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# Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials

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# Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials

by

### Christopher D. Wight

### Dissertation

Presented to the Faculty of the Graduate School of The University of Texas at Austin in Partial Fulfillment of the Requirements for the Degree of

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### Dedication

Dedicated to Yogi and Allison. I love you both more than anything.

"I am among those who think that science has great beauty [she told her interlocutors.] A scientist in his laboratory is not only a technician: he is also a child placed before natural phenomena which impress him like a fairy tale."

Marie Curie, Nobel Prize in Physics (1903), Nobel Prize in Chemistry (1911)
 Excerpt from *Madame Curie: a biography. By Eve Curie, translated by Vincent Sheean*. Doubleday, Doran: New York, 1939

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#### Abstract

# Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials

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Supervisor: Brent L. Iverson

There is still a great deal to learn about the assembly and dynamic properties of solid-state supramolecular architectures. The higher order structure of solids imposes severe limitations on molecular motion and dynamics. Yet, there is growing interest in creating dynamic solids that assemble in predictable ways for functional applications, including sensing and energy conversion. An understanding of the interplay between all of the relevant non-covalent interactions is fundamental for the rational design of such architectures. Electrostatic interactions of all types, including hydrogen bonding and van der Waals interactions, combine to determine the exact intermolecular geometries adopted by organic molecules and assemblies in solids, liquids, and mesophases.

A significant portion of work in the Iverson group has broadly focused on the self-assembly of aromatic units, both in solution and more recently, in the solid-state. This dissertation builds on this body of research and describes fundamental investigations into intermolecular interactions that give rise to functional supramolecular architectures, driven by the self-assembly of organic molecules in the solid-state. The majority of this

work describes the stimuli-responsive colorimetric switching of polymorphic monoalkoxynaphthalene-naphthalimide (MAN-NI) donor-acceptor dyads in the solid-state, with a primary focus on a detailed mechanistic analysis that allowed us to discover how this dramatic mechanism operates in the solid-state.

Chapter 1 provides an introduction to non-covalent interactions, polymorphism, and stimuli-responsive materials. Chapter 2 describes the synthesis of 14 new MAN-NI dyads, and goes on to provide an in-depth structural and spectroscopic characterization illustrating the different polymorphs that can be formed by symmetric and asymmetric dyads, as well as the photophysical origins for the differences in color between various polymorphs. Chapter 3 details the stimuli-responsive properties of dyads, with particular focus on the thermochromic orange-to-yellow transition seen when dyads are heated. Detailed structural, spectroscopic, thermal, and morphological analyses are described in the context of characterizing the two different states. Chapter 4 goes on to describe the mechanistic analysis that uncovered the presumptive molecular switching mechanism, and the key interactions that enable polymorphic switching mechanisms. Chapter 5 details the application of aromatic interactions for the rational design of supramolecular assemblies in perylene diimides (PDI) for novel energy conversion materials.

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## CHAPTER 1

## Aromatic Interactions in Supramolecular Chemistry: Dynamics and Properties of Self-Assembled, Stimuli-Responsive Materials

#### **1.1 NON-COVALENT INTERACTIONS**

Non-covalent forces are a requirement for life as we know it. Hydrogen bonding between water molecules provides the solution that enables interactions between organic molecules and vital biological machinery. These hydrogen bonds also contribute to the stability of complementary double-stranded DNA (dsDNA) that allow for compact and valuable storage redundancy, yet are weak enough to allow the "unzipping" of dsDNA by topoisomerases, and the "reading and writing" of sequences by polymerases in growing or expressing cells.

Yet, the complexity seen in nature relies on an ensemble of dynamic intermolecular interactions, not just hydrogen bonds. Hydrophobic and entropic effects further help to keep DNA assembled, and as chemists, we have learned to better understand and characterize intermolecular interactions, including those that stabilize the double helix of DNA. Specifically, we can attribute stability of dsDNA to conformational preferences of the sugar phosphate backbone combined with aromatic interactions, an encompassing interaction including the hydrophobic effect, dispersive, and electrostatic interactions. Aromatic interactions between DNA bases provide favorable interbase interactions, while also minimizing the exposure of hydrophobic nucleobases to water, and maximizing the entropically favorable solvation of the sugar phosphate backbone.

Medicinal chemists have come to exploit the same aromatic interactions as a way to target DNA for pharmaceutical therapies. Aromatic interactions enable lifesaving chemotherapeutics like Doxorubicin to kill cancer cells by intercalating into dsDNA, blocking the unzipping action of topoisomerases as well as the reading and writing of DNA by polymerases.<sup>1</sup> Driven by non-covalent interactions, the intercalating drug kills cancer cells by stopping the dynamic molecular machines required for life.

While individually weak and operating on the atomic scale, accumulation of various noncovalent interactions can create stable structures that can be visualized, as in the case of the microscopic supramolecular assemblies of DNA with various histone proteins that form chromosomes. Yet even larger manifestations of weak intermolecular interactions can be seen at the macroscopic level, as in the case of a gecko fixed to a vertical wall, held against gravity by van der Waals interactions.<sup>2</sup>

Although dispersive interactions are critical for the gecko to adhere, the interaction alone provides little benefit to its vitality without the *dynamic* ability to change it, for example, in order to avoid predation. The geckos' ability to run relies on the concerted and cooperative movements of myosin molecular machines along actin filaments, powered by ATP. Macroscopic movement is achieved when energy derived from ATP is coupled to the molecular machine,<sup>3</sup> in turn driving *collective and dynamic conformational changes between various forms, each being accessible by varying an ensemble of non-covalent interactions*. While natural selection has had great success in manipulating numerous dynamic, non-covalent interactions that enable life, chemists are only beginning to combine non-covalent interactions in dynamic, supramolecular assemblies.

In organic molecules, the ability to rationally predict conformational preferences in solution, or packing geometries in the solid-state becomes increasingly difficult with size. An understanding of the interplay between covalent constraints and non-covalent interactions is fundamental for the rational design of molecules that interact with predictable geometries. In order to achieve the complexity observed in nature, we must not just learn to understand and

2

utilize the collective ensemble of non-covalent interactions, we must also learn how to alter and access various conformations through dynamic molecular motions.

#### **1.2 INTERACTIONS BETWEEN ALKANES**

Alkanes and other hydrophobic organic molecules are attracted to one another primarily through dispersion forces, as there is no permanent electrostatic attraction between alkanes.<sup>4</sup> Specifically, London dispersion forces represent the attractive term in the interaction described by the van der Waals potential,<sup>5</sup> and reflect induced dipole-induced dipole interactions that underlie favorable intermolecular interactions in polarizable alkanes.

The hydrophobic effect can also drive the association of hydrophobic, organic molecules in certain environments. The self-association of hydrophobic molecules in aqueous environments is known as the hydrophobic effect, and is primarily responsible for the folding of proteins, the assembly of phospholipids into membranes, and sometimes the binding of small molecules to receptors in water.<sup>4</sup> The hydrophobic effect primarily arises from the exposed organic surface area and two primary mechanisms decrease exposed organic surface: self-aggregation of organics and shape changes to decrease hydrophobic surface area. Shape changes result from conformational rotations in simple alkanes, with changes from staggered-anti to gauche conformations decreasing the surface area presented by an alkane.

While other intermolecular effects are often invoked when rationalizing stability preferences (e.g. orbital interactions, aromatic interactions, etc.), it is valuable to note the strength of dispersion forces. For example, the most energetically favorable packing of *n*-pentane dimers has a binding energy of 3.6 kcal mol<sup>-1</sup>, significantly stronger than the binding of the benzene dimer (2.7 kcal mol<sup>-1</sup>).<sup>5</sup> When packed as trans isomers in the solid-state that limit their conformational flexibility, alkanes are held together in part by homonuclear R-H···H-R dihydrogen interactions.<sup>6</sup> While individually weak, accumulations in longer, rigid packed alkanes can yield significant association energies, as high as 4.6 kcal mol<sup>-1</sup> in *n*-hexane,<sup>7</sup> and

even higher in alkyl polyhedranes.<sup>6</sup> These weak van der Waals interactions differ from weak hydrogen bonds as, unlike the latter, these induced dipole-induced dipole interactions do not have directionality requirements.<sup>6</sup>

An interesting phenomenon seen in alkanes is the "odd-even" effect, where the melting points of alkanes are seen to increase in a 'zig-zag' shape, rather than a continuous increase.<sup>8</sup> While Baeyer noted this experimental observation in 1877,<sup>9</sup> the basis for this behavior was not understood fully until the start of the 21<sup>st</sup> century.<sup>10</sup> Single-crystal structures of *n*-alkanes longer than six carbons show characteristic differences in packing between even and odd numbered alkanes. In even numbered alkanes, methyl groups on each chain end have optimal intermolecular contacts to adjacent alkanes, whereas odd numbered chains have optimal distances only at one end of the chain, and longer distances at the other. Thus, a "packing effect" is seen to give rise to the odd-even effect, and can be explained by a simple geometric model for crystal packing, where odd alkanes have lower density, fewer intermolecular contacts, and thus have lower melting points.

#### **1.3 AROMATIC INTERACTIONS & AROMATIC SELF-ASSEMBLY**

#### 1.3.1 Modern Theory: Local, Direct Interaction Model

Interactions between aromatic units have been well known and increasingly studied over the last half-century. Our current understanding of aromatic interactions has enabled the application of this fundamental non-covalent interaction to numerous fields including catalyst design,<sup>11, 12</sup> optical monitoring and self-assembly,<sup>13</sup> and molecular sensing.<sup>14</sup>

Yet, interactions between aromatic units have not been as widely studied as other noncovalent interactions. In 1960, Patrick and Rosser published a short report describing a 1:1 complex that formed when benzene and hexafluorobenzene are mixed.<sup>15</sup> A model for understanding the formation of this complex as well as rationalizing the geometries adopted by interacting aromatic was put forth by Hunter and Sanders in 1990.<sup>16</sup> This model, known as the "polar/ $\pi$  model", is an often invoked rationale for understanding the relative geometries adopted by aromatic units. The "polar/ $\pi$  model" model rationalizes aromatic stacking as resulting from maximizing favorable quadrupole-quadrupole interactions between aromatic units<sup>16</sup> and found apparent support in subsequent experimental work.<sup>17-19</sup> Qualitatively, analysis of quadrupolequadrupole interactions can be visualized by comparing calculated electrostatic potential maps (ESPs) between the relevant aromatic units (Figure 1.1).



Figure 1.1 Calculated electrostatic potential maps (ESPs) for the indicated molecules, scaled for relative comparison. Bottom: common aromatic stacking geometries and some of the descriptions often encountered to describe each.

Based on analysis of quadrupole moments, a molecular complex between benzene and hexafluorobenzene could be rationalized as having a 'face-centered' aromatic stacking geometry because complementary charges within each respective aromatic ring would be maximized in this geometry (Figure 1.1)

While the "polar/ $\pi$  model" provides a nice description for the face-to-face stacking interactions of complementary aromatic units, as in the case of benzene and hexafluorobenzene, the model does not accurately describe the favorable self-associations of electron rich aromatics. For example, the "polar/ $\pi$  model" would expect unfavorable face-to-face interactions between two methoxybenzene (anisole) molecules (top right Figure 1.1), as the methoxy group is a known electron donor, and the interaction of two electron rich aromatics based on quadrupole-quadrupole interactions would thus be unfavorable. Yet, numerous examples have shown that all substituents stabilize the substituted benzene dimers in the gas phase,<sup>20-25</sup> and a more accurate model to describe interactions between various aromatic units must account for such interactions.

Later work by Rashkin and Waters,<sup>26</sup> as well as computational work by Wheeler and Houk,<sup>27, 28</sup> and more recently Wheeler,<sup>20, 29-31</sup> has provided strong evidence in favor of a different model, known as the "local, direct interaction" model.<sup>20</sup> This model postulates that the substituents on aromatic rings dictate aromatic stacking geometries as a result of local, through-space electrostatic interactions from polarized bonds. Whereas previous model has rationalized stacking geometry based on polarization of the  $\pi$ -electron cloud, the "local, direct interaction" model poses that aromatic geometry results from the local, direct interaction between substituents and the other ring. Said differently, strong electrostatic dipoles on the periphery of aromatic units dictate aromatic interaction geometries. This "local, direct interaction" model has since been expanded to include various interaction geometries, including edge-to-face interactions, as well as other aromatic interactions, including the cation/ $\pi^{28}$  and anion/ $\pi$  interactions.<sup>32</sup>

Elegant computational work supporting this model has been reported, and an example of such work is shown in Figure 1.2. Computational work revealed that the interaction in the

benzene dimer with varying substituents (e.g. X-C<sub>6</sub>H<sub>5</sub> ··· C<sub>6</sub>H<sub>6</sub>) can be modeled simply by the interaction between a hydrogen capped substituent and an aromatic ring, without the substituent being itself bound to an aromatic ring (e.g. (X-H ··· C<sub>6</sub>H<sub>6</sub>). Shown in the top of Figure 1.2 is a plot of the computed interaction energy of dimers made between benzene and one of 25 different monosubstituted benzenes plotted versus the Hammet  $\sigma_{meta}$  parameter, which is taken to reflect the inductive electron-donating or withdrawing ability of a given substituent.<sup>27</sup> The overall correlation between aromatics can be qualitatively understood in terms of the electron donating or withdrawing characteristics of a given substituent.<sup>27</sup>

To understand the nature of this interaction, a simple change was made to the benzene dimer, where the benzene ring in the substituted benzene derivative was replaced with a simple hydrogen atom (e.g. Cl-C<sub>6</sub>H<sub>5</sub> becomes Cl-H). Shown in the bottom of Figure 1.2, a remarkably similar correlation exists is shown for the dimer formed from a hydrogen-capped substituent-benzene dimer (X-H  $\cdots$  C<sub>6</sub>H<sub>6</sub>) and the substituted benzene-benzene dimer (X-C<sub>6</sub>H<sub>5</sub>  $\cdots$  C<sub>6</sub>H<sub>6</sub>) shown above. For the 25 different substituents in each case, a strong correlation is seen between the two different interaction energies (r = 0.91).<sup>27</sup> This remarkable similarity was the basis for the "local, direct interaction" model, where the substituent effects can be described simply from the direct interaction between the substituent and the other ring, and did not need to involve the  $\pi$ -system of the substituted ring.<sup>27</sup>



Figure 1.2 The "local, direct interaction" model of aromatic interactions shows that the same relative interaction energy exists between a substituted benzene-benzene dimer, and a hydrogen bound substituent-benzene dimer when plotted against  $\sigma_{meta}$ . Reprinted with permission from Ref. <sup>30</sup>, <u>https://pubs.acs.org/doi/10.1021/ar300109n</u>. Copyright 2012 American Chemical Society.

#### **1.3.1.1 Electrostatic Potential Maps and Aromatic Interactions**

In the previous section, electrostatic potential maps (ESPs) were used in order to qualitatively understand interactions between aromatic units. As ESPs will be referenced throughout this dissertation, a few brief comments are necessary in order to clearly explain what they can and cannot tell us, as well as how they can be qualitatively 'predicted'.

Briefly, ESPs are *a priori* quantum mechanical calculations that reflect the attractive or repulsive force calculated from moving a positive point charge around the surface of a given molecule.<sup>4</sup> In this work, all ESPs are calculated using an isodensity surface with an electronic distribution of 0.002 electrons au<sup>-3</sup>, corresponding to over 99.5% of total electron density. In plotted ESPs, the magnitude of the interaction (plotted as energy) between the point charge and the molecule is shown, and a red color will always refer to an attractive force.

Substitutions on benzene rings that result in changes to ESPs are often used to rationalize local changes to electronics following substitution. For example, addition of electron donating substituents resulting in changes to calculated ESPs are sometimes said to reflect a more "electron rich" system, when that is not necessarily the case. Wheeler and Houk have noted that<sup>33</sup> "While negative ESPs often do correspond to electron-rich regions, the assumption that changes in ESPs necessarily indicate local changes in the electron density is incorrect.", and thus, caution must me made when evaluating ESPs. While the calculated ESP is a function of electron density in all surrounding space with an inverse dependence on distance, even small differences in charge distribution can have significant effects on calculated ESPs. For example, a charge of 0.1 e results in changes of over 10 kcal mol<sup>-1</sup> to the ESP at a distance of 3 Å.<sup>33</sup> Wheeler has gone on to note that simply considering the sign of the ESP above the center of aromatic rings when trying to predict aromatic interactions may lead to conclusions that are not supported by accurate computational predictions,<sup>20</sup> and that ESPs do not necessarily provide reliable indication of the strength of electrostatic components of stacking interactions.<sup>20</sup> This is in agreement with our earlier discussion, noting that there is actually a favorable interaction in the formation of a methoxybenzene dimer, despite the red color central to the ESP shown in Figure

1.1. It is the C-O bond dipole of anisole that dictates the aromatic geometry adopted between the two units, and in a face-to-face dimer, the preferred interaction geometry for would avoid overlapping the strong C-O bond dipoles, either by adopting an off-set parallel geometry, or having rotational differences, such that the C-O bonds are oriented away from one another.

ESPs can provide a qualitative tool for understanding the interactions between substituted aromatic rings when used in appropriate ways, and can even be qualitatively envisioned in many simple cases with prior knowledge of certain reference ESPs. Wheeler and Houk have shown a valuable method for predicting ESPs for substituted benzenes by the additive construction from simpler ESP components.<sup>28</sup> In this method, illustrated in Figure 1.3, the ESP for various substituted benzene derivatives are shown to be remarkably similar to the "additive ESPs" constructed by adding the individual benzene and substituent ESP together. This method shows that ESPs can be predicted from the addition of hydrogen-capped substituent ESPs to benzene, and allows for a quick 'back of the envelope' tool to quickly and qualitatively evaluate electrostatic charges on substituted aromatics that can be valuable when rationalizing aromatic interaction geometries.

Note the ESP for cyanobenzene (Figure 1.3) shows a more positive ESP compared to unsubstituted benzene (see Figure 1.1). As discussed above, the origins for this relative increase in positive ESP above the center of the cyanobenzene are not the result of a decrease in electron density of the pi-system from the cyano substituent. Rather, this effect *to the ESP* arises from through-space effects caused by the appended cyano group, whereby the positive local dipole from the CN substituent "overwhelms" the negative character provided by the aryl pi-system. Thus, changes in ESPs should not be taken as an indication of local changes in electron density.<sup>28, 30</sup>



Figure 1.3 Calculated ESPs for substituted aromatics (top) strongly resemble ESPs generated by adding separately computed ESPs for benzene and each substituent (bottom). Reprinted with permission from Ref. <sup>30</sup>, <u>https://pubs.acs.org/doi/10.1021/ar300109n</u>.Copyright 2012 American Chemical Society

### **1.3.2** Aromatic Interactions in Solution

Aromatic interactions are derived from a combination of electrostatic, dispersive, and solvophobic interactions.<sup>34</sup> Because of the combination of different physical interactions, aromatic interaction energetics can show large variation depending on the aromatics involved, as well as the surrounding conditions (e.g. water versus chloroform). Aromatic interactions have been experimentally studied in the solution using a number of different platforms that rely on the same basic premise: rigid systems that can force aromatic interactions, and measuring a distribution interacting and non-interacting geometries using <sup>1</sup>H NMR.

Work in the early 1990s by Cozzi, Siegel, and coworkers investigated the influence of substituent effects on solution-based aromatic interactions in cofacial 1,8-diarylnaphthalene

systems using <sup>1</sup>H NMR (Figure 1.4).<sup>17-19</sup> In this rigid naphthyl framework, appended aromatic rings are be forced into a face-to-face type interaction which would be this lost based on rotation around the indicated biaryl-type bond (Figure 1.4). NMR was used to quantify the rotation barrier, which in turn was used as a proxy for the strength of the parallel interaction. The authors reported that polar/ $\pi$  electrostatic interactions were the determinant in understanding the geometry adopted by the two appended arenes, as opposed to charge-transfer based interactions.<sup>17-19</sup> Rashkin and Waters<sup>26</sup> went on to provide experimental work to explain that the magnitude of offset parallel interactions as resulting from orientational effects between substituents and hydrogen atoms on adjacent rings (Figure 1.4). More recent work by Shimizu and coworkers<sup>34-36</sup> using atropisomeric molecular torsion balances have studied positional and additive substituent effects, and trends were found to agree with the "local, direct interaction" model put forth by Wheeler and Houk, yet could not definitively rule out indirect substituent effect interactions.



Figure 1.4. Examples of systems used to experimentally study aromatic interactions in solution.

Other strategies to study and quantify aromatic interactions in solution have been put forth by Cubberley and Iverson. Using aromatic donor 1,5-dihydroxynaphthalene (DAN) and acceptor 1,4,5,8-naphthalenetetracarboxylic diimide (NDI), association constants were determined for donor-acceptor complexes as well as respective self-association complexes in solvents of varying polarities, as measured by the empirical solvent parameter  $E_T(30)$ . Results from <sup>1</sup>H NMR binding studies are shown in the top of Figure 1.5. In general, association constants are larger in solvents of increasing polarity for DAN-DAN, NDI-NDI, and DAN-NDI complexes. The increase in association constant as a function of solvent polarity was interpreted as a consequence of the hydrophobic effect, whereby the larger aromatic faces are driven to associate more in higher polarity solvents as a way of decreasing unfavorable exposure of aromatic surface area to the surrounding environment. Noteworthy, larger binding constants are seen for the NDI-NDI self-association complexes compared to the DAN-DAN complexes can be attributed in part to the larger NDI surface area, thus engendering a larger net hydrophobic effect. It is worth mentioning at this point that the strongly polarized carbonyls of NDI (Figure 1.6) distributed around the ring would allow for more favorable aromatic stacking geometries, for example in an off-set parallel stacking geometry, compared to DAN.

		K <sub>a</sub> (M <sup>-1</sup> )	K <sub>a</sub> (M <sup>-1</sup> )	K <sub>a</sub> (M <sup>-1</sup> )	$-\Delta G^{\circ}$ (kcal/mol)	<i>E</i> <sub>T</sub> (30)
	Solvent	(donor-donor)	(acceptor-acceptor)	(donor-acceptor)	(donor-acceptor)	(kcal/mol)
1	CDCl <sub>3</sub>	(1)	(1)	$2 \pm < 0.5$	0.4	39.1
2	acetone-d6	$1 \pm < 0.5$	$1 \pm < 0.5$	$8 \pm < 0.5$	1.2	42.2
3	DMSO-d6	$1 \pm 1$	$2 \pm < 0.5$	$3 \pm < 0.5$	0.7	45
4	CD <sub>3</sub> CN	$1 \pm 1$	$3 \pm < 0.5$	$11 \pm < 0.5$	1.4	45.6
5	$CD_3OD$	$1 \pm < 0.5$	$8 \pm < 0.5$	$30 \pm < 0.5$	2	55.5
6	3:1 CD <sub>3</sub> OD/D <sub>2</sub> O	$1 \pm < 0.5$	$15 \pm < 0.5$	$63 \pm 2$	2.5	57
7	1:1 CD <sub>3</sub> OD/D <sub>2</sub> O	$2 \pm < 0.5$	$28\pm2$	$254 \pm 41$	3.3	58.9
8	1:3 CD <sub>3</sub> OD/D <sub>2</sub> O	$10 \pm 2$	$101 \pm 28$	$952 \pm 64$	4.1	60.8
9	D <sub>2</sub> O	$20 \pm 4$	$245 \pm 101$	$2045 \pm 63$	4.5	63
н		н Н{о~}		H 3 4 4 3 4 4 5 4 4 7 2 6 (kcal/mol) 2 - 2 4 2 4 - 2 4 - 2 4 - 2 4 - 2 4 - 2 4 - 2 4 - 2 4 - 2 4 - 2 2 4 2 2 4 2 2 4 2 2 4 2 2 4 2 2 4 2 2 4 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 4 2 3 - 2 4 2 4 2 4 3 - 2 4 2 4 2 3 - 2 4 2 4 2 4 2 4 2 3 - 2 4 2 4 2 4 - 2 4 - 2 - 2 - 2 - 2 - 2	6 5, 4, 3,	9 8 7
	Donor	, 7 <u>3</u>	Acceptor	0 35 40	45 50 55 Ε <sub>τ</sub> (30)	

Figure 1.5. Electron rich DAN and electron deficient NDI association constants as measured by <sup>1</sup>H NMR in indicated solvents. Plotted is the measured free energy for the 1:1 NDI:DAN complex versus solvent polarity, with stronger complex formation being observed in increasingly polar solvents. Adapted with permission from Ref.<sup>37</sup> Copyright 2001 American Chemical Society.

#### 1.3.3 Supramolecular Self-Assembly of DAN-NDI in Foldamers

#### 1.3.3.1 Lokey's AEDAMER

The aforementioned association constants computed for DAN and NDI followed early work by the Iverson group to use complementary aromatic units as a means to assemble the first abiotic foldamers, that is, molecules that would spontaneously fold into an ordered structure in water. In 1995, Lokey and Iverson reported the first <u>a</u>romatic <u>e</u>lectron <u>d</u>onor-<u>a</u>cceptor fold<u>amer</u> (*aedamer*) (Figure 1.6).<sup>38</sup> The foldamer design was built around a DAN-NDI co-crystal having alternating face-centered stacking of DAN-NDI units. Molecular mechanics modeling assisted the design of a semi-rigid hydrophilic peptide back bone in between complementary DAN and NDI shown in Figure 1.6. Once synthesized, proof of the folded complex came from NMR spectral studies and an observed broad charge-transfer (CT) band that was seen, resulting in a characteristic plum color due to electronic donor-acceptor interactions between the high lying HOMO of DAN, and the low-lying LUMO of NDI.



Figure 1.6. Lokey and Iverson foldamer seen to fold into a pleated secondary structure in aqueous media.<sup>38</sup> ESPs for dimethyl DAN and NDI are shown (B3LYP, 6-31G\*).

#### 1.3.3.2 Irreversible Foldamer to Amyloid Fibril – Nguyen, Bradford, and Peebles

Following this initial foldamer, subsequent work in the Iverson group investigated additional secondary structures that could be assembled based on the complementary interactions of DAN and NDI.<sup>39-42</sup> Nguyen and Iverson<sup>43</sup> introduced amphiphilicity into the peptide backbone, by replacing a single aspartic acid with leucine, conceptually similar to the biologically relevant leucine zipper motif. While the molecule still folded into a pleated structure in water, a unique, irreversible conformational change was noticed after the foldamer was heated to 80°C, resulting in a gel that persisted indefinitely. The formation of an irreversible aggregate was thought to result from a mechanism initially involving unfolding, followed by a kinetically irreversible conversion to a tangled aggregate.

In 2008, Bradford and Iverson<sup>44</sup> reported a follow-up report on a structure activity relationship of a series of amphiphilic aedamers, with variation in side chains. Notably, the leucine introduced by Nguyen was replaced with other hydrophobic residues, including norleucine, isoleucine, and valine. Upon heating, the three leucine isomers were found to form hydrogels following irreversible aggregation. Characterization of the aggregates using rheology, circular dichroism, and scanning electron microscopy revealed that the aggregates were actually highly ordered intermolecular assemblies, analogous to amyloid formation in proteins. Further, the three different leucine isomers formed assemblies with significant differences in hydrogel properties, while the valine derivative did not form a hydrogel. Taken together, the differences in supramolecular aggregate formation and hydrogel properties were reported to reflect the sensitivity of the nature and geometry of intermolecular interactions adopted by the self-assembled aggregates.

A follow up report by Peebles and Iverson<sup>45</sup> sought to better characterize the nature of the intermolecular interactions that gave rise to the highly ordered aggregate formed upon heating. Upon heating the amphiphilic, alternating DAN-NDI foldamer shown in Figure 1.7 generated a highly ordered amyloid like fiber as previously observed.<sup>43-45</sup> Structural characterization of the fibrils using transmission electron microscopy (TEM) and atomic force microscopy (AFM)

revealed the width of the fibrils was equal to the length of the extended, unfolded molecule. Further, AFM measurements revealed a helical pitch, consistent with previous observations for 1-dimensional fibers seen formed from the offset face-to-face self-stacking of NDI.<sup>46</sup>



Figure 1.7. Transformation of a kinetically stable, soluble foldamer to an irreversible aggregate from upon heating, driven by conformational switching of alternating DAN-NDI aromatic stacking to NDI-NDI stacking geometries. Adapted from Ref.<sup>45</sup>, Reprinted with permission from<sup>47</sup> Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

A conformational change from the soluble, kinetically stable folded state to a more thermodynamically stable fibril aggregate was found to result from NDI moieties switching from DAN-NDI alternating stacking in the folded state to NDI off-set self-stacking in the aggregate.<sup>45</sup>

An understanding of the conformational change could not be explained using the polar/ $\pi$  model, as it would predict a repulsive interaction between two NDI units based on quadrupolequadrupole repulsion. On the other hand, using the local, direct interaction model, one can rationalize NDI offset self-stacking as a favorable electrostatic interaction resulting from the overlap of the electron rich carbonyl oxygen atom of one NDI molecule with the electron deficient carbonyl carbon atom of an adjacent NDI. Previously not resolved, an understanding of the mechanism of conformational switching in this foldamer-to-aggregate transformation helped illuminate aromatic packing modes that can be accessed by NDI.

#### 1.3.3.3 Ikkanda's Nucleotidomimetic DNA, DAN, & NDI Foldamers

Following success using NDI as a threading intercalator for binding of DNA sequences,<sup>48-57</sup> subsequent investigations sought to explore and quantify aromatic interactions between NDI, DAN, and DNA in the context of nucleic acid containing foldamers. These nucleotidomimetic foldamers have the same sugar-phosphate backbone of DNA and assemble into a double helical heteroduplex in solution, thus falling under the umbrella 'foldamer' classification.<sup>58</sup> In 2014, Ikkanda and Iverson<sup>59</sup> reported a nucleotidomimetic foldamer assembly where several internal bases were replaced with DAN and NDI (Figure 1.8). In order to maintain the double helical backbone, a spacer was introduced on the complementary strand, opposite of DAN/NDI, such that for the 6 total bases replaced across the two strands, three were spacers, and the other three were combinations of DAN and NDI derivatives. The general trends for the DAN-DAN-DAN and NDI-NDI-NDI duplexes shown in Figure 1.8 track with self-stacking preferences reported by Cubberley and Iverson<sup>37</sup> previously discussed (section 1.3.2), and further highlight the ability of DNA to have favorable aromatic stacking interactions with other aromatic molecules.



Figure 1.8 DAN and NDI directed assembly of nucleic acid showing an internal NDI-DAN-NDI sequences has similar melting points to the same sequence with three A-T base pairs. Adapted with permission from Ref. <sup>59</sup> <u>https://pubs.acs.org/doi/10.1021/jo402704z</u> Copyright 2014 American Chemical Society.

### 1.3.4 Solid-State Supramolecular Assemblies of DAN & NDI

Previously described work highlighted the ability for DAN and NDI to have favorable aromatic interactions in solution. Other work in the Iverson group explored the ability for these aromatic units to assemble in the solid-state. Early work by Reczek and coworkers<sup>60</sup> explored the ability for DAN and NDI derivatives to assemble into columns with alternating DAN-NDI face-centered stacking in the solid-state. Alkyl substituted DAN and NDI derivatives were found to

form stable mesophases, as well as soft/plastic crystals, and derivates with liquid-crystalline properties made from alternating DAN-NDI stacks within columns. Later work by Alvey and coworkers<sup>61</sup> explored a structure activity relationship related to thermal properties, and reported controllable thermochromism in the mixtures based on side chain substitution

Both of these works using alkyl substituted DAN and NDI derivatives revealed thermochromic changes that accompany the reorganization of some DAN and NDI mixtures.<sup>60-62</sup> Shown in Figure 1.9, cooling of certain DAN and NDI mixtures from the isotropic phase produced a deep red colored mesophase, attributed to the formation of a CT complex, with DAN-NDI adopting an alternating face-centered stacking geometry. Even more interesting, a dramatic thermochromic change occurred in some derivatives with additional cooling, when the red mesophase cooled to form a yellow crystalline solid (Figure 1.9), with the color change taken as an indication that CT interactions were lost upon crystallization. Various structural, optical, and thermal characterizations indicated this color change was the result of the self-sorting of NDI and DAN. Meaning, during cooling, the alternating face-centered NDI-DAN stacking geometries switched to NDI off-set parallel self-stacking and DAN self-stacking in a herringbone geometry (Figure 1.9). Unique to this system, little observable morphological change was seen following this self-sorting behavior.



Figure 1.9 Cooling of a 1:1 isotropic melt of certain DAN and NDI derivatives would initially form a maroon mesophase that would turn into a yellow crystalline solid upon cooling, with retention of the overall crystalline morphology. The process was shown to be due to self-sorting of alternating DAN and NDI monomers, shown by representative crystal structures, showing alternating DAN-NDI face-centered stacking switching to NDI-NDI offset parallel self-stacking and DAN-DAN edge-to-face (herringbone) self-stacking.<sup>60</sup>

### 1.3.5 Variation in Solid-State Packing Geometries: DAN and NDI

The polar/ $\pi$  model does provide an intuitive rationale for the face-centered stacking geometry adopted by the relatively electron rich 1,5-dialkoxylnaphthalene (DAN) and relatively electron poor 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) pioneered by our group in the context of aqueous foldamers (Figure 1.10).<sup>37-45</sup> Contrary to what the polar/ $\pi$  model would

predict but consistent with the local, direct interaction model and previously described results, NDI has been shown to exhibit highly favorable NDI-NDI associations in solution,<sup>37</sup> as well as adopt NDI offset self-stacking in a variety of contexts (Figure 1.10).<sup>45, 46, 60-65</sup>



Figure 1.10 a) NDI and DAN with calculated electrostatic potentials (B3LYP, 6-31G\*). Bottom, representative crystal structures of DAN and NDI stacking modes with hydrogen atoms omitted for clarity<sup>60</sup> b) Alternating DAN-NDI face-centered stacking. c) NDI-NDI offset parallel self-stacking d) DAN-DAN self-stacking in an edge-to-face stacking geometry. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

The favorable self-stacking of NDI can be thought of as being derived from its strong carbonyl C-O bond dipoles (Figure 1.10). As predicted by the "local, direct interaction model", aromatic stacking geometries adopted by NDI are expected to result from the favorable direct, through space interactions of polarized groups. Note the positive charge shown on the ESP in between each carbonyl. Off-set NDI-NDI self-stacking that places the electronegative carbonyl oxygen in this very location, making for an energetically favorable interaction. Shown in the

crystal structure in Figure 1.10c, the measured intermolecular distance between a carbonyl oxygen of one NDI molecule and the carbonyl carbon of an adjacent NDI measures 3.30 Å, indicative of a very close intermolecular contact for two face-to-face stacked aromatics. It is this type of interaction between the most polarized carbonyl groups that is believed to underlie the favorable self-stacking of NDI in the thermochromic mesophases, as well as the previously described foldamer forming fibrils. Thus, NDI can be thought of as having a "split personality" in terms of its favorable stacking modes: alternating face-centered stacking with electron rich aromatics like DAN, and offset NDI self-stacking.

#### **1.4 POLYMORPHISM**

Polymorphism is defined as the ability of a single chemical entity to exist in the solidstate in multiple different crystalline structures, and is a commonly occurring property among organic molecules.<sup>67-71</sup> While made of the same chemical components, polymorphism can enable a single molecule to form materials with different properties,<sup>72</sup> including different solubilities,<sup>73</sup> melting points,<sup>63</sup> crystalline morphologies,<sup>66</sup> as well as differences in electronic,<sup>74</sup> optical,<sup>75</sup> and mechanical properties.<sup>76</sup> The ability to access different properties from a single chemical entity have resulted in an increase in research into polymorphism as a functional tool for materials applications.<sup>68, 74</sup> Yet, despite the vast improvements in our understanding of polymorphism, targeted polymorphism still remains a highly desirable goal.<sup>70</sup>

While a newer area of research in the functional materials community, research into polymorphism has been a long standing area of research interest in metallurgy<sup>77</sup> and the pharmaceutical industry.<sup>78</sup> Pharmaceutical interests in polymorphism stem from the different physical properties between polymorphs and the effects different polymorphs have on the use and efficacy of a drug. Different polymorphs can dramatically change the properties of a drug and change how a given drug is manufactured, influence its chemical stability and shelf-life, and

arguably most important, determine how the drug behaves inside the body, including the rate and extent to which the drug is absorbed.<sup>69,72</sup>

One of the most famous examples of polymorphism affecting the pharmaceutical industry came in the summer of 1998 with the antiretroviral drug ritnovair, marketed under the name Norvir, used for the treatment of Acquired Immunodeficiency Syndrome (AIDS).<sup>73</sup> Only being bioavailable in the solution phase, ritnovair was packaged as a liquid and semi-solid capsules with the drug dissolved in an ethanol/water mixture. It was not until after drug development and manufacture that various batches of the pharmaceutical failed dissolution tests. A second, previously unobserved polymorph was seen to precipitate out that was significantly less soluble than the previously known crystalline form, and this ultimately resulted in the product's recall.<sup>73</sup>

## 1.4.1 Time-Dependent Polymorphism in Monoalkoxynaphthalene-Naphthalimide Donor-Acceptor Dyad

Most often, different polymorphs are found by varying crystallization parameters, including different methods for crystal growth, specific crystallization conditions, and even time. The presence of multiple polymorphs can sometimes be detected through optical analyses looking for different crystalline morphologies, but more definitive proof can come from quantitative spectroscopic or structural characterization methods.

In 2014, Peebles, Iverson, and coworkers reported the time-dependent polymorphism in a series of conjugated monoalkoxynaphthalene-naphthalimide (MAN-NI) donor-acceptor dyads (Figure 1.11).<sup>63</sup> While different packing modes were observed, aromatic dyad cores were found to stack in columns in all polymorphs, as is often the case with aromatic molecules.



 Figure 1.11 Structures and electrostatic potential maps of monoalkoxynaphthalenenaphthalimide (MAN-NI) donor acceptor dyads, with corresponding ESPs (B3LYP, 6-31G\*). Reprinted with permission from Ref <sup>63</sup>. Copyright 2014 American Chemical Society.

In contrast to independent DAN and NDI units described previously, the covalently linked conjugated MAN-NI dyads do not have C2 symmetry, and thus the conjugated aromatic dyad core has directionality. Within a column, adjacent dyads can be stacked in one of two general ways. If adjacent aromatic cores align in the same orientation (e.g. MAN unit above another MAN unit) the stacking can be referred to as having a head-to-head (NI-NI, or MAN-MAN) stacking geometry. On the other hand, if adjacent dyads within a column are in opposite orientations, they are said to a head-to-tail (NI-MAN) stacking geometry.

Several of these MAN-NI dyads showed a difference in solid-state packing between relatively faster (yellow crystals) and slower (orange crystals) evaporation times from solution. While the photophysical basis for differences in color was unclear, analysis of single-crystal X-ray diffraction structures and powder X-ray diffraction (PXRD) patterns indicated that the differences in optical properties resulted from differences in head-to-head and head-to-tail packing.

Rationalizing these two different polymorphs can be done using the same "local, direct interaction" model introduced earlier in this chapter. It is critical to note the most polarized

bonds present in the aromatic dyad core, as shown by the electrostatic potential map in Figure 1.11, are as predicted from previous discussions involving NDI. In an analogous manner, the carbonyl C-O bonds have the strongest dipole, and so each NI component can be thought of having favorable interactions between other adjacent NI units, when stacked in an off-set parallel fashion (similar to NDI-NDI offset stacking). Conversely, alternating face-centered stacking between the MAN core and an adjacent NI unit in the case of head-to-tail stacking is favored because of the general electrostatic complementarity of the MAN and NI core (similar to DAN-NDI face centered stacking).

#### 1.4.2 Mechanisms of Polymorphic Transitions

In the previous example, polymorphs were said to have different optical properties, yet they were accessed by varying crystallization parameters. An ability to access different colored polymorphs, by transforming one polymorph into the other with the application of an external stimulus, could enable different colored polymorphs to become a colorimetric sensor. As mentioned at the beginning of section 1.4, numerous different properties beyond color (electrical, physical, etc.) can change between two given polymorphs. Thus, polymorphism can become a functional design principle for materials when combined with the ability to *form and interconvert* various polymorphs,<sup>68</sup> where dynamic materials can be formed from simply the interconversion of individual chemical entities.

A number of different classification systems exist<sup>69, 79</sup> to characterize and describe polymorphic transitions, that is, the interconversion of multiple polymorphs, and a few of these systems will be described for the sake of completeness. In the late 19<sup>th</sup> century, Lehmann characterized two different types of polymorphism: "Monotropic" polymorphism, was said to be when one polymorph irreversibly transforms to a second and "enantiotropic" polymorphism, is when two polymorphs can undergo a reversible phase transition.<sup>72</sup> Ehrenfest's classifications<sup>80</sup> are instead based on thermodynamic quantities (e.g. entropy), and how those quantities change

during the polymorphic transitions. First order transitions are defined as those that have entropy, or volume changes and are further characterized by having an infinite heat capacity at the transition point, as all energy being added to the system is driving the transition, as opposed to increasing the temperature of the system.<sup>69</sup> Second order transitions do not involve entropy or volume changes, and have a continuous first order derivative of free energy, but do have second order discontinuities in heat capacity, thermal expansivity, and compressibility.<sup>69</sup> Other classifications put forth are based on structural relationships between the two phases, or the continuity of phase transitions. In the latter, put forth by Ubbelohde,<sup>79</sup> continuous transitions are those that have continuous, "smooth" transitions from one phase to the other, while discontinuous transitions are just that.<sup>69</sup> A final note on terminology, this dissertation treats the terms *polymorphic transition* and *polymorphic transformation* as synonymous and will use them interchangeably, following the work of Anwar and Zahn.<sup>69</sup>

While previously mentioned classification systems provide a very brief introduction to terms used to classify polymorphic transitions throughout the literature, a different type of classification dominates the most recent descriptions of polymorphic transitions in functional materials. In materials related fields, polymorphic transitions are divided into two general transition types: either nucleation and growth transitions, or cooperative/martensitic transitions. Martensitic transitions are named after the transition that accompanies the rapid cooling of the austenite form of iron to yield the hard steel known as martensite.<sup>81</sup> This transition is a rapid, diffusionless, first-order transition that is accompanied by the cooperative movement of atoms<sup>82</sup> and may also be referred to as a displacive or cooperative transformations.<sup>69, 83</sup>

Most phase transitions are believed to begin through initiation mechanisms that, in general, resemble nucleation and growth processes.<sup>69, 82</sup> In martensitic transitions, the transition initiates in an activated process displaying first order kinetics.<sup>82, 84</sup> Nucleation and growth transitions operate similarly to the nucleation of crystals in solution, where nucleation of a 'daughter' phase in the solid-state initiates polymorphic phase transitions.<sup>85, 86</sup> Nucleation mostly occurs at 'preferred sites', that in general provide accessible degrees of freedom in the form of

edges, surfaces, grain boundaries, or point defects in a solid<sup>69</sup> and growth of this nucleated phase is noted to often disrupt the integrity of the initial crystal.<sup>83</sup>

In general, polymorphic transitions are believed to operate at a phase contact interface, that involves the simple relocation of molecules from the parent phase to the new daughterphase, where the movement occurs between a small gap between phases, and not through an intermediate amorphous layer (Figure 1.12).<sup>69, 85, 86</sup> However, polymorphic crystal-to-crystal transitions that do proceed through a transient amorphous phase have been reported.<sup>87</sup>



Figure 1.12 General scheme for polymorphic transitions operating at a transition interface, where by simple translational and rotational movements allow for molecule by molecule transition. A single molecule highlighted in green is seen detaching from the parent phase then reattaching and aligning to the growing daughter phase.<sup>81</sup>

Recent work has shed light on the variable nature of phase transition interfaces and these interfaces are noted to vary in nature. In some cases, transitions are sharp boundaries, modeled to operate on length scales of 0.1-1 nm, with an average transition front of approximately half a molecular layer.<sup>69</sup> However, more diffuse transition boundaries have been proposed in the past two decades. Molecular dynamics (MD) simulations of phase transitions in ionic compounds, have been reported to propagate through the "liquid-like" movement of individual components, followed by "freezing" the newly formed daughter phase expanding through multiple molecular layers.<sup>88</sup> While shown in ionic compounds involved in high pressure simulations, these more diffuse transition phase boundaries seem plausible with the conditions that can favor the liquid-like movement of individual species.

Support for transition boundaries that expand length scales beyond 10 nm have found support from in recent MD simulations for organic molecules in the phase transition seen in DLnorleucine.<sup>89</sup> In 2013, Zahn and Anwar used MD simulations to show that the  $\beta \rightarrow \alpha$  phase transition in DL-norleucine crystals involved concerted molecular displacements, and not a nucleation and growth mechanism. The authors reported that the mechanism was likely to involve a compression wave that has a wavelength larger than the 10 nm simulation cell, and that the length scale for other molecular displacements would have a dependence "on the compressibility of all the molecules along the displacement direction and be limited by defects within the crystal structure."<sup>89</sup>

An excellent summary detailing the key differences between the two polymorphic transition mechanisms (nucleation and growth or cooperative/martensitic) is shown in Figure 1.13. Martensitic (cooperative) transitions can be characterized by fully cooperative, diffusionless transitions that proceeds in a layer-by-layer manner, moving very fast (rates of  $10^3 - 10^7$  mm s<sup>-1</sup>) with near perfect correspondence in orientation between the parent and daughter phases and often small changes in lattice parameters between the two phases. In contrast, nucleation and growth transitions operate through significantly slower, diffusion-based reorganizations that move through the material in a molecule-by-molecule fashion, with relatively large overall changes in packing, and no orientational relationship between the parent and daughter phase.



Figure 1.13 General properties seen in the two different polymorphic transition mechanisms encountered in polymorphic materials literature. Republished with permission of Royal Society of Chemistry from Ref<sup>82</sup>; permission conveyed through Copyright Clearance Center, Inc.

Park and Diao have classified<sup>82</sup> the relatively small changes seen in Martensitic transitions as being translational, conformational, or rotational in nature, and as shown in Figure 1.14, the daughter phase produced after the transition shows strong similarities to the parent phase.



Figure 1.14 Three different types of changes give rise to Martensitic (cooperative) polymorphic transitions, all of which result in relatively small changes to the unit cell parameters. Republished with permission of Royal Society of Chemistry from Ref <sup>82</sup>; permission conveyed through Copyright Clearance Center, Inc.

It is worth noting that, Christian<sup>77</sup> and others have noted that many transitions do not cleanly fit into this binary nomenclature created to describe transitions very different than that seen in metallurgic contexts. Additional nomenclatures have been employed across the literature, and this dissertation does not serve as a comprehensive review. Yet one important example is worthy of being mentioned. Transformations that have correspondence between the parent and daughter lattice (a martensitic property) but also operate through long range diffusion (a nucleation and growth property) have been observed, and can be referred to as diffusional displacive transformations.<sup>77, 90</sup>

While a vast majority of polymorphic transition research is focused on materials applications, it is valuable to note biological examples of polymorphic transformations. Arguably the most interesting example is the martensitic transformation of the T4 bacteriophage virus,<sup>91</sup> a double stranded DNA tailed virus that infects *E. coli*, and is said to be "one of the most complex viruses".<sup>92</sup> The virus has a long viral sheath made up of six interacting helices, where each helix is assembled by monomeric gp18 proteins (Figure 1.15), and this viral sheath has two different conformations. In the elongated conformation, gp18 protein monomers that make up the viral sheath store energy like a stretched spring (Figure 1.15).<sup>92</sup> Compression of the outer viral sheath utilizes the rapid rotation and radial expansion of gp18 monomers that make up the sheath, releasing 25 kcal mol<sup>-1</sup> of energy per monomer.<sup>92</sup> The cooperative, martensitic transformation of this viral sheath enables a rapid compression of the cylindrical viral sheath, shrinking it from 925 to 420 Å in length.<sup>93</sup> This transition drives a rigid, viral DNA containing central tube, surrounded by the viral sheath, through the bacterial outer membrane, and enabling the viral DNA delivery and subsequent infection.



Figure 1.15 The T4 bacteriophage viral sheath contracts following a martensitic transformation, resulting in compression of the viral sheath, enabling the delivery of viral DNA to the host. Gp18 proteins in three of the six helices shown in pink, blue, and green. Reprinted with permission from Ref.<sup>93</sup> Copyright 2009 European Molecular Biology Organization.

#### **1.5 POLYMORPHIC STIMULI-RESPONSIVE MATERIALS**

Many materials exploit polymorphism as a functional property that allows some form of reporting.<sup>68</sup> Polymorphic phase transitions have been thoroughly reviewed<sup>82</sup> including in experimental,<sup>94</sup> computational,<sup>69</sup> and theoretical contexts.<sup>95</sup> Stimuli induced polymorphic color switching has been achieved in the solid-state following the application of various types of external stimuli including heat,<sup>64</sup> pressure,<sup>96</sup> mechanical force,<sup>87, 97-99</sup> electric potential,<sup>100</sup> and exposure to various analytes including salts<sup>101</sup> and solvent.<sup>102</sup> Stimuli-responsive materials that induce macroscopic and photophysical changes have been extensively investigated and reviewed,<sup>103-105</sup> and show promise for mechanical applications including actuators<sup>106-109</sup> and self-
healing materials.<sup>110, 111</sup> Covalent modifications of polymorphic systems have been effectively used to impart tunability in various color changing, stimuli-responsive systems.<sup>60, 112</sup>

Computational efforts have successfully modeled polymorphic transformations, but have been limited to small molecules<sup>81, 109, 113</sup> or larger, rigid systems<sup>107</sup>. Experimental insights into the mechanisms by which polymorphs interconvert would better inform the future design of novel polymorphic systems. While numerous examples for color changing materials that rely on polymorphism exist, elucidating the molecular mechanisms by which these materials change is experimentally challenging because many experimental techniques employed only provide a time and space average of structural information.<sup>69</sup> Application of external stimuli to polymorphic systems containing flexible substituents (e.g. alky chains) often involve switching between crystalline and non-crystalline states, with structures of the latter often being inferred from structural information like powder XRD.<sup>64, 101</sup> A subset of reports on polymorphic transitions have been able to correlate macroscopic changes to specific nanoscopic reorganization.<sup>83, 84, 109, 111, 114-120</sup>

A recent example of this was when Ito and co-workers correlated molecular rearrangements to macroscopic mechanical motion from the anisotropic strain release in thermosalient crystals.<sup>120</sup> This thermosalient effect is a rapid, cooperative displacement of molecules, and thus falls within the class of martensitic (or displacive, cooperative) transformations.<sup>69, 83</sup>

# 1.5.1 Amphiphilic Dipolar Luminescent Materials via Metastable States

Although it is the aromatic  $\pi$ -system that directly influences the electronic and photophysical properties of the system, substituents appended to aromatic molecules are a critical and determining factor in the solid-state electronic,<sup>121</sup> spectroscopic and stimuli-responsive properties of solid-state stimuli-responsive systems.<sup>122</sup> An example of utilizing substituents on aromatic systems to influence photophysical properties in the solid-state came

from Yagai, Ito, and co-workers, presenting a design principle for stimuli-responsive color switching materials that exploit polymorphism through competing interactions between aromatic lumiphores and appended side-chains (Figure 1.16).<sup>101</sup> By constructing amphiphilic and dipolar characteristics into a single molecule, different metastable polymorphic states were stabilized through competing intermolecular interactions of the dipolar aromatic core, a hydrophilic sidechain, and a hydrophobic sidechain. It is worth noting that this system self-assembled through the formation of alternating aromatic, hydrophilic, and hydrophobic layers. The same group has also reported stimuli-responsive systems that exploit the switching between multiple accessible polymorphs through mechanically induced crystal-to-crystal transformations.<sup>87, 94, 99, 123</sup>



Figure 1.16 Structures representative of Ito's amphiphilic dipolar luminescent materials<sup>101</sup> and Lam's fused ladder thioarenes,<sup>118</sup> both of which show thermally induced polymorphic phase transitions.

#### 1.5.2 Reversible Crystal-to-Crystal Transition in Ladder Thienoarenes

Abe, Lam, and coworkers<sup>118</sup> characterized reversible crystal-to-crystal transitions involving two distinct reorganizations in donor dithienocyclopenta-thieno-[3,2-b]thiophene (DTCTT) derivatives with variable side chains (Figure 1.16). Their work highlighted the influence of multiple different intermolecular interactions on thermally induced polymorphic transitions, specifically noting the role of side chain size and flexibility as well as the influence of heteroatoms in this polymorphic system.

Disc shaped DTCTT derivatives were seen to assemble as 1-dimensional columns, and certain derivatives were seen to undergo reversible crystal-to-crystal transitions when heated. Upon heating the di(HTh2BT)DTCTT derivative, shown in Figure 1.16, a continuous reorganization between columns was seen to precede a second, discontinuous phase transition, characterized by a change in DTCTT aromatic stacking and further intercolumnar reorganizations. The multiple transitions observed in the di(HTh2BT)DTCTT derivative (Figure 1.16) was attributed to a complex interplay between various intermolecular interactions, including stabilizing aromatic and S-S interactions between adjacent stacked DTCTT cores, competing with repulsive interactions derived from bulky spirocyclic phenyl groups, and rotationally flexible benzo-[2,1,3]thiadiazole (BT) and thiophene (Th) end groups.

In contrast to the reversible transition in the dithiophene containing derivative di(H<u>Th2</u>BT)DTCTT in Figure 1.16, a derivative only differing by a single thiophene unit in each side chain (diH<u>Th</u>BT side chains) did not show reversible solid-state polymorphism. This difference in transition behavior was reported to reflect the critical role of side chains for imparting the structural flexibility required for this solid-state polymorphic transition, highlighting the role that small structural changes can impart on polymorphic transitions.

### 1.5.3 Alkyl Rotor Driven Crystal Deformation

Systems containing alkyl groups are noted to be instrumental for many thermally induced polymorphic transitions. In the previous example, aromatic and alkyl side chains provided the flexibility for imparting polymorphic transition behavior. Yet in other systems, polymorphic transitions have been attributed to rotational motion of relatively small alkyl chains, with possible applications as molecular rotors. Su, Sato, and coworkers reported single crystals capable of reversible and repeatable crystal expansion and contraction by exploiting thermally induced rotational isomerization of an *n*-butyl ester containing cobalt (II) complex (Figure 1.17).<sup>116</sup> Analysis of single-crystal structures showed that the Co(II) complex formed 1D columns stabilized by aromatic and shape-complementary van der Waals interactions, and 3D molecular packing was dominated by non-conventional C-H…O hydrogen bonding. Heating of this complex resulted in rotational isomerization of the butyl side-chain, form anti in the lower temperature polymorph to a gauche conformation in the higher temperature polymorph (Figure 1.17). Increased intermolecular repulsion following isomerization, causing contraction about the crystal long axis in a repeatable fashion.



Figure 1.17 Anisotropic crystal expansion seen following conformational isomerization of an *n*-butyl ester cobalt complex, with reversible and repeatable cycling in successive heating-cooling cycles. Adapted from Ref.<sup>116</sup>

# 1.5.4 Peebles' Donor-Acceptor MAN-NI Dyads

As part of the Iverson groups comprehensive supramolecular program focused on NDI and its analogs and introduced previously, a series of molecules were synthesized incorporating naphthalene monoimides (NI) covalently linked via an alkyne to monoalkoxynaphthalenes (MAN) with *n*-alkyl side chains (Figure 1.18). As noted previously, several of these MAN-NI donor-acceptor dyads showed a dramatic difference in solid-state color between solids created from relatively faster (yellow, Figure 1.18g) and slower (orange, Figure 1.18f) evaporation from solution.<sup>63</sup> However, in addition to these different optical properties, interesting color changing properties were found when external stimuli was applied.



b) Yellow crystals of 1f



c) Yellow-orange crystals of 1s



d) Orange crystals of 4s





Figure 1.18 Proposed packing of MAN-NI dyad polymorphs with different optical properties and the formation of different polymorphs of **4** shown in the bottom, either grown as an orange solid with red emission when grown by slower evaporation (panel f), or grown as a yellow solid with green emission from faster evaporation (panel g). Reproduced from Ref. <sup>64</sup> with permission from The Royal Society of Chemistry. In the solid-state, one of the dyads (dyad **4** in Figure 1.18a) was found to change color in response to grinding (orange to yellow, Figure 1.19a-b), heating (orange to yellow, Figure 1.20), and vapor fuming (yellow to orange, Figure 1.19c-e), with repeatable cycles of color changing.<sup>64</sup>



Figure 1.19 Mechanochromic and halochromic -responsive properties of the octyl MAN-NI dyad. a) grinding of the letters "UT" convert the drop cast orange material yellow, and b) vapor fuming with DCM reverts back to the orange form. c-e) POM images show thermally heated yellow material return to an orange form following exposure to DCM vapor. Reproduced from Ref. <sup>64</sup> with permission from The Royal Society of Chemistry.

Similar to the thermochromic behavior of independent DAN and NDI mixtures previously described, the change in color was determined to result from a conformational change of the aromatic units. Based upon single crystal data, X-ray diffraction (XRD) patterns, and modeling, the stimuli-responsive behavior was reported to result from a conformational switch between the two stable polymorphs previously accessed by varying crystal growth time (section 1.4.1).

When ground or heated, the orange crystalline form, possessing a head-to-head (NI-NI) stacking geometry (Figure 1.19d), interconverted to a yellow soft crystalline mesophase with a head-to-tail (NI-MAN) stacking geometry (Figure 1.19e) that persisted at room temperature in the absence of solvent vapor, an indication that both packing geometries have kinetic stability. Figure 1.20 shows the conversion of the orange crystalline form to the yellow soft crystalline mesophase, while maintaining macroscopic morphology, when heated at 110°C for 30 seconds. Interestingly, and in contrast to many of the polymorphic systems previously described, the stimuli-induced thermochromic transition of this MAN-NI dyad proceeded without altering the microscopic morphology of the original crystal (Figure 1.20).



Figure 1.20 Overall proposed dyad packing and stimuli-responsive properties seen in the octyl MAN-NI dyad. Adapted from Ref. <sup>64</sup> with permission from The Royal Society of Chemistry.

From this initial dyad series, it was clear that both substitution position and side chain identity played a role in the stimuli-responsive properties, as only the 1,4-substituted MAN with n-Octyl chains (dyad 4, Figure 1.18) was capable of stimuli-responsive colorimetric switching behavior. However, the photophysical basis for the differences in polymorph color as well as the

structural basis for stimuli-responsive colorimetric switching was unclear, as a single-crystal structure of the yellow polymorph was not yet solved.

# **1.6 INFLUENCE OF MOLECULAR PACKING ON SPECTROSCOPIC AND STIMULI-RESPONSIVE PROPERTIES**

Variations in optical and spectroscopic properties in different polymorphs arise from various photophysical processes. Differences in color of aromatic molecules packed in the solid-state are often attributed to general differences in intermolecular packing and specific photophysical origins for these differences have been reported to arise from numerous different mechanisms. Photophysical origins for differences in color have been in hundreds of examples and have been attributed to changes in types and extent of and intermolecular charge-transfer complex formation,<sup>60, 61, 124-127</sup> changes to H/J aggregate formation, <sup>123, 101, 128</sup> on-off switching of FRET in bicomponent mixtures,<sup>129</sup> excimer<sup>98</sup> and exciplex formation,<sup>130</sup> changes to aurophilic interactions in organo-gold complexes,<sup>87, 131</sup> aggregation induced emission (AIE)<sup>96, 132</sup>, as well as being attributed to general conformational or packing differences between the two states that change overlap of  $\pi$ -systems. <sup>98, 133-136,</sup>

In contrast to intermolecular mechanisms that give rise to different optical properties, intramolecular processes can also change optical properties, including from intramolecular charge-transfer mechanisms<sup>137</sup> as well as conformational based changes. For example, Minakata and co-workers reported a tri-color mechanically responsive polymorphic system that had multiple colors resulting from changes in rotations of terminal donor units within a three component donor-acceptor-donor complex.<sup>138</sup> Rotations of these terminal units resulted in changes in the relative energies of frontier orbitals, and the different colors were attributed to these changes in frontier orbital energies.

In the solid-state, slight changes in molecular packing can dramatically alter the optical and electronic properties of conjugated materials through various mechanisms that can operate in isolation or parallel.<sup>139-141</sup> For example, long-range electronic coupling between molecules, that is dependent on the alignment of transition dipole moments, can alter the spectroscopic properties of solid-state systems compared to free molecules.<sup>141</sup> In addition, short-range intermolecular interactions that manifest through direct orbital overlap, especially through LUMO-LUMO and HOMO-HOMO overlap, can facilitate the delocalization of locally excited states into delocalized excitonic charge-transfer (CT) states.<sup>140, 141</sup> While these intermolecular excitonic interactions are distinct, the net electronic coupling experienced is a product of the interference between short- and long-range coupling.<sup>141</sup>

# **1.6.1** Chung's Switch in Mechanism of Polymorphic Switching: Cooperative or Nucleation and Growth Mechanisms

Previously, side chain size was shown to influence the reversibility of polymorphic transitions in fused ladder thienoarenes. In addition to the influence side chains can have on accessing various polymorphs, size chain differences can alter the mechanisms by which polymorphs interconvert.

Chung, Diao, and coworkers have investigated cooperative polymorphic transitions in single crystals of ditert-butyl [1] benzothieno[3,2-b][1]1benzothiophene (ditBu-BTBT) and 13-bis(triisopropylsilylethnyl) pentacene (TIPS-pentacene).<sup>119</sup> Single crystals of either semi-conductor were shown to undergo a reversible, thermally induced phase transitions characterized by a rapid, concerted movement of the polymorphic phase boundary through the crystal, resulting in a small shape change. In ditBu-BTBT crystals, the cooperative phase transition initiated from rotation of the tert-butyl side chains and, interestingly, was seen to move through crystals two distinct pathways, moving either parallel or perpendicular to the (001) crystal face. Using TIPS-pentacene, they showed a similar martensitic transition took place, and concluded

that rotational motion caused by the order to disorder transition of bulky tert-butyl side chains was a generalizable mechanism to induce cooperative transitions.

Follow-up work by the same group highlighted the sensitivity of the transition mechanism.<sup>83, 142</sup> A single atom substitution in BTBT side chains, from tert-butyl to trimethylsilyl (TMS), changed the mechanism from a cooperative, rapid transition (average transition speed 176  $\mu$ m s<sup>-1</sup>) to a slower nucleation and growth mechanism (average transition speed 1.8  $\mu$ m s<sup>-1</sup>) (Figure 1.21).



Figure 1.21 Different side chains on BTBT derivatives yield materials that have polymorphic transitions that proceed through different transition mechanisms. Nucleation and growth mechanisms proceed in variable orientations, at rates 2 orders of magnitude slower. Adapted with permission from Ref.<sup>83</sup> Copyright 2019 American Chemical Society.

Changes to unit cells following the nucleation and growth transition in the TMS derivative, and the cooperative transition in the tert-butyl derivative are shown in Figure 1.22a and 1.22b, respectively. Importantly, the cooperative transition involving the tert-butyl derivative is seen to result in smaller changes to unit cell parameters, as well as a smaller change in the edge-to-face interaction angle between BTBT cores when compared to the nucleation and growth pathway (Figure 1.22a-1.22b).



Figure 1.22 Different side chains on BTBT have polymorphic transitions that proceed through different transition mechanisms. Nucleation and growth mechanisms in TMS side chain derivatives. show larger unit cell changes with interlocked side chains. Cooperative transitions (martensitic) reveal *t*-butyl side chains with rotational motion and no contacts to adjacent neighbors. Adapted with permission from Ref.<sup>83</sup> Copyright 2019 American Chemical Society.

As expected, the larger silicone atom and longer bonds in the TMS group result in a ca. 15% increase in the side chain radius compared to the tert-butyl group. The larger TMS group packs closer to adjacent molecules with short contacts to adjacent molecules, whereas no short contacts exist to the tert-butyl side chain. These differences prevent the TMS side chain from rotating freely (Figure 1.22c), while allowing rotational motion of the smaller tert-butyl side chain to rotate (Figure 1.22d).

As described previously, the trigger to initiate this rapid, cooperative transition was attributed to cooperative rotations of the bulky side chains appended to aromatic cores. Nucleation and growth pathways were reported from bulkier side chains, and attributed to decreased rotational motion thereby disfavoring the cooperative transition pathway. Further, the bulkier TMS groups decreased overall crystal packing density, which was said to in turn allow for multiple thermally accessible packing orientations, favoring nucleation and growth pathways. In contrast, cooperative transitions were said to arise from polymorphs with more dense packing that can allow for rotational motion, and said to be favored when changes in herringbone packing geometry are minimized between two polymorphs. Taken together, these works highlight the sensitivity of polymorphic transitions mechanisms to subtle structural modifications and underscore the role that thermal motion and side chain flexibility have on enabling various polymorphic transition pathways.

# CHAPTER 2

# Monoalkoxynaphthalene-Naphthalimide Donor-Acceptor Dyads: Synthesis, Structural and Spectroscopic Characterization<sup>1</sup>

# **2.1 CHAPTER SUMMARY**

## **2.1.1 Introduction**

Previous work on conjugated monoalkoxynaphthalene-naphthalimide (MAN-NI) donoracceptor dyads revealed multiple polymorphs that could be accessed by varying crystal growth parameters, and further, that stimuli-responsive properties could be achieved with certain sidechain substituents. Only one dyad in the initial series (symmetric, *n*-octyl side-chains) demonstrated dynamic and reversible stimuli-responsive behavior in the solid-state: colorimetric switching from orange to yellow when heated (thermochromic) or ground (mechanochromic), and reversal from yellow to orange following exposure to solvent vapor (solvatochromic). Previous comparative structural and spectroscopic studies led to the conclusion that the structure of both the grown and thermally generated yellow material had head-to-tail packing although the structure of the yellow polymorph was unknown. Key questions remained: can the amount of stimuli that induces the colorimetric switch be tuned by changing side-chain lengths, and what is the photophysical basis for the two differently colored polymorphs? This chapter describes the synthesis and characterization of new dyad derivatives, the materials they form in the solid-state,

<sup>&</sup>lt;sup>1</sup> This chapter was adapted in part from the published article: Wight, C. D.; Xiao, Q.; Wagner, H. R.; Hernandez, E. A.; Lynch, V. M.; Iverson, B. L., Mechanistic Analysis of Solid-State Colorimetric Switching: Monoalkoxynaphthalene-Naphthalimide Donor–Acceptor Dyads. *J. Am. Chem. Soc.* **2020**, 142 (41), 17630-17643. CDW designed and conducted experiments and wrote the manuscript with BLI.

and the photophysical origins for the differences in color displayed by various colored polymorphs.

#### 2.1.2 Scientific Questions

This work sought to answer the questions: *What is the definitive structure of the yellow polymorph? Can other dyad derivatives with different side-chain lengths form polymorphic materials? What are the photophysical origins of the differences in color between polymorphs? What colors are possible?* Understanding these effects will better elucidate the intermolecular interactions that help enable the emergence of stimuli-responsive properties and inform the design and synthesis of new solid-state materials with desirable properties, including tunable stimuli-responsive and colorimetric properties.

#### 2.1.3 Approach

The goal of this work was to investigate a structure activity relationship (SAR) of new MAN-NI dyads with varying alkyl chain lengths. This SAR would first investigate the ability of various MAN-NI dyads to form polymorphs before later evaluating how different side chains affect stimuli responsive properties (Chapter 3). The MAN-NI dyads explored were focused around the most promising MAN-NI dyad from the initial series: the 1,4-substituted MAN with *n*-octyl alkyl chains that showed promising stimuli-responsive behavior. As such, the SAR was focused around making derivatives with side chains longer and shorter than the octyl derivative. In addition, asymmetric dyads were explored to further investigate the role of side chain variation in polymorphic and stimuli responsive systems. This SAR involved the synthesis of various derivatives in order to solve single-crystal structures of the materials, something that had not previously been achieved. The overarching goals of this work were to understand what structural features in MAN-NI dyads (1) enable derivatives to form various colored polymorphs and (2) what is the structural and photophysical basis for the differences in color.



Symmetric Naming Convention: **R** 

Figure 2.1 Structure-activity relationship for investigating new monoalkoxynaphthalenenaphthalimide (MAN-NI) donor-acceptor dyads.

# 2.1.4 Results

A structure activity relationship study with 10 new MAN-NI dyads was carried out in order to better understand polymorphism in this series of molecules. Following synthesis, reproducible methods to readily grow crystals for nine derivatives were found, including accessing multiple polymorphs for four different symmetric dyad derivatives. Structural characterization using single-crystal X-ray diffraction allowed for eleven single-crystal structures to be solved for nine derivatives (eleven symmetric dyad crystals: 1 bright orange, 5 orange, 5

yellow; three asymmetric dyad crystals: 1 yellow-orange, 1 gold, 1 yellow). Spectroscopic analysis of dyads in solution and in the solid-state was completed. The photophysical basis for the various colored dyads was determined based on a combination of structural, theoretical, and spectroscopic analyses.

#### **2.2 RESULTS**

# 2.2.1 Synthesis of Dyads

Dyads were synthesized following previously reported procedures.<sup>63</sup> A synthetic scheme detailing intermediates and dyads synthesized is shown in Scheme 2.1. General information and detailed synthetic procedures and characterizations for each dyad and intermediate can be found in sections 2.5.1 and 2.5.6, respectively.

Access to 4-bromo-1-naphthol could be achieved on a 30 g scale in decent yield. From this common intermediate, the MAN portion (Figure 2.1) of each dyad could be accessed in 3 steps: alkylation with Williamson ether synthesis, Sonogashira cross-coupling to install the alkyne coupling partner, and deprotection to afford the terminal alkyne MAN unit. On the other side of the dyad, the NI portion was accessed in a single step from commercially available 4-bromo-1,8-naphthalic anhydride.



Scheme 2.1 Synthetic scheme for the synthesis of all dyads. Note, dyads with symmetric alkyl side chains are named with a single number (e.g. 6, for hexyl side-chains), while asymmetric dyads are named according to the length of alkyl chain on the Monoalkoxynaphthalene unit as well as the side chain on the Naphthalimide (e.g. M6N8, see Figure 2.1).3

#### 2.2.2 Crystal Growth

Consistent with initial reports of MAN-NI dyads, several of the dyads in this study crystallized as orange (**o**) or yellow (**y**) polymorphs, and different crystallization methods were employed to grow either the orange or yellow crystals. High-quality X-ray diffraction capable single crystals were grown primarily using slow-evaporation or vapor diffusion. Crystal growth conditions for crystals that resulted in single-crystal structures are shown in Scheme 2.2.



Scheme 2.2 Crystal growth conditions that formed crystals yielding single-crystal structures with the exception of **80**. \*Crystal structure previously reported<sup>64</sup> and grown via indicated slow conditions. Vapor diffusion conditions provide the same **80** polymorph.



Figure 2.2 Top: Side-by-side pictures of yellow, orange, and bright orange crystals grown from solution highlight color differences between individual crystalline samples. Bottom: Z-stacked optical micrographs of various derivatives representative of yellow and orange polymorphs.

Pictures and Z-stacked optical micrographs of various crystals are shown in Figure 2.2. A side-by-side comparison of crystal colors shown at the top highlights the subtle variation in colors that exists in yellow symmetric crystals **6y**, **7y**, and **8y**. Note that **1bo** has both a very unique orange color compared to other dyad crystals, and also it forms characteristic thread like needles, in stark contrast to all orange crystals with two dimensions of obvious growth. Symmetric orange crystals had nearly identical color to the naked eye, although larger orange crystals often appeared more red when compared to smaller crystals.

Hundreds of different crystal growth conditions were screened during the course of this work, and a few general trends stand out. Orange crystals were best formed using vapor diffusion methods, and a single method could be used to form all orange crystals: vapor diffusion of the dyad in a solvent of *p*-xylenes with acetonitrile as the precipitant. In general, for a given symmetric dyad, orange crystals grew as shorter and wider crystals that had more structural integrity compared to their longer, more brittle, needle-like yellow counterparts. However, symmetric orange crystals tended to become shorter and narrower as alkyl side chain length increased: crystals of **60** over 1 cm in length could be consistently prepared using the conditions shown in Scheme 2.2. In contrast, and despite a variety of conditions, variations in concentration, and crystal growth temperature, most crystals of **100** and **120** were smaller than 1 mm in their longest dimension. Uniquely, and despite examining dozens of growth conditions, **1** only crystallized as a single polymorph (**1b0**), forming bright orange needles (Figure 2.2).

Yellow crystals could be formed by a combination of slow evaporation and vapor diffusion methods. Slow evaporation often yielded crystals with multiple different colors and morphologies, a likely indication of the formation of multiple different polymorphs within a single crystal growth vial. Symmetric yellow crystals were exceptionally brittle for derivatives with alkyl chains longer than heptyl. Yellow crystals of **9** and **10** were formed using slow evaporation methods, but even the slightest manipulation of these soft crystals would bend/break them.

Symmetric orange crystals grown from solution were better diffracting, higher quality crystals with smaller R-factors and no atoms with multiple site occupancies. In contrast, yellow symmetric polymorphs had more disorder, especially in alkyl side chains. Asymmetric dyad crystals displayed dramatic differences in optical and microscopic characteristics between the M6N8/M8N10 derivatives and M8N6/M10N8 derivatives, yet certain similarities were observed within each set of derivatives. The M8N6 and M10N8 derivatives grew crystals that had colors of gold and yellow-orange, respectively, although liquid and plastic crystals of these could be formed in several solvent conditions. Both of these derivatives with the longer alkyl chain on the

MAN unit grew more structurally robust crystals than most yellow symmetric crystals, and had more structural integrity than most orange crystals with side chains longer than 8 carbons. Between **M8N6** and **M10N8**, the **M8N6** crystals consistently had more growth in two dimensions compared to **M10N8** derivatives. While not as big, **M10N8** was able to form several subtly different colored crystals ranging from canary yellow to yellow-orange; however, characterization of yellow-most derivatives was not possible, as these crystals were extremely flexible and would easily bend/break when a small amount of pressure was applied.

Within the asymmetric series shown at the bottom of Figure 2.2, **M8N6** and **M10N8** are noted to have formed sturdy gold and yellow-orange crystals, respectively. These crystals were both different in color and had more structural integrity compared to symmetric yellow crystals and yellow crystals of **M6N8**. In contrast to all three other asymmetric derivates that formed materials with yellow hues, **M8N10** was unique in the asymmetric series: it would only grow as very small (ca. 100 µm) flexible, thread like needles that were orange to red-orange in color.

#### **2.2.3 Single-Crystal Structures**

In addition to the single-crystal structure of **80** previously reported,<sup>64</sup> 14 additional unique crystal structures were solved for the 12 dyads in this study by means of single-crystal X-ray diffraction analysis. A summary of the crystallographic data for all dyad single-crystal structures is presented in Table 2.1 (orange and bright orange) and Table 2.2 (yellow and asymmetric). Before commencing a discussion of crystal packing and features of different dyad crystals, descriptors that will be used to describe dyad packing in the solid-state will be described.

	Dyad Crystal Structure									
	60	70	80	90	100	120	1bo			
a (Å)	4.69	4.68	4.67	4.67	4.67	4.67	17.81			
b (Å)	38.87	41.44	43.93	46.58	49.08	54.24	26.10			
c (Å)	15.56	15.42	15.52	15.39	16.71	15.48	3.85			
$\alpha$ (deg)	90	90	90	90	90	90	90			
$\beta$ (deg)	96.18	94.88	96.88	94.23	112.97	96.01	90.00			
γ (deg)	90	90	90	90	90	90	90			
Volume [Å <sup>3</sup> ]	2,818	2,978	3,163	3,340	3,524	3,896	1,790			
Space Group	Сc	Сc	Сc	Сc	Сc	Сc	<b>P</b> n a 2 <sub>1</sub>			
Chemical Formula	C <sub>36</sub> H <sub>37</sub> NO <sub>3</sub>	$C_{38}H_{41}NO_3$	C40H45NO3	$C_{42}H_{49}NO_3$	C44H53NO3	$C_{48}H_{61}NO_3$	$C_{26}H_{16}NO_3$			
MW [g mol <sup>-1</sup> ]	531.67	559.72	587.77	615.82	643.87	699.98	391.41			
Density [g cm <sup>-3</sup> ]	1.253	1.248	1.235	1.225	1.214	1.193	1.452			
Z	4	4	4	4	4	4	4			
R (reflections) [%]	5.09	6.26	19.05	6.84	9.47	8.17	11.72			
wR2 (reflections) [%]	11.96	17.58	33.77	21.19	29.52	20.03	35.40			

Table 2.1Crystallographic information for all orange and bright orange dyad single-crystal<br/>structures.

	Dyad Crystal Structure										
	6y	6y'	7y	7 <b>y'</b>	8y	M10N8	M8N6	M6N8			
a (Å)	8.78	10.76	53.03	15.60	56.52	24.61	24.73	10.76			
b (Å)	13.46	10.79	7.44	7.44	7.43	5.03	4.94	10.78			
c (Å)	24.03	24.71	15.49	105.36	15.49	56.37	50.62	26.51			
a (deg)	88.39	95.31	90	90	90	90	90	85.57			
$\beta$ (deg)	87.33	98.74	94.61	90.96	95.81	99.55	101.29	85.58			
γ (deg)	81.92	93.19	90	90	90	90	90	87.08			
Volume [Å <sup>3</sup> ]	2,809	2,816	6,090	12,223	6,470	6,886	6,069	3,053			
Space Group	P -1	P -1	P 21/C	I 2/a	Сç	C 2/c	C 2/c	P -1			
Chemical Formula	C <sub>36</sub> H <sub>37</sub> NO <sub>3</sub>	C <sub>36</sub> H <sub>37</sub> NO <sub>3</sub>	$C_{38}H_{41}NO_3$	$C_{38}H_{41}NO_3$	C40H45NO3	C42H49NO3	$C_{38}H_{41}NO_3$	$C_{38}H_{41}NO_3$			
MW [g mol <sup>-1</sup> ]	531.67	531.67	559.72	559.72	587.77	615.82	559.72	559.72			
Density [g cm <sup>-3</sup> ]	1.257	1.254	1.221	1.217	1.207	1.18	1.225	1.218			
Z	4	4	8	16	8	8	8	4			
R (reflections) [%]	5.46	7.72	5.73	22.25	9.89	16.55	15.49	10.74			
wR2 (reflections) [%]	16.11	23.45	17.54	57.59	29.05	44.40	41.27	33.33			
Multiple Side Chain Occupancy	52:48 for last 3 C atoms in one MAN chain of asymmetric unit	N/A	57:43 for last 6 C atoms in one MAN chain of asymmetric unit	50:50 for last 5 C atoms in one MAN chain; 50:50 for last 6 C atoms in NI unit below that MAN	N/A	N/A	N/A	N/A			

 Table 2.2
 Crystallographic information for all yellow and asymmetric dyad single-crystal structures.

# 2.2.3.1 Descriptors for Dyad Packing in the Solid-State

In general, polycyclic aromatic molecule stack together in the solid-state in a way that maximizes aromatic interactions. As such, in the solid-state, MAN-NI dyads form 1-dimensional columns (or stacks) from the stacking of aromatic dyad cores. It is useful to describe the stacking of dyads using two different terminologies to describe both the orientational and translational relationship between adjacent dyads within columns.

Dyad cores are asymmetric with a long and short molecular axis. Adjacent dyads within a column are always seen to stack with alignment of long and short molecular axes, respectively. Thus, two different orientations of dyad stacking are possible: head-to-head, with adjacent NI-NI

stacking, or head-to-tail, with adjacent NI-MAN stacking. Figure 2.3 shows a cartoon depiction of these two dyad aromatic stacking geometries. It is worthwhile to note that despite the relatively low rotation barrier around the internal alkyne, all crystal structures were solved with the two naphthyl rings of the aromatic core in the *trans* conformation.



Figure 2.3 Aromatic stacking geometries and molecular slip are two ways to describe how dyad cores stack in columns.

A second description to describe stacking geometry is based on the translational relationship between adjacent dyads (top right of Figure 2.3). Translational movements of adjacent dyads that maintain alignment of the respective molecular axes will be discussed as having a 'molecular slip' or having an 'offset slip-stacking geometry'. Molecular slip for dyad crystal structures was calculated using a MATLAB script that involves the input of crystallographic parameters, defining a crystallographic coordinate system, and calculating centroids for each dyad core, as shown in in Figure 2.3.

In order for molecular slip calculations to be comparable, a consistent coordinate system must be defined, as shown in Figure 2.3. The long axis slip was defined by an axis made from the atoms 'X1' and 'X2' of the NI unit. The short axis was defined by the carbon atoms labeled 'Y1' and 'Y2'. As the dyad is not symmetric about the defined axis, an arbitrary designation was chosen for orienting the reference dyad in order to consistently define positive and negative slip values (unambiguously highlighted by the distorted perspective shown in Figure 2.3). After defining a coordinate system and the reference dyad, the last necessary task is to define a centroid for both dyads, which was chosen to be defined by the 39 atoms of each aromatic dyad core. Finally, the translational slip can then be calculated for the dyad above the reference dyad, based on the relative translation displacement between the two centroids.

This calculation also yields the distance between dyad cores (Z axis displacement), although this dimension was the most consistent packing dimension for all dyad crystals. The spacing between aromatic cores is similar in all crystals, with an average distance of  $3.36 \pm 0.05$  Å for all 14 crystal structures. The major differences in crystal packing have to do with translations about the long and short molecular axis, and orientation differences, which are discussed in detail in the following sections.

#### 2.2.3.2 Symmetric Dyad Crystal Structures

Symmetric Crystal Packing Overview: Orange is Head-to-Head, Yellow is Head-to-Tail. For the derivatives 6, 7, and 8, multiple polymorphs were found. For these three molecules, two general packing motifs were consistently observed: orange crystals (O) were always observed to be stacked with the dyad cores in a head-to-head geometry and yellow crystals (Y) were always observed to be stacked with the dyad cores in a head-to-tail geometry. Two structures were solved for yellow hexyl (6y and 6y') and heptyl (7y and 7y') polymorphs, with each set of polymorphs having similar packing of aromatic cores and the largest differences being manifest in side-chain packing. It is critical to note that all of the solved crystal structures only contain the pure dyad; *solvent was never observed within the crystalline lattice*.

**Orange Symmetric Dyad Crystals.** With the notable exception of 1, all symmetric dyads formed orange crystals with strikingly similar packing features that will be discussed in terms of the three special dimensions. In all six orange crystals (**60**, **70**, **80**, **90**, **100**, and **120**), dyads were found to adopt a head-to-head stacking geometry with remarkably similar slip-stacking: an average long axis displacement of  $3.07 \pm 0.03$  Å and a short axis displacement of  $1.0 \pm 0.1$  Å (Figure 2.4). Alkyl side-chains in these crystals were found to be exclusively in the staggered-anti conformation (torsional angles of  $180 \pm 5^{\circ}$ ) of with one notable exception. The side chain adopts a gauche conformation coming off of the MAN oxygen atom, with the O-C-C-C dihedral angle (shown in magenta in Figure 2.4) averaging  $72 \pm 3^{\circ}$  for all six crystal structures.



Figure 2.4 Single-crystal structures of **60**, **70**, **80**, **90**, **100**, and **120** shown as head-to-head stacked dimers. Side-chains are exclusively in staggered-anti conformations, except the C-C bond extending off of the MAN oxygen atom.

In the six orange polymorph crystals, adjacent columns are nearly perpendicular about the long axis of the dyad (Figure 2.5). Columns have intercolumnar angles of  $87.53^{\circ}$  for **60**,  $86.97^{\circ}$  for **70**,  $87.66^{\circ}$  for **80**,  $87.03^{\circ}$  for **90**,  $87.81^{\circ}$  for **100**, and  $87.42^{\circ}$  for **120**, and an average intercolumnar angle of  $87.5 \pm 0.4^{\circ}$  for all six orange crystals (Figure 2.5). As shown in the upper portion of Figure 2.5, side chains (pointing up) are seen to pack in close proximity with side chains of dyads in adjacent columns in one direction of the column.



Figure 2.5 Dyads stack in one-dimensional columns, and in all orange crystals, adjacent columns are roughly orthogonal. A single dyad has aromatic contacts to four other dyads (blue dashed lines), and a unique -OCH<sub>2</sub>- to carbonyl oxygen hydrogen bond shown in the top right (green dashed line). Hydrogen atoms are omitted for clarity.

Several short-range contacts exist between adjacent columns and are believed to stabilize the orthogonal intercolumnar relationship. In the orange crystals, a single dyad molecule has short contacts (2.45 - 2.65 Å) to four different dyads, in two adjacent columns (shown in Figure 2.5 as blue dashed lines for **60**). For a single molecule, each NI carbonyl oxygen interacts with C-H bond(s) on adjacent MAN units in two different columns, and each side of the MAN unit has C-H contact(s) to NI units in adjacent contacts. Thus, these four contacts stabilize a given dyad in two dimensions and help enable the assembly of columns into layers. Within individual layers, three sub-layers exist: two alkyl chain layers on each side of a central aromatic layer.

In addition to interactions with four adjacent aromatic cores, unique non-typical hydrogen bonds are seen in all orange dyad crystals between alkoxy C-H bonds of alkoxy O-CH<sub>2</sub>- groups and adjacent NI carbonyl oxygens. As shown in the top right of Figure 2.5, the previously mentioned gauche conformation involving the MAN unit puts one hydrogen atom of the -OCH<sub>2</sub>methylene unit in close proximity to the carbonyl oxygen of a dyad in the adjacent column. This short-range interaction is consistent in all orange crystals, with an average separation of 2.63  $\pm$ 0.03 Å. The interaction is the most notable intermolecular contact between dyads and adjacent columns, and is believed to stabilize the interaction between adjacent columns, by 'locking' potentially rotationally flexible side chains into a static conformation. Freezing of these side chains aids in assembly in the third dimension required for crystal packing: the assembly of 2dimensional layers into 3-dimensional 'stacks' of layers.

Beyond the rotational 'locking' of the alkyl side chain, the gauche conformation forces the side-chain to 'turn' with the adjacent column, and allows for intimate side chain packing within layers.



Figure 2.6 Single-crystal structures of the indicated dyad derivatives with Hydrogen atoms omitted for clarity. In all orange crystals, alternating alkyl and aromatic layers are formed. The single gauche conformation in orange crystal side chains allows for the are interdigitation with the dyad side chains in the layer above and below, in a 'cork' and 'bottle' fashion. Hydrogen atoms are omitted for clarity.

As shown in Figure 2.6, side chain interactions between adjacent layers give rise to alternating alkyl and aromatic layers. A directionality in side chain packing is apparent when looking at two columns from above, as shown by the crystal structures in the upper portion of Figure 2.6. One side of the dyad long axis has side chains packed towards a specific column, and the other alkyl side chain then packs towards the opposite column. In doing so, the side chains can interdigitate with adjacent dyad layers, in a 'cork' and 'bottle' type analogy (shown in the top left of Figure 2.6) that allows side chains to 'zip up'. The dominant staggered-anti

conformations of side chains maximize alkyl side chain van der Waals contact between adjacent columns and further stabilizes the third dimension of crystal growth.

Figure 2.7 shows an overlay of four orange polymorphs – 70, 90, 100, and 120 – both as trimers and as two columns of trimers. Despite the dramatic difference of 10 carbon atoms, 70 and 120 have nearly identical packing within columns, highlighted by the hexamer overlay on the right of Figure 2.7.



Figure 2.7 Overlay of **70**, **90**, **100**, and **120** single crystals shows the remarkable similarity in 2D packing, with a common offset along the long-axis much like the offset of stairs in a stair case. Crystal structures shown as displacement ellipsoids set to the 50% probability level, and hydrogen atoms are omitted for clarity.

## Yellow Dyad Crystals.

Yellow symmetric dyad crystals were all found to have dyads packing in a head-to-tail geometry with two molecules in the asymmetric unit of the unit cell and similar molecular slip stacking geometries, as shown in Figure 2.8.



Figure 2.8 Symmetric dyads that form yellow crystals are shown to pack in one-dimensional columns with head-to-tail stacking geometries. Crystal structures shown as displacement ellipsoids set to the 50% probability level with multiple side chain occupancy shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

In head-to-tail **Y** polymorphs, slip-stacking can be calculated relative to either one of the two molecules in the asymmetric unit. As discussed in section 2.2.3.1, the method for calculating molecular slip requires defining a coordinate system and a single reference dyad. Thus, yellow symmetric crystals with two molecules in the asymmetric unit will have at least two slip stacking geometry values, because each molecule can be defined as the reference dyad for calculating the slip of the other. To complicate things further, symmetry operations that define each unit cell can add additional slip stacking possibilities. For example, triclinic cells with the P-1 space group (the space group for **6y**, **6y**', and **M6N8**) possess a center of inversion and have a total of four different unique slip stacking geometries for the two dyads of the asymmetric unit.

In light of multiple calculated slip-stacking geometries for several head-to-tail polymorphs, a new convention is needed to minimize the number of molecular slips that describe the overall column orientation and make results comparable across derivatives. The reason for the need to simplify is because the dyad is asymmetric about the long axis and the translational displacement between two centroids in head-to-tail stacking geometries is not an ideal indicator of the general way the column packs. Restated, head-to-tail stacked dyads can have calculated slips that are not reflective of the overall stacking within the column. The goal of this convention

is to yield a minimum number of calculated molecular slips that provide insight into how dyads stack overall as they build within columns. This new convention for molecular slip in head-totail dyads will provide comparative metrics for how dyads are assembled within columns, rather than how each individual dyad sits above another as determined by translational displacements of the centroid.

Shown in Figure 2.9 is a column made from stacked derivatives of **6y**, and going across the figure to the right, the column is sequentially rotated in 90° increments, showing all 4 sides of the column. With a goal of understanding how slip is calculated and the need for a new convention in head-to-tail dyads, we begin by first choosing the reference for the measurement. The initial choice for which dyad to begin calculating slip stacking geometry is arbitrary; the only requirement is the orientation requirement defined previously (MAN unit on left, NI on right, MAN unit projecting toward the observer, see Figure 2.3). Shown on the bottom of the left most column is a red colored dyad fulfilling this requirement.



Figure 2.9 Dyads packed in head-to-tail columns have challenges associated with calculating slip values that easily convey overall column orientation and yield values that are comparable across different derivatives. A convention for reporting head-to-tail molecular slip is defined to address these challenges.

Before a discussion of calculating dyad slip, qualitative comments on the column orientation are relevant. In the left most column, the red dyad could function as a reference for calculating slip for the above dyad. In this same column, the green dyad cannot itself function as a reference because the dyad does not have the correct orientation for the convention used to define positive and negative slip. When using the red dyad as a reference and the convention for positive and negative slip already defined, the long axis is noted to have a negative slip, and the short axis is seen to have a positive slip.

Note that a simple 180° rotation about the Y-axis of the first column is all that is required to make the green dyad properly oriented to function as a reference. Also note that the qualitative view of dyads stacking within the column is exactly the opposite if the green dyad was used as a reference instead (shown in the right two columns of Figure 2.8).

Consider again the red reference dyad of **6y** in the left most column, and note that centroids for each dyad are shown for the bottom four dyads of each column, represented by black spheres near the alkyne. The molecular slip for the dyad above the red reference dyad can be calculated by the translational displacement between the two centroids. Note that, qualitatively, the slip is expected to be negative along the long axis, and positive along the short axis. Quantitative results of this agree with the prediction, as shown for the calculated molecular slip labeled as "1" in Figure 2.9. In order to calculate the next slip moving up the column, the green dyad must now become the reference, and thus be oriented following the defined reference convention. Thus, in the third column, the green dyad is then in the right orientation to be used as a reference for the calculation of the slip labeled by "2". The calculated slip maintains a negative long axis slip, however the short axis slip value has the opposite sign from the first slip calculation. Continuing this process of defining a new reference and calculating the additional unique molecular slips in the column ("3" and "4") yield unique slips with similar alternating values as slip "1" and "2". Thus, even though the column orientation never changed, the convention for how slip is defined and calculated using translational displacements of centroids creates slip values that have varying sign, yet describe the same overall column. This challenge in slip calculation for head-to-tail derivatives is further compounded with the use of a centroid defined for an asymmetric dyad core, and also the use of the NI core (that can have small variations out of planarity) to define the axes.

In light of this, a new convention is defined in order to (1) describe the overall orientation of dyad packing within head-to-tail columns and (2) enable the relative comparison of packing between different head-to-tail derivatives. Because the original convention consistently defines the correct value for long axis slip, the long axis slip will be reported as the simple average of all unique long axis molecular slips. In contrast, the short axis slip was seen to vary as the reference changed. In light of this, the convention takes an "orientation average", meaning that this average will describe the overall column structure by alternating the sign of alternating short axis slip values in order to maintain the overall column structure. To clarify, in Figure 2.9, the short axis slip starting with the red reference dyad is clearly consistently positive to the naked eye, yet the calculations varied between positive and negative values by convention. So, this orientation average will multiply the second and fourth short axis value by negative one to have all short axis slips have the same sign prior to averaging. In doing so, the average of the four unique short axis slips becomes representative of the overall column orientation.

Because the choice of reference is arbitrary and the presence of an inversion center allows for equal and opposite slips to be calculated, the convention further details the average for both perspectives. Therefore, two different values will be used to describe slip stacking for headto-tail polymorphs in order to make comparisons across derivatives clear. With a detailed understanding of how slip stacking is calculated for these more challenging head-to-tail derivatives, the slip stacking geometry for yellow symmetric derivatives can now be discussed and is shown in Figure 2.10.


Figure 2.10 Slip stacking of symmetric dyads that form yellow crystals, packing in a head-totail fashion. Bottom: overlay of **7y** and **7y**' single-crystal structures shows remarkable similarities in packing of cores despite variation in side chain packing. Crystal structures shown as displacement ellipsoids set to the 50% probability level with multiple side chain occupancy shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

As briefly mentioned at the beginning of this section describing yellow symmetric dyad crystals, there is similar slip-stacking within all yellow polymorphs, with an average long axis displacement of  $1.11 \pm 0.09$  Å and a short axis displacement of  $-1.47 \pm 0.06$  Å. All five polymorphs are closely grouped, and further grouping within each set can be seen (Figure 2.10).

This is especially pronounced for the two heptyl polymorphs, **7y** and **7y'**, which also have remarkable similarity in packing, including the alignment of alkyl side chains on the overlaid trimer of **7y** and **7y'** shown in the bottom left of Figure 2.10. Similar molecular slip stacking is seen between both yellow polymorphs and that of **8y**. Greater variation is seen in the two hexyl polymorphs. Yet, general to all five symmetric yellow polymorphs, derivatives with the same side chain length have nearly identical packing along the short axis, and the majority of difference between individual polymorphs in packing manifests along the dyad the long axis.



Figure 2.11 Symmetric dyads that form yellow crystals have variable intercolumnar relationships, with adjacent columns being either parallel (**6y** and **6y'**) or rotated about the short axis of the dyad between 48 – 49° (**7y**, **7y'**, **8y**). Reprinted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

In stark contrast to orange crystals with perpendicular columns about the long axis, aromatic cores in adjacent columns of **Y** crystals are either parallel or rotated about the short axis of the dyad (Figure 2.11). Adjacent columns are parallel to one another in both polymorphs of **6**, while adjacent columns are rotated about the short-axis in **7y** (48.570 – 48.98°), **7y'** (48.09 – 48.10°), and **8y** (48.45 – 48.59°).



Figure 2.12 View from above dyad columns in yellow crystals (4 dyads/column). Symmetric dyads that form yellow crystals have alternating aromatic and aliphatic layers, with segregated side-chains that have increasing disorder further from dyad cores. Crystal structures shown as displacement ellipsoids set to the 50% probability level. Multiple side chain occupancy in **6y**, **7y**, and **7y**' shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

As shown in Figure 2.12, alternating alkyl and aromatic layers are formed in all yellow crystals, similar to orange crystals, but with key differences. Side chains within the alkyl layer adopt staggered-anti and gauche conformations. Further, side chains in between layers are segregated and not interdigitated, as was the case with orange crystals. All yellow side-chains have increasing disorder in their side-chains with increased distance from the dyad core. It is important to note that **6**y, **7**y, and **7**y' had side chains with multiple site-occupancy in terminal carbon atoms of the alkyl chains (additional details in Table 2.2), indicating that disorder was present within the alkyl layers.



Figure 2.13 Single-crystal structure of **1bo** as viewed from various perspectives indicated. In a) and c), crystal structures shown as displacement ellipsoids set to the 50% probability level. Hydrogen atoms omitted in b) for clarity.

**Bright Orange Dyad Crystals.** The methyl dyad 1 was only found to crystallize as bright orange needles. Denoted as being bright orange (**bo**), this derivative had many differences compared to symmetric orange crystals and as such is put in a category of its own. The only commonality between **1bo** and the other orange derivatives was head-to-head stacking. However, the slip stacking was significantly different. Orange crystals were slipped  $\sim$ 3 Å along the long axis of the dyad, and  $\sim$ 1 Å along the short axis; **1bo** was found to have shorter offset along the long axis (0.8078 Å) and a longer offset along the short axis (-1.695 Å). Unique in **1bo**, two different packing motifs are seen in adjacent columns, where adjacent columns have interactions between either the short- or long-axis of dyads in a given adjacent column. Most

notable, **1bo** does not form alternating alkyl and aromatic sheets (Figure 2.13c) in contrast to all other crystals in this report. While **1bo** stacks in a head-to-head geometry, it has a unique slip-stacking geometry with its largest offset along the short axis of the dyad, in contrast to the head-to-head stacked **O** dyads (**6o**, **7o**, **8o**).

#### 2.2.3.3 Asymmetric Dyad Single-Crystal Structures

Three high-quality asymmetric dyad single-crystal structures were solved. These structures had several distinct differences compared to all symmetric dyads, with a few common features. In common with their symmetric counterparts, all asymmetric dyads stacked in one-dimensional columns, either in head-to-head or head-to-tail geometries as shown in Figure 2.14. Unique to the asymmetric series, altering the position of asymmetric alkyl substituents resulted in a change in aromatic stacking geometries, with head-to-tail packing in **M6N8** and head-to-head packing in **M8N6** (Figure 2.14).

**M6N8** was the single asymmetric dyad that exhibited a head-to-tail stacking geometry. As was the case with **6y** and **6y'**, **M6N8** had two molecules in the asymmetric unit, and four different possible column packing motifs: two different dimers of **M6N8** are shown in Figure 2.14. It should be noted, a single **M10N8** yellow crystal was found to have head-to-tail packing, but a refined single-crystal structure could not be solved for this derivative. A large enough data set was collected to conclusively determine head-to-tail packing of the aromatic core, but limited resolution and the absence of a number of reflections made refinement of a resolved, publishable structure impossible.



Figure 2.14 Asymmetric dyads form crystals that span from yellow to gold. Dyad molecules are shown to pack in columns with both head-to-head and head-to-tail stacking geometries. Crystal structures shown as displacement ellipsoids set to the 50% probability level with hydrogen atoms omitted for clarity.

Nevertheless, **M10N8** and its shorter counterpart, **M8N6**, were able to grow high-quality yellow-orange and gold crystals, respectively, and single-crystal structures of each were solved. Both of these structures had unique head-to-head packing, distinctly different from orange polymorphs and **1bo**. Both **M10N8** and **M8N6** exhibited remarkably similar molecular slips with an average long axis displacement of  $0.78 \pm 0.01$  Å and a short axis displacement of  $3.69 \pm 0.08$  Å.



Figure 2.15 Single-crystal structures of asymmetric dyad crystals reveal various intercolumnar relationships, with adjacent columns being either parallel (M6N8) or rotated about the short axis of the dyad between 84-85° (M8N6, and M10N8).

Adjacent columns are parallel to one another in the structure of **M6N8**, reminiscent of **6y** and **6y'.** The other asymmetric derivatives had adjacent columns that were rotated almost perpendicular about the short-axis in **M8N6** (85.15°) and **M10N8** (84.10°). Similar to orange head-to-head polymorphs that were stabilized by four different dyads (two stabilizing MAN, two stabilizing NI units), **M10N8** and **M8N6** had intermolecular contacts (intermolecular contacts here are defined by Mercury software as being shorter than the sum of the van der Waals Radii) to five adjacent aromatic units due to close proximity in packing that accompanied herringbone, also called "edge-to-face", type aromatic interactions. Also similar, the nonconventional alkoxy - OCH<sub>2</sub>- to carbonyl oxygen hydrogen bond was present in both derivatives, with an average length of  $2.50 \pm 0.06$  Å. The torsional angle of the alkyl chain coming off the MAN unit (O-C-C-C torsion) was also in a gauche conformation in these two derivatives, with an average torsion of  $56 \pm 6°$ . In the shorter **M8N6**, the rest of the side chain exists in a staggered-anti conformation,

whereas in **M10N8**, each alkyl side chain has a gauche conformation part way down the alkyl chain.



Figure 2.16 Asymmetric dyad crystals form alternating aromatic and alkyl layers, but alkyl layers can have complete segregation of side-chains between layers (M6N8), or a mix of interdigitated and segregated side-chains (M8N6 and M10N8). Crystal structures shown as displacement ellipsoids set to the 50% probability level with hydrogen atoms omitted for clarity.

Asymmetric dyads all formed alkyl and aromatic layers in the third dimension of crystal packing. Interestingly, among **M10N8** and **M8N6** there was a mix of interdigitated and segregated side chains. Uniquely, asymmetric **M10N8** and **M8N6** form a unique hybrid alkyl/aromatic sublayer due to the offset of adjacent aromatic cores, and this hybrid sublayer has the net effect of decreasing the overall width of the alkyl layer. In contrast, side chains of **M6N8** were entirely segregated from the adjacent layer.

An overlay of **M10N8** and **M8N6** shown in Figure 2.17 highlights the remarkable similarity in packing of the aromatic cores and the NI side chains between the two derivatives. These NI side chains are the segregated side chains seen in between interdigitated pairs in Figure 2.16. While the first carbon atoms of the MAN side-chain have similar placement, deviation occurs between more terminal atoms of MAN alkyl chains.



Figure 2.17 Similar crystal packing seen in single-crystal structures of M10N8 and M8N6. a) Overlay of single-crystal structures of M10N8 (green) and M8N6 (gold) with accompanying cartoon depicting the perspective being viewed. b) Similar sidechain packing seen in both derivatives, with a mix of interdigitated and segregated side chain packing between layers. In all cases, crystal structures shown as displacement ellipsoids set to the 50% probability level with hydrogen atoms omitted for clarity.

A single-crystal structure for **M8N10** was never obtained, as this dyad would always crystallize as small, flexible crystalline needles/threads within polycrystalline aggregates despite efforts to grow crystals under numerous different crystal growth methods and conditions. In light of this, powder X-ray diffraction (PXRD) was carried out to gain structural insight into the packing of **M8N10** crystals grown via vapor diffusion (toluene, acetonitrile). Shown in the top of Figure 2.18 is a crystal structure of **90** with select crystallographic planes shown in magenta and unit cell axes shown in black. In the bottom of Figure 2.18, normalized PXRD for **M8N10**, **90**, and **80** are shown, where the PXRD patterns for **80** and **90** shown are the calculated powder patterns based the respective single-crystal structure.



Figure 2.18 Crystal structure of **90** with certain crystallographic planes indicated by magenta colored lines. Hydrogen atoms omitted for clarity. Bottom: stacked normalized PXRD spectra with calculated spectra for **90** and **80**.

A visual comparison of **M8N10** and **90** PXRD shows several peaks with similar spacing. The low angle peak for **M8N10** falls in between the low angle peak for **90** and **80**. This low angle peak corresponds to the largest crystallographic spacing in the crystal. The observed peak in between that of **80** and **90** supports a proposed packing model for **M8N10** that has interlayer spacing (e.g. length of alkyl chain layer) at a value between that of **80** and **90**. The broad peak width for the **M8N10** low angle peak may be an indication of variation in interlayer spacing across the sample or within different crystalline domains.

Correspondence between the (002) and (022) crystallographic planes of 90 and 80 can also be seen. Note the (002) and the (022) plane in the 90 crystal structure shown in the top of Figure 2.18. The (002) plane passes through the alkyne of dyads in columns with the same displacement along the b-axis of the crystal but occupies different layers. The (022) plane passes a dyad also a layer above, but in the adjacent column (e.g. b-axis offset). Thus, taken together, these two planes provide an indication of the relationship between columns within the crystal. A correspondence in peak location for the (002) and (022) planes of 90 and 80 and peaks seen in the PXRD spectrum of **M8N10** is believed to reflect a similar relationship between columns in M8N10. The broad peaks seen in the M8N10 spectra could be an indication of slight variation in crystal packing dimensions for the given planes across the polycrystalline sample, or even within different crystalline domains. The lack of an appreciable (061) plane in M8N10, may indicate variation in interlayer spacing and/or the absence of longer-range order in M8N10 crystals. While it is possible this peak is not observed in the PXRD of M8N10 due to preferred orientation effects, its absence could arise from variation in alkyl chain packing, causing changes in interlayer spacing within a single layer while maintaining order between adjacent columns within individual layers. Thus, it is believed from PXRD analysis that M8N10 has packing that is similar to its constitutional isomer, 90, with similar ordering between adjacent columns, and similar interlayer spacing. In agreement with observations that M8N10 forms small needles, the lack of appreciable crystal growth in three dimensions could result from variability in the packing of the side chains in the alkyl layer, or a lack of stabilizing intercolumnar interactions.

#### 2.2.3.4 Comparison of Dyad Slip Stacking

A single combined plot of all different dyad slip stacking geometries is shown in Figure 2.19. Grouping can be observed between all orange dyads (squares), asymmetric **M10N8** and

**M8N6** (blue and purple diamonds), as well as yellow symmetric (circles) and asymmetric **M6N8** (yellow diamond) head-to-tail crystals. Packed in a head-to-head fashion unlike yellow crystals with similar stacking, **1bo** has its own very unique molecular slip.



Figure 2.19 Calculated molecular slip for all dyad crystals.

## 2.2.3.5 Preferred Orientation

With an understanding of how dyads stack in three dimensions in the crystalline state, analyses of the molecular orientations within crystals was carried out in an effort to understand how various crystal packing forces manifest as observable microscopic differences in crystal growth.



Figure 2.20 Preferred orientation for dyad molecules in symmetric orange crystals based on BFDH morphology calculations using single-crystal data.

Orientations of dyad molecules in the crystals was determined using Bravais, Friedel, Donnay, and Harker (BFDH) calculations from single crystal data and is shown in Figures 2.20 and 2.21. In all cases, molecular orientation of dyad molecules corresponds to the direction of aromatic stacking of dyads within columns.

As stated previously, the longest dimension of all crystals was the direction of aromatic stacking. In **60**, the thinnest crystal dimension was found to arise from the relationship between columns, and the dimension from side-chain interactions is the second largest dimension. The preferred orientation for **60** shown in Figure 2.20 was calculated from the crystal dimensions that yielded the **60** single-crystal structure, where the thinnest crystal dimension to be made from interactions between column (e.g. rectangular prism). Other **60** crystals were seen that had nearly identical dimensions in the two smaller crystal axes (e.g. square prism). In longer derivatives, there is a reversal in the preferred orientation shown for **60** in Figure 2.20: longer derivatives form wider and thinner crystals, in which the width is made from the interactions of columns, and the height is made from the stacking of layers held together by alkyl chains.



Figure 2.21 Preferred orientation for dyad molecules in symmetric yellow crystals and **M10N8** based on BFDH morphology calculations using single-crystal data.

#### 2.2.4 Thin Films

Thin Films. Dyads were deposited onto quartz substrates using physical vapor deposition. During deposition, copper tape was used to hold the quartz substrates upside-down during the sublimation process, resulting in areas around the perimeter of films not having deposited material. These vacancies can be seen on all corners of the thin films shown in Figure 2.22, and create unique crystal boundaries that will be discussed later.

Sublimation of all deposited dyads (1, 7, and 10) generated amorphous yellow thin films (Figure 2.22a, c). Vapor annealing of yellow thin films in a fuming chamber with dichloromethane (DCM) yielded polycrystalline orange thin films (Figure 2.22d) and displayed orange emissions when irradiated with 365 nm light (Figure 2.22e). Vapor fuming of yellow films had slight variation in the amount of time required for the film to fully convert. Shown in Figure 2.22e, an initially yellow film of 10 fully converts to an orange film over two days. Films would almost always begin on a film boundary, and proceed inward.

It is important to note the fine balance that must be present when fuming these dyad films. If the chamber was not tightly sealed, DCM would evaporate quickly, and the film would not convert without continual replenishment of DCM. If too much DCM was present in a sealed chamber, DCM would visibly condense on the film surface, causing it to fully dissolve and concentrate into a single spot in the middle of the substrate. In general, films would be fumed in a non-sealed cylindrical chamber (diameter and height ca. 10 cm) with DCM (ca. 10 mL) that was replenished roughly every 24 hours until complete conversion occurred.

Using fuming chambers, polycrystalline thin films made of discrete microcrystals were characterized by structural, optical, and spectroscopic measurements. GIWAXS of a **70** thin film (Figure 2.22f) showed that polycrystalline orange thin films had diffraction spots matching single-crystal structures, while also informing about preferred orientation of thin film samples. The location for diffraction spots can be calculated based on input of crystallographic parameters and GIWAXS parameters (e.g. sample-detector distance, wavelength) in a reported MATLAB script: GIXSGUI.<sup>143</sup> The calculated spots for **70** match a preferred orientation of **70** to have the

long molecular axis of the crystal perpendicular to the substrate,<sup>144</sup> indicated by the presence of the in-plane (020) reflection.



Figure 2.22 Dyad thin film preparation, structure, and optical properties. a) Dyad 7 seen deposited as a yellow material inside the physical vapor deposition chamber following sublimation. b) GIWAXS of 70 thin film shows a polycrystalline thin film with calculated reflections that match 70 and show preferred orientation with the crystallographic long axis (020) perpendicular to the substrate. c) Methyl dyad 1 deposited as an amorphous yellow film. d) Polycrystalline 70 thin film formed following exposure of 7 to DCM vapor in a fuming chamber. e) UV irradiation shows fluorescence of a 100 film. f) From left-to-right: an amorphous, yellow thin film of 10 converts to 100 over two days when exposed to DCM vapor in a fuming chamber.

Optical micrographs of a **70** thin film on quartz are shown in Figure 2.23 with varying magnification. Note that on the film boundaries, individual crystals can be distinguished.



Figure 2.23 Optical micrographs of **70** thin film shows a polycrystalline surface with distinguishable individual crystals seen on boundaries.

#### 2.2.5 Spectroscopic Characterization

#### 2.2.5.1 Solution Phase Spectroscopic Properties

In solution, all dyads had nearly identical spectroscopic properties, as the alkyl side chains do not affect electronic properties of the aromatic cores, exhibiting significant solvatochromism (Figure 2.24), with a strong bathochromic shift with solvents of increasing polarity (hexanes  $\lambda_{em-max} = 444$  nm, acetonitrile,  $\lambda_{em-max} = 593$  nm, Figure 2.24). This shift is consistent with a highly charge-separated excited state due to electron transfer from the electron rich MAN core, where the HOMO is primarily localized, to the electron deficient NI core, where the LUMO is localized (Figure 2.24a). This is further supported by 7 having a calculated excited state dipole of 14.64 Debye in the first electronically excited state, compared to just 7.21 Debye in the ground state ( $\omega$ B97X-D, 6-311+G\*\*).



Figure 2.24 (a) Calculated dyad electrostatic potential, molecular dipole, HOMO, and LUMO of 7 (ωB97X-D, 6-311+G\*\*). (b) 7 in solvents of increasing polarity from left to right. Bottom: UV irradiated samples, showing positive solvatochromism. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

Absorbance and emission of Dyad 7 in a variety of solvents is shown in Figure 2.25. Absorbance profiles are similar for dyads in each solvent, with a range in the observed absorbance max of 15 nm (hexanes  $\lambda_{abs-max} = 408$  nm, DCM  $\lambda_{abs-max} = 423$  nm). Vibronic peaks are only observed for 7 in hexanes. A shift in emission wavelength is seen when the solvent polarity increases from non-polar hexanes to polar acetonitrile (hexanes  $\lambda_{em-max} = 444$  nm, acetonitrile  $\lambda_{em-max} = 593$  nm). Plotting emission maxima versus ET(30), an empirically derived solvent polarity parameter, shows a general trend of increasing emission wavelength in more polar solvents.



Figure 2.25 Normalized absorbance and emission spectra for 7 in a variety of solvents and emission max plotted versus solvent polarity (E<sub>T</sub>(30)). Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

In addition to changes in emission wavelength with varying solvent, other shifts are seen in emission wavelength when even small amounts of polar solvent are added to a dyad in nonpolar solvent. Shown in Figure 2.26, as ethanol is added to dyad 7 dissolved in hexanes, the initial emission maxima of 444 nm shifts dramatically to 551 nm ( $\Delta = 107$  nm) once the solution is 50% ethanol by volume. A 44 nm shift (37% increase) in the emission wavelength was seen with only 2.0% ethanol by volume.



Figure 2.26 Absorbance and emission spectra of 7 in mixtures of hexanes and ethanol.

A summary of dyad spectroscopic properties in solution, including quantum yields and fluorescence lifetimes, can be found in Table 2.3. Additional experimental details for solution-based measurements can be found in section 2.5.3. Dyads are strong absorbers ( $\varepsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )

and have high quantum yields in non-polar solvents. Quantum yields (QY) were determined using the relative determination method following reported protocols,<sup>145</sup> using a Coumarin-153 standard. To calculate molar absorption coefficients, concentration dependent measurements (3, 5, 10, 25, 50  $\mu$ M) of each dyad in a given solvent were carried out. Molar absorption coefficients were calculated by the slope made from plotting the absorbance value (at  $\lambda_{abs-max}$ ) versus concentration. The molar absorption coefficient for 7 in acetonitrile is not shown because limited solubility in higher concentrations hindered concentration-based measurements.

Solvent	$\lambda_{abs-max}(nm)$	$\boldsymbol{\varepsilon}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{em-Max}(nm)$	FLT (ns)	QY
EtOAc	417	$2.36 \times 10^4$	538	3.96	0.68
PhMe	414	$1.97 \ge 10^4$	489	2.58	0.73
Hexanes	408	$2.57 \times 10^4$	444	2.34	0.73
DCM	426	$2.27 \times 10^4$	558	4.40	0.68
Acetone	419	$2.46 \times 10^4$	587	2.00	0.22
MeCN	418	-	593	0.94	0.07

Table 2.3 Summary of spectroscopic data for 7 in a variety of solvents. Absorbance maxima  $(\lambda_{abs-max})$ , emission maxima  $(\lambda_{em-max})$ , fluorescence lifetime (FLT) and fluorescence quantum yield (QY). FLT was determined from fitting the sample decay to a single-exponential function.

Time-correlated single photon counting measurements were conducted in order to determine solvent effects on fluorescence lifetime (FLT) of dyads in solution. A plot of the decay for **7** in a variety of solvents is shown in Figure 2.27, and the calculated FLT based upon of fitting a single exponential function to the decay is shown in Table 2.3. While **7** had the two shortest FLTs in the most polar solvents used, acetonitrile and acetone, the least polar solvents used, hexanes and toluene, had FLTs in the middle of the distribution. Chlorinated solvents gave rise to the longest FLTs, with DCM having the longest measured FLT (4.40 ns), and CHCl<sub>3</sub> (not shown) having a measured FLT of 3.94 ns, nearly identical to that of ethyl acetate (3.96 ns).



Figure 2.27 Fluorescence lifetime of 7 in various solvents as measured by time-correlated single photon counting (TCSPC).

### 2.2.5.2 Solid-State Spectroscopic Properties

Shown in Figure 2.28 are pictures of crystals viewed under ambient visible light and also when irradiated by a 365nm lamp. Crystals are shown in groups, where pictures were taken sideby-side to allow for comparison of symmetric orange, symmetric yellow, bright orange **1bo**, and the four asymmetric derivatives.

Spectroscopic characterization of solids was completed by carefully sandwiching the solid material between two cleaned quartz slides. Absorbance of solids was calculated by measuring both diffuse reflectance and transmittance of the quartz 'sandwich'. Measurement of the quartz sandwich without material allowed a blank absorbance for the quartz holder to be calculated, and this blank absorbance was subtracted from sample data. Solid fluorescence emissions were collected using a front facing accessory that enabled the light source to be perpendicular to the sample, and emission to be collected at 22.5° relative to the light source in order to reduce reflected light from the material surface. Additional information including instrumentation, and additional parameters for data collection can be found in section 2.5.4.

# Symmetric Orange Crystals



Figure 2.28 Color of all crystals under visible light and when irradiated at 365 nm.



Figure 2.29 Solid-state absorbance and emission for symmetric orange crystals grown from solution. Inset near the legend is the respective emission maxima (nm).

All orange crystals had very similar color to the naked eye under visible light and when irradiated with a 365nm lamp (Figure 2.28) absorbance and emission of these crystals are indeed similar (Figure 2.29). All orange crystals have similar red shifted absorbance and emission profiles compared to yellow crystals, which are shown in Figure 2.30. Note that the exact emission maxima of orange crystals showed variability that appears correlated to crystal size to at least some extent, with some observed red-shifting as crystal size increases (Table 2.4).

Compound	$\lambda_{abs-Max} (nm)$	$\lambda_{em-Max} (nm)$
1bo	371	590
60	371	625
<b>7o</b>	360	617
80	296	613
9o	428	624
<b>10o</b>	357	615
120	359	615
6y	392	569
7y	390	554
8y	395	554
M6N8	293	561
<b>M8N6</b>	357	568
M8N10	430	616
M10N8	402	564

Table 2.4Solid-state absorbance and emission for dyad derivatives.



Figure 2.30 Solid-state absorbance and emission for symmetric yellow crystals grown from solution. Inset near the legend is the respective emission maxima (nm).

In general, all three symmetric yellow crystals had similar color judged by the naked eye; however, **6y** did appear to have a slight orange hue compared to **7y** and **8y** when irradiated with a 365 nm lamp (Figure 2.28). Spectroscopically, **7y** and **8y** showed nearly identical absorbance and emission spectra (Figure 2.30, Table 2.4). In comparison, the emission of **6y** has a small bathochromic shift relative to **7y** and **8y**, as would be expected from the observed yellow-orange hue upon excitation with longwave UV light.



Figure 2.31 Solid-state absorbance and emission for asymmetric crystals, with colors ranging from yellow to orange-red grown from solution. Inset near the legend is the respective emission maxima (nm).

Asymmetric dyads had large variation in absorbance and emission profiles compared to the respective orange and yellow symmetric derivatives as shown in Figure 2.31. Three distinct absorbance profiles can be seen on the red-edge of the absorbance profiles, with similarity between **M8N6** and **M10N8**. In comparison to these two derivatives, **M6N8** had a hypsochromic shift in both absorbance and emission profiles, and **M8N10** displayed bathochromic shifts in both its absorbance edge and the emission profiles.



Figure 2.32 Comparison of solid-state absorbance and emission crystals grown from solution, where overlap between certain asymmetric derivatives is seen. Inset near the legend is the respective emission maxima (nm).

A comparison of several selected derivatives is shown in Figure 2.32 in order to highlight a few commonalities. Not all derivatives are shown in order to provide clarity. Nevertheless, it is hoped that the following discussion will describe trends across all of the derivatives, even if each spectra is not shown in Figure 2.32. Head-to-tail derivatives, which includes yellow symmetric crystals **6y**, **7y**, and **8y**, as well as **M6N8**, are seen to have similar absorbance and emission profiles, with the most blue-shifted absorbance edges of all crystals. Unlike the similarity in head-to-tail derivatives, the three different groups of head-to-head derivatives were all distinct. Head-to-head **M6N8** and **M8N10** have a unique absorbance edge, although emission profiles for these two derivatives fall within the range of yellow symmetric crystals. Similar to how **1bo** had a molecular slip unlike all other derivatives, the absorbance and emission of **1bo** is also truly unique, with an emission in between yellow and orange derivatives. Further, all symmetric orange derivatives had similar spectroscopic behavior to one another, and uniquely, **M8N10** displayed nearly identical absorbance and emission profiles.



Figure 2.33 Comparison of **7y** and **7o** absorbance and emission spectra relative to thin films of **7** either yellow (**7y**<sub>Thin Film</sub>) or orange (**7o**<sub>Thin Film</sub>) in color.

Finally, a spectroscopic comparison was carried out between crystals grown from solution and thin films produced via physical vapor deposition. The **7y** thin film shown in Figure 2.33 is an amorphous film of **7** following deposition via sublimation. The **7o** thin film was formed from vapor annealing of a **7y** thin film with DCM, as discussed previously. Thin films of **7** had differences in absorbance compared to their crystal counterparts. Despite these differences in absorbance spectra, similar emission profiles were seen between crystals and thin films of **7** in their yellow and orange forms, respectively.

#### **2.3 DISCUSSION**

#### 2.3.1 Dyad Packing in the Solid-State

**Dyad Packing.** The dyads described in this chapter all pack in stacked columns, but they exhibit diversity in terms of both translational molecular slip and packing orientation (head-to-head versus head-to-tail). The geometries adopted by dyads within columns are in part due to aromatic stacking interactions, which are primarily guided by electrostatic, through-space interactions between the relatively strong dipoles on the periphery of the aromatic core, <sup>30</sup> with a smaller dispersive component also contributing to the stability of aromatic stacks.<sup>146</sup>

Before a discussion on how aromatic interactions result in different geometries, the role of van der Waals, i.e. dispersive interactions, should be considered. Dispersive forces play a major role in stabilizing alkyl chains on adjacent dyads in the solid-state. The staggered-anti geometry of alkyl chains in the orange crystals maximizes the surface area and thus provide a large number of relatively weak dispersive forces that can stabilize all three dimensions of crystal packing. In contrast to the orange forms, a larger number of gauche conformations decreases side chains surface area in the yellow and asymmetric derivatives. This loss of surface area results in a decrease in dispersive interactions. Further, an analysis of voids in the orange and yellow crystals shows more empty space (voids) within the yellow crystals, specifically in locations adjacent to side-chain gauche conformations. For example, calculating the volume of a unit cell that has room to fit a 1 Å spherical "probe" shows that 2.0% of the **7y** unit cell can fit 1 Å probes, and they are all localized near gauche interactions close to the aromatic core. In contrast, none of these 1 Å probes can fit within the unit cell of **7o**.

Multiple side chain occupancy sites (6y, 7y, 7y') further hinder three-dimensional growth and add to the number of voids. For example, calculating the number of probes that can fit in 7yafter removing atoms that have multiple site occupancy further increases the number of voids to 2.4% of the unit cell. The voids likely decrease stability of the crystal as well by allowing more accessible degrees of freedom thereby reducing contact surface area. These vacancies also likely hinder three-dimensional growth for the same reason. While molecular geometric constraints can limit what atomic configurations are possible for a given molecule in the solid-state, other configurations that maximize alkyl side chain surface area may improve three-dimensional growth. For example, the other yellow polymorph, **7y**', had a calculated void volume of 0.5% of the unit cell. While not indicative of stability in three dimensions, the crystal that yielded the structure of **7y**' was 0.83 mm in length, over three times longer than any other yellow crystal that yielded a single-crystal structure. Additionally, minimal side chain overlap in **1bo** (Figure 2.13) provides a plausible explanation for 1 dimensional, needle-like crystal growth observed (Figure 2.2).

As discussed previously, the long axis of the crystal corresponds to the axis of aromatic stacking interactions. Therefore, on average longer yellow crystals may be an indication that aromatic interactions between yellow crystals are stronger than those in orange. Aromatic interactions between dyad cores have dominant energetic interactions based on the local, direct, through-space interactions of bond dipoles. In chapter 1, a discussion of relevant dyad bond dipoles highlighted differences between dipoles on the MAN and NI unit of the dyad, and an electrostatic potential map of **7** is shown in Figure 2.34 for convenience. Briefly, on the NI unit, the two strong carbonyl C-O bond dipoles, and to a lesser extent, five C-H bonds on the aromatic ring periphery influence stacking geometry. The C-H bonds on the MAN unit can also influence aromatic stacking geometry, as these bonds are noted to have significantly stronger bond dipoles than NI C-H bonds. In addition to the five aromatic C-H bonds the one alkoxy C-O bond on the MAN unit also has a significant bond dipole and will influence aromatic stacking geometries in accordance with modern theory.



Figure 2.34 Calculated electrostatic potential map of **7** in the conformation from the **70** singlecrystal structure (ωB97X-D, 6-311+G\*\*). Note the most polarized bonds are on the periphery of the aromatic core, as well as the alkoxy bound methylene unit.

The NI carbonyl is believed to have the strongest single bond dipole in the dyad, and thus, should have the largest single effect on aromatic stacking geometry. The offset self-stacking of NI units in head-to-head geometries of orange crystals places adjacent dyads with an average of a 3.1 Å offset along the long axis and 1.0 Å on the short axis. This placement aligns one of the NI carbonyls above the electron deficient NI aromatic core, with the oxygen atom roughly above the NI carbon-1. The other carbonyl is positioned slightly off-set (ca. 0.1 Å) from the C-H bond coming off of the NI carbon-7. This same carbonyl oxygen sits directly above a C-H bond coming off of the imide N-CH<sub>2</sub>-, and while not a true aromatic-aromatic interaction, this is believed to be a stabilizing force that helps maintain the relative translational slip of the dyad. On the other side of the dyad core, the MAN unit with a 3.1 Å offset positions C-H bonds of the MAN carbon-6 and carbon-8 near C-H bonds on the adjacent NI carbon-3 and MAN carbon-6,

although the angle adopted by each respective pair approximates  $\sim 120^{\circ}$ . Most notable however is the relative position of the C-H bonds on the MAN carbon-8 with the adjacent MAN unit carbon-5 C-H bond. These two bonds align almost directly on top of each other, and are exactly 180° in opposition, in perfect alignment for a strong intermolecular interaction. In these orange symmetric crystals, the ensemble of interactions between aromatic cores is believed to stabilize cores within a column.

In other head-to-head derivatives, dramatic differences in translational displacement exist. For example, **1bo** had a smaller long axis offset (0.81 Å) and a longer offset along the short axis (-1.7 Å). In this stacking geometry, the larger short axis offset perfectly positions the carbonyls in the ideal geometry to interact favorably with carbonyls on a single adjacent dyad. Thus, within a column, each NI has strong dipolar interactions with four other NI carbonyls, where one carbonyl oxygen will sit between two carbonyl carbons. Beyond just aromatic-aromatic interactions, the slip in **1bo** places the alkoxy oxygen directly above a C-H bond of the methyl ether, and the NI carbonyl oxygen directly above a C-H bond of the N-Methyl imide, further stabilizing this conformation.

The head-to-head **M6N8**, and **M10N8**, as discussed earlier, have an average long axis slip of 0.8 Å and a short axis displacement of 3.7 Å. This short axis offset is dictated by the intercolumnar packing in these asymmetric derivatives, where columns are roughly orthogonal about the short axis of the dyad (see Figure 2.15). In this geometry, a given dyad has a dyad from an adjacent column interacting in an edge-to-face geometry on one side of that dyad. In this way, any dyad that is stacked on top of the original dyad will be offset at least the width of the dyad (~3.4 Å). The relative increase in short axis slip compared to **1bo** results in the loss of each NI carbonyl interacting with carbonyls on adjacent dyads. In this geometry, a single NI carbonyl oxygen is favorably positioned over a single electron deficient NI carbonyl carbon. This larger short axis slipped geometry results in new interactions between two head-to-head MAN units. The 3.7 Å slip along the short axis puts the second MAN ring of one dyad half-way over the

adjacent MAN unit. In this configuration, the alkoxy C-O bond is positioned in between the carbon-6 and carbon-7 C-H bonds.

Importantly, all of the interactions described above for these head-to-head geometries are dependent on translational slip. In all cases, stabilizing interactions were described related to the stability brought about specific, often NI carbonyl dipoles. Calculated slip stacking geometries for head-to-head stacks showed three different translational slips that were found, and of those with multiple geometries (all symmetric orange, and **M8N6/M10N8**), tight grouping was observed with minimal offset in aromatic slip stacking geometry (see Figure 2.19).

While geometric constraints can always minimize the number of possible orientations that a molecule can stably adopt in the solid state, the tight grouping of head-to-head packing and crystal structures that lack multiple side-chain occupancies is perhaps a result of a narrow packing range for these geometries. Said differently, perturbation of the NI-NI stacking geometry is likely to result in a strong energetic penalty when considering dipolar interactions, especially of the carbonyl. Small shifts in translational displacement would result in the loss of favorable interactions, and often times an increase in repulsive interactions, highlighting our groups previous reports on the role of the NI carbonyl as a dictating force in aromatic stacking geometry.<sup>47, 60, 61, 63, 64, 66</sup>

In contrast to the strongly polarized NI carbonyls localized on one side of the NI core, the MAN aromatic core has a larger number of strong bond dipoles oriented all around both rings. This is believed to allow for the MAN unit to have greater flexibility in terms of the geometry that can be adopted when stacked with NI units. For example, the average offset of 1.1 Å and - 1.5 Å along the long and short axis, respectively, result in each unit being slightly offset along the short axis relative to the adjacent dyad. Perturbations in short axis offset would be energetically costly, as the alkoxy oxygen would come in proximity to the NI carbonyl; however, these would not be nearly as energetically costly as translation of a carbonyl oxygen above another carbonyl oxygen. In addition, as the MAN unit has many more strong dipoles, small

translations along either axis would still retain some degree of favorable dipolar interactions, whereas loss of stabilizing NI-NI dipolar interactions could occur with similar translations.

While head-to-tail yellow crystals are seen to also have clustered molecular slip stacking geometries, a greater deviation is seen in long axis slip (0.09 Å in the yellow crystals versus 0.03Å in the orange crystals). In addition, three different crystal structures with multiple side chain occupancies and minimal side chain interactions between adjacent layers is taken as evidence that side-chain interactions are not a necessary component of head-to-tail stacking. The wide variation in side-chain packing that exists in all yellow structures (see Figure 2.12) is believed to reflect the role of aromatic interactions guiding crystal growth, rather than from side-chain packing.

The existence of multiple diverse intercolumnar relationships (parallel columns or rotated  $\sim 45^{\circ}$  along the short axis) that exist around similar translational geometries is taken further to indicate that head-to-tail stacking geometries are able to allow for greater translational diversity in solid-state packing motifs.

In contrast, the conserved nearly perpendicular relationship between columns in all orange crystals appear to be stabilized through a combination of favorable side chain packing and electrostatic interactions between the most polarized bonds in the dyads, namely the imide carbonyl C–O bonds and the C–H bonds of alkoxy O–CH<sub>2</sub> groups (dashed green lines in Figure 2.4). An average distance of ~2.6Å is indicative of a weak hydrogen bond, with an energy of less than 4 kcal mol<sup>-1</sup> and contributions from both electrostatic and dispersive interactions likely.<sup>147</sup> This conserved intercolumnar feature further introduces stability into higher order structures, and is believed to enable the growth of large, three-dimensional, macroscopic crystals. As noted earlier, this non-conventional hydrogen bond is one of four significant contacts each orange dyad makes with adjacent columns on either side. These four contacts are believed to lock the dyad in place and prevent any motion that may result in translational movements.

Previously, it was noted that the single-crystal structure of **M8N10** (orange-red) was never obtained, as the dyad would crystallize out as orange-red polycrystalline needles/threads.

Crystal packing of **M8N10** was proposed to be similar to **90** based on indexing of the **M8N10** PXRD, and comparison to the **90** single-crystal structure derived PXRD pattern (Figure 2.18). The growth of thin, thread like crystals, morphologically similar to that seen in **1bo** is attributed to variation in side chain packing within the layer, or a lack of stabilizing intercolumnar interactions, including the aforementioned non-conventional hydrogen bond.

Different crystal growth methods should be able to provide insight into the role of side chain packing in dyad crystal growth of orange and yellow polymorphs. Yellow symmetric crystals could be grown using slow evaporation or vapor diffusion. When grown by slow evaporation, the dyad crystals would almost always grow along the wall of the vial as the solvent level decreased. In contrast, orange crystals grown using slow evaporation would grow in solution the vast majority of the time, rarely adhering to the outer walls as evaporation progressed. This is very similar to how orange crystals are produced using vapor diffusion. Yellow crystals could also be grown via vapor diffusion, and it is noted that sometimes a single condition can yield orange or yellow polymorphs, often exclusively in each individual batch. The emergence of both polymorphs in a single vial may reflect the stochastic process of crystal growth, and following nucleation, the derivative that has been nucleated continues to grow in the most favorable way.

As previously noted, orange crystals almost always grew in solution. Further, for many longer derivatives, a single vapor diffusion solvent system would enable the formation of orange crystals: *p*-xylenes as the solvent, and acetonitrile as the precipitant. It is valuable to note the fact that the solvents hexanes and acetonitrile are immiscible under standard conditions. This helps inform how the process for orange crystal growth may begin: Nucleation in solution occurs as the concentration of acetonitrile increases, thereby causing alkyl side chains to decrease their solubility. When controlled, the slow increase in acetonitrile concentrations would allow for a dynamic equilibrium to allow for the assembly and subsequent dissolution of derivatives that do not pack in the most favorable ways. Only once thermodynamically stable packing motifs are formed, for example with all alkyl side chains in staggered-anti conformations, the dynamic
equilibrium shifts so that crystal growth is favored as the acetonitrile is not capable of dissolving the stable structure. This perspective for acetonitrile driving orange crystal growth by driving alkyl side chain appended dyads out of solution is also supported by the observation that longer dyads form many more, smaller crystals (see Figure 2.3). Longer derivatives have lower solubility in similar acetonitrile concentrations, and perhaps result in the kinetics for nucleation exceeding the kinetics for crystal growth.

In contrast to the dynamic sampling of crystal packing enabled by crystal growth in solution, crystal growth down the vial wall following decreasing solvent levels are not afforded the same ability. As the solvent level decreases and the concentration of dissolved dyad increases, solubility limits drive dyads out of solution and into packing motifs that are stable when not given chances to reorganize. In this way, head-to-tail packing produced from slow evaporation can be rationalized as allowing thermodynamically stable crystals to form in spite of not having all of the higher order stability requirements needed for orange crystal growth (e.g. intercolumnar packing, interlayer side chain interdigitation). Fewer intermolecular interactions may enable head-to-tail crystal growth from solution, supported by the more flexible aromatic stacking geometry afforded in head-to-tail packed dyads.

Interestingly, dimensional changes were seen in the preferred orientation of crystals as side chain lengths increased, with derivatives with longer side chains in general being seen to have a relative increase in crystal width (made from intercolumnar stacking) and a relative decrease in crystal height (made from the stacking of layers) (Figure 2.20 & 2.2). This morphological shift in crystal growth patterns may reflect a difference in intercolumnar and interlayer stabilization provided by longer side chains (thermodynamic) or change growth rates of different crystal faces. In agreement with these observations, it is possible that longer side chains may better stabilize adjacent columns (increasing crystal width) more than they stabilize adjacent layers, despite the presumed benefit that longer side chains would increase stability of interlayer, 'cork' and 'bottle', packing (Figure 2.6). While longer side chains presumably have more thermodynamically favorable 'cork' and 'bottle' packing, longer side chains likely

significantly decrease the rate for layered crystal growth, due to a greater extent of side chain order required for the 'cork' and 'bottle' packing of longer, more flexible side chains.

In summary, a stable head-to-head stacking geometry in orange crystals of symmetric dyads is seen to have maximized van der Waals interactions between the perfectly ordered and close-packed staggered-anti, interdigitated alkyl chains, and is thought to be the more thermodynamically stable form overall. It is believed that aromatic stacking interactions are slightly more favorable in the head-to-tail yellow form, stabilized by more complementary electrostatic interactions on the periphery of the aromatic units. Yet in the head-to-tail yellow crystals, the alkyl chains are no longer all staggered-anti, highly ordered, close-packed, or interdigitated. The bottom line is that there is an energetic and structural trade-off between the two forms; more stable side chain packing but less stable aromatic stacking geometry in the orange form, yet more stable aromatic stacking geometry with less favorable alkyl chain packing in the yellow form. Finally, the head-to-tail form is also believed to be more 'forgiving' of slight translational motion within columns, where aromatic stacking interaction as a function of translational motion can be thought of as having a broader potential well, compared to a steeper potential well in the head-to-head orange form. A steeper potential well in head-to-head symmetric dyad orange crystals is reflective of a presumptive larger energetic penalty for slight translational perturbations in stacking geometry, a consequence of the fine balance of through space interactions observed in the consistent geometries of self-stacking NI units.

# 2.3.2 Photophysical Properties in Solution

All dyads have nearly identical photophysical properties in solution, as differences in dyads are not on the aromatic core. Absorbance of visible light by a dyad molecule results in the intramolecular electron transfer from the HOMO, centered largely on the electron rich MAN unit (see Figure 2.24) to the LUMO, centered largely on the electron deficient NI unit. In so doing. a

large excited state dipole moment forms, explaining the striking solvatochromic behavior of the dyads in solvents of different polarities and is expected for such highly polarized excited states.

As the process for absorption of a photon is much faster ( $10^{-15}$  sec) than solvent reorganization ( $10^{-10}$  sec), the ground and excited states are not significantly affected by solvent polarity, as a molecule experiences the same local environment before and after absorption of a photon. This nicely explains the small 15 nm range in solution-state absorbance maxima, shown seen in Figure 2.25 (hexanes  $\lambda_{abs-max} = 408$  nm, DCM  $\lambda_{abs-max} = 423$  nm). In stark contrast, the fluorescence emissions showed far greater sensitivity to solvent polarity (Figure 2.26), with emission maxima spanning 149 nm (hexanes  $\lambda_{em-max} = 444$  nm, acetonitrile  $\lambda_{em-max} = 593$  nm).

On the other hand, fluorescence emissions are far more sensitive to solvent polarity and viscosity compared to absorption processes because of the longer fluorescence lifetimes (10<sup>-8</sup>-10<sup>-9</sup> sec). Such a slow process means the solvent can 'relax' around the excited state and stabilize it, resulting the red-shifted emission (smaller energy gap).

Stabilization of the large excited state dipole moment by bulk solvent molecules is considered a general solvent effect, whereby the overall solvent polarity and refractive index of the solvent stabilize the excited state, and thus cause a red shift in emission. This type of general solvent effect does not explain the dramatic shift in emission seen for dyad 7 upon adding small additions of ethanol (Figure 2.20). The addition of 2% ethanol caused a shift in emission from 444 nm to 488 nm, while a further increase to 50% ethanol shifted the emission further to 551 nm. The addition of only 2% ethanol in conjunction with a bathochromic shift of 44 nm is thus attributed to specific solvent interactions that stabilize the dyad excited state likely through hydrogen bonding, as 2% is too small of a volume to alter bulk solvent properties.<sup>148</sup>

# 2.3.3 Photophysical Basis for Different Colored Solid-State Materials

The key structural difference in solid-state between symmetric orange and yellow polymorphs is the orientation of adjacent dyads within a given aromatic stack. Adjacent dyads in

orange polymorphs have offset head-to-head stacking geometries, while yellow polymorphs exhibit head-to-tail stacking geometries. In other words, in the dyad stacks of orange polymorphs, a given MAN unit is situated above and below MAN units of adjacent dyads, and NI units are adjacent to NI units on adjacent molecules. In this head-to-head packing arrangement, there is a small short-axis offset and a larger ~3 Å offset along the long axis of the molecule, where dyads shift unidirectionally in a column, much like the offset of stairs in a staircase (Figures 2.19, 2.4-2.7). The offset head-to-head stacking geometry in the orange form will lead to mixing of LUMO orbitals since orbital lobes of similar phase are in close proximity (Figure 2.35). This LUMO mixing can facilitate the dissociation of an initial locally excited state into charge-transfer states, where electrons and holes are delocalized onto multiple molecules. This is believed to be the basis for the red-shift seen in all orange crystals. At the quantitative level, differences in the precise geometry of LUMO orbital overlap due to slightly different displacements along the short and long molecular axes can be used to explain subtle differences between the optical properties of orange polymorphs.



Figure 2.35 Overlay of calculated LUMO of a **70** monomer ( $\omega$ B97X-D, 6-31G\*) with the **70** crystal structure. A long-axis slip of 3Å in all orange polymorphs allows for favorable orbital overlap in the NI-localized LUMO, as seen by a match in orbital phasing with adjacent dyads. Reprinted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

While dipolar coupling may be in play, it is not expected to be the basis for the red-shift seen with orange crystals, and this is rationalized by comparisons of head-to-head crystal structures for **1bo** (Figure 2.13), asymmetric **M8N6** (gold crystals) and **M10N8** (yellow-orange) (Figure 2.17) and all orange polymorphs (Figures 2.4-2.7). Across these three groups, a larger slip along the short axis is correlated to smaller extent of red shifting compared to yellow polymorphs. Compared to all orange polymorphs (short axis slips of 1.0 Å), the smaller red-shift in **1bo** is attributed to a decrease in short-range coupling derived from orbital overlap. The 1.7 Å short axis slip in **1bo** still allows for the possibility of orbital overlap, as ca. 3 Å of overlap is present between adjacent NI unites. In contrast to **1bo**, a 3.7 Å short axis slip in head-to-head

stacked **M8N6** (gold crystals) and **M10N8** (yellow-orange) has smaller (~1.5 Å) overlap between head-to-head stacked NI units, yet these asymmetric dyads are still seen to have a significant red shift compared to yellow, head-to-tail polymorphs (Figure 2.32).

The observable red-shift in **1bo**, as well as **M8N6** and **M10N8**, compared to all head-totail yellow polymorphs is believed to result from a combination of dipolar coupling within headto-head stacked crystals and/or orbital overlap effects, with a larger orbital mixing component possible in **1bo** compared to the two asymmetric head-to-head dyads. Computational efforts would be required in order to resolve the respective contributions.

All yellow polymorphs exhibit head-to-tail stacking geometries and show greater variation in slip-stacking geometry compared to the orange polymorphs (Figure 2.19). The absence of a red shift in yellow polymorphs is interpreted to indicate that MAN-NI dyads do not form CT complexes in head-to-tail packing geometries, almost certainly due to energetic differences that minimize HOMO-LUMO orbital mixing.

While no single-crystal structure was solved, indexing of the **M8N10** (orange-red) PXRD pattern revealed similar packing to **90**, and the red shift in emission is consistent with head-to-head packing similar to symmetric orange derivatives. Differences in optical properties between symmetric orange crystals (Figure 2.29) were attributed to small differences in slip stacking geometries (Figure 2.19). Thus, the red hue seen in **M8N10** could be the result of small (ca. 0.1 Å) differences in dyad slip stacking compared to symmetric orange crystals.

# **2.4 CONCLUSION**

Small changes in packing resulted in shifts in spectroscopic properties, and an understanding of the differences in dyad solid-state color was put forth. In the solid-state, dyads were crystallized in multiple different polymorphs, and a detailed understanding of their crystalline morphologies has been described. A qualitative understanding of the thermodynamics of dyad packing was proposed, in agreement with modern theory and prior results. A model to understand differences in crystal growth propensities as a function of method was put forth, and in agreement with changes in preferred orientation changes seen in dyads with different side chain lengths.

MAN-NI donor-acceptor dyads are incredibly sensitive to their surrounding environment, and as such, make appealing candidates for future study. Solution-phase spectroscopic measurements showed that dyad fluorescence operates through an electron-transfer process that makes the dyad highly sensitive to the surrounding solvent environment, through both general (e.g. polarity) and specific (e.g. hydrogen-bonding) solvent-solute interactions.

# **2.5 EXPERIMENTAL**

#### 2.5.1 General Methods

All reagents were purchased from commercial vendors and used without further purification unless otherwise noted. NMR solvents were purchased from Cambridge Isotope Laboratories and used as received. All NMRs were completed in CDCl<sub>3</sub> and the chemical shift in parts per million ( $\delta$ ) is referenced relative to the residual solvent peak: 7.26 ppm for <sup>1</sup>H-NMR and 77.16 for <sup>13</sup>C-NMR. <sup>1</sup>H and <sup>13</sup>C NMRs were obtained using a Bruker AVIII HD 500 with a BBFO Prodigy liquid nitrogen CryoProbe or an Agilent MR 400 MHz NMR spectrometer. High-resolution mass spectrometry was performed using a either a Waters AutoSpec GC/MS for chemical ionization (CI) or an Agilent Q-TOF LC/MS for atmospheric pressure chemical ionization (APCI).

# 2.5.2 X-ray Crystallography

Single-crystal structure data for 6y, 6y', 7y', 8y, 1bo, 6o, 7o, 9o, 10o, and 12o was collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu

K $\alpha$  radiation source ( $\lambda = 1.5418$  Å) with collimating mirror monochromators. The data were collected at 100 K using an Oxford Cryostream low temperature device.

Single-crystal structure data for **7y** was collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength of 0.97741 Å. The data were collected at 100 K using an Oxford Cryostream low temperature device.

# 2.5.3 Solution-State Spectroscopy

Absorbance measurements in solution were made using a Cary 100 UV-Vis spectrophotometer. Steady-state fluorescence measurements were collected on a Horiba Jobin Yvon Fluorolog3. Time resolved fluorescence measurements were made using Horiba NanoLEDs (402 nm or 442 nm) on a Horiba Jobin Jyvon Fluorolog3. FLT was calculated from fitting the sample decay to a single-exponential function. QY was determined relative to a Coumarin-153 standard solution following established protocols<sup>145</sup>, with maximum absorbance values at or below 0.1 absorbance units.

## 2.5.4 Solid-State Spectroscopy

Spectroscopic characterization of solid material was completed by very carefully sandwiching the solid between cleaned quartz (fused quartz microscope slides, 1mm thick, Technical Glass Products, Inc.). Two cleaned quartz substrates were sandwiched together and the absorbance and emission spectra of this blank was subtracted from the sample data.

Solid-state absorbance measurements were made using Shimadzu UV-2600 UV-vis spectrometer with an integrating sphere attachment. Absorbance of solid-state samples were calculated from diffuse reflectance and transmittance measurements and calculated using the following formula,

$$A = 2 - Log_{10}(R+T)$$

where A is absorbance, R is reflectance (%), and T is transmittance (%).

Absorbance of thin-films was calculated using the same formula, except specular reflectance was measured instead of diffuse reflectance. Solid-state emission spectra were collected using the front-facing accessory on a Horiba Jobin Yvon Fluorolog3 and collected 22.5° from the incident beam.

# 2.5.5 Thin Film Deposition

Thin films were made via physical vapor deposition (AMOD Thermal Deposition System, Ångstrom Engineering Inc.) onto rigorously cleaned quartz substrates. All films were deposited in order to achieve 100nm thick thin films. Vapor annealing of thin films were done in sealed fuming chambers with volumes of DCM between 150  $\mu$ L (using a hermetically sealed chamber) and 10 mL (using a non-sealed chamber) to generate the orange film.

#### 2.5.6 Synthetic Procedures and Characterizations

**4-bromonaphthalen-1-ol (4-bromo-1-naphthol):** To a solution of 1-naphthol (20.8 g, 144 mmol) in dry acetonitrile (145 mL) was added freshly recrystallized NBS (27.0 g, 152 mmol) in several portions at room temperature over 30 min. After complete addition of the NBS, the reaction was allowed to stir at room temperature for an addition 4 hours. The reaction solution was then poured into H<sub>2</sub>O (100 mL) and extracted with diethyl ether twice (2 x 100 mL). The organic layers were then combined and washed with H<sub>2</sub>O (3 x 500 mL) and sat. NaCl (3 x 500 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of diethyl ether by rotary evaporation yielded the crude product which was then subjected to column chromatography (20%/80% DCM/hexanes to 100% DCM) to yield 4-bromo-1-naphthol as an off-white powder after rotary evaporation (22.3 g, 99.8 mmol, 69 % yield).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (t, *J* = 9.5 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  151.38, 132.87, 129.53, 128.02, 127.22, 126.18, 125.75, 122.30, 113.61, 109.31. HRMS (CI, positive): Calc. for C<sub>10</sub>H<sub>7</sub>BrO [M]<sup>+</sup> 221.9680, found 221.9674.

**1-bromo-4-methoxynaphthalene (MAN 1.1):** To a solution of 4-bromo-1-naphthol (3.0 g, 13.4 mmol) in dry acetonitrile (80 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (5.5 g, 39.8 mmol) and methyl iodide (1.2 mL, 19.3 mmol) and the solution was heated to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug, which was then rinsed with DCM (500 mL). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography (100% hexanes) to yield **MAN 1.1** as a clear oil (2.15 g, 9.07 mmol, 67.4% yield).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.35, 132.53, 129.57, 127.87, 126.97, 126.91, 126.06, 122.54, 113.35, 104.61, 55.78. HRMS (CI, positive): Calc. for C<sub>11</sub>H<sub>9</sub>BrO [M]<sup>+</sup> 235.9837, found 235.9835.

4-(4-methoxynaphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 1.2): To a stirring solution of MAN 1.1 (1.65 g, 6.96 mmol) in triethylamine (70 mL) was added 2-methyl-3-butyn-2-ol (2.05 mL, 20.9 mmol) and Nitrogen was bubbled through the solution for 10 min. After degassing the solution, CuI (66 mg, 5 mol %), PPh<sub>3</sub> (91 mg, 5 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (244 mg, 5 mol %) were added and the reaction was brought to 90 °C and left to reflux overnight. The reaction was then filtered, washed with diethyl ether (100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and sat. NaCl (3 x 300 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 1.2 as a yellow-white solid (851 mg, 3.54 mmol, 50.1% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.51 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.01 (s, 3H), 2.10 (s, 1H), 1.72 (s, 6H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.11, 134.33, 131.16, 127.42, 125.93, 125.83, 125.48, 122.39, 112.51, 103.58, 97.22, 80.58, 66.10, 55.76, 31.92. HRMS (CI, positive): Calc. for C<sub>16</sub>H<sub>1602</sub> [M]<sup>+</sup> 240.1150, found 240.1156.

1-ethynyl-4-methoxynaphthalene (MAN 1.3): To a round bottom flask containing MAN 1.2 (850 mg, 3.54 mmol) was added finely ground KOH (595 mg, 10.6 mmol) and toluene (35 mL). The reaction was then refluxed for 6 hours and upon cooling, the KOH was filtered, and washed with DCM until the filtrate was colorless (~100 mL). The solution was concentrated under reduced pressure and subsequent purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded MAN 1.3 as a brown oil (511 mg, 2.80 mmol, 79.2% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 – 8.25 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H), 3.38 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  156.47, 134.57, 132.05, 127.58, 125.98, 125.92, 125.44,

122.41, 111.98, 103.52, 82.23, 80.40, 55.79. HRMS (APCI, positive): Calc. for C<sub>13</sub>H<sub>10</sub>O [M+H]<sup>+</sup> 183.08040, found 183.08110.

**6-bromo-2-methyl-1***H***-benzo**[*de*]isoquinoline-1,3(*2H*)-dione (NI 1): To a solution of 4-bromo-1,8-naphthalic anhydride (1.0 g, 3.6 mmol) was added Methylamine (40 wt. % in H<sub>2</sub>O; 10 mL) and 5 mL of Ethanol to aid in the dissolution of starting materials. The vial was purged with Nitrogen, then briefly sonicated before leaving the solution to stir at 35°C overnight. After the reaction was deemed complete by TLC the following morning, 5mL of cold ethanol was added. The reaction was then filtered and the filtered solids were washed with H<sub>2</sub>O until the filtrate was colorless. To recrystallize the crude product, the washed solid was dissolved in boiling ethanol, then left to cool at room temperature for 3 hours, before being moved to the freezer to sit overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give **NI 1** as pale-yellow needles (0.69 g, 2.4 mmol, 66% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (d, *J* = 7.3 Hz, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 3.54 (s, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.94, 163.91, 133.38, 132.11, 131.29, 131.20, 130.68, 130.40, 128.91, 128.17, 123.06, 122.19, 27.22. HRMS (CI, negative): Calc. for C<sub>13</sub>H<sub>8</sub>BrNO<sub>2</sub> [M]<sup>-</sup> 288.9738, found 288.9737.

#### 6-((4-methoxynaphthalen-1-yl)ethynyl)-2-methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione

(1): To an oven-dried three neck flask containing NI 1 (1.12 g, 3.85 mmol) and MAN 1.3 (540 mg, 2.96 mmol) was added dry triethylamine (30 mL) and toluene (30 mL) and the solution was degassed for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (39 mg, 5 mol %), CuI (28 mg, 5 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (104 mg, 5 mol %). The reaction solution was purged with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir overnight. After allowing the reaction to cool, the reaction was filtered to

obtain the product which was rinsed with H<sub>2</sub>O (150 mL) and dried under vacuum. Recrystallization of the crude product in toluene yielded 1 as a bright, neon orange crystals (865 mg, 2.21 mmol, 74.7 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.88 (dd, J = 8.4, 1.3 Hz, 1H), 8.68 (dd, J = 7.2, 1.2 Hz, 1H), 8.61 (d, J = 7.6 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.70 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.59 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 4.09 (s, 3H), 3.59 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.56, 164.29, 157.25, 134.27, 132.81, 132.47, 131.78, 131.75, 130.72, 128.58, 128.28, 128.01, 127.57, 126.23, 125.85, 125.63, 123.07, 122.78, 121.75, 112.09, 103.92, 98.37, 90.01, 55.95, 27.24. HRMS (CI, negative): Calc. for C<sub>26</sub>H<sub>17</sub>NO<sub>3</sub> [M]<sup>-</sup> 391.1208 , found 391.1212.

**1-bromo-4-(hexyloxy)naphthalene (MAN 6.1) :** To a solution of 4-bromo-1-naphthol (4.0 g, 17.9 mmol) in dry acetonitrile (106 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (7.4 g, 53.7 mmol) and 1-bromohexane (3.02 mL, 21.5 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (~100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug which was then rinsed with DCM till the filtrate was colorless (~500 mL). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography (100% hexanes) to yield **MAN 6.1** as a white solid (4.32 g, 14.1 mmol, 78.4% yield).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.60 – 1.52 (m, 2H), 1.44 – 1.32 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.73, 132.50, 129.60, 127.71, 127.03, 126.86, 125.84, 122.62, 112.93, 105.23, 68.37, 31.73, 29.25, 26.01, 22.75, 14.20. HRMS (CI, positive): Calc. for C<sub>16</sub>H<sub>19</sub>BrO [M]<sup>+</sup> 306.0619, found 306.0612.

4-(4-(hexyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 6.2): To a stirring solution of MAN 6.1 (2.5 g, 8.1 mmol) in triethylamine (62 mL) was added 2-methyl-3-butyn-2-ol (1.1 mL, 11.4 mmol) and Argon was bubbled through the solution for 10 min. After degassing the solution, CuI (154 mg, 10 mol %), PPh3 (212 mg, 10 mol %) and PdCl2(PPh3)2 (569 mg, 10 mol %) were added and the reaction was brought to 90 °C and left for 20 hrs. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether (2 x 100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and brine (3 x 300 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 6.2 as a brown oil (1.023 g, 3.3 mmol, 40.8% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, J = 8.3 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.60 - 7.54 (m, 2H), 7.50 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.14 (t, J = 6.4 Hz, 2H), 2.08 (s, 1H), 1.97 – 1.88 (m, 2H), 1.72 (s, 6H), 1.61 – 1.54 (m, 2H), 1.45 -1.32 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.62, 134.37, 131.25, 127.34, 125.90, 125.70, 125.63, 122.51, 112.14, 104.28, 97.11, 80.67, 68.45, 66.11, 31.93, 31.76, 29.32, 26.07, 22.77, 14.20. HRMS (CI, positive): Calc. for C<sub>21</sub>H<sub>2602</sub> [M]<sup>+</sup> 310.1933, found 310.1936.

**1-ethynyl-4-(hexyloxy)naphthalene (MAN 6.3):** To a round bottom flask containing **MAN 6.2** (0.913 g, 2.9 mmol) was added finely ground KOH (0.460 g, 8.2 mmol) and toluene (22 mL). The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded **MAN 6.3** as a brown oil (0.647 g, 2.6 mmol, 87% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 – 8.27 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H),

4.15 (t, J = 6.4 Hz, 2H), 3.38 (s, 1H), 1.93 (p, J = 6.8 Hz, 2H), 1.56 (dd, J = 10.6, 4.7 Hz, 2H), 1.45 – 1.32 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.98, 134.63, 132.14, 127.50, 125.95, 125.79, 125.59, 122.53, 111.61, 104.22, 82.33, 80.28, 68.49, 31.75, 29.30, 26.06, 22.77, 14.20. HRMS (CI, positive): Calc. for C<sub>18</sub>H<sub>20</sub>O [M]<sup>+</sup> 252.1514, found 252.1516.

**6-bromo-2-hexyl-1***H***-benzo**[*de*]isoquinoline-1,3(2*H*)-dione (NI 6): To a solution of 4-bromo-1,8-naphthalic anhydride (1.0 g, 3.6 mmol) in ethanol (10 mL) was added 1-hexyylamine (0.57 mL, 4.3 mmol). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol (50mL). To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature for 3 hours, before being moved to the freezer where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 6 as off-white needles (0.367 g, 1.0 mmol, 28% yield).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.66 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.57 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.85 (dd, *J* = 8.5, 7.3 Hz, 1H), 4.16 (t, *J* = 7.7 Hz, 2H), 1.72 (q, *J* = 7.9, 7.3 Hz, 2H), 1.46 – 1.29 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.78, 163.76, 133.36, 132.16, 131.35, 131.24, 130.80, 130.33, 129.19, 128.23, 123.35, 122.49, 40.78, 31.69, 28.18, 26.93, 22.71, 14.20. HRMS (CI, negative): Calc. for C<sub>18</sub>H<sub>18</sub>BrNO<sub>2</sub> [M]<sup>-</sup> 359.0521, found 359.0513.

#### 2-hexyl-6-((4-(hexyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(6): To an oven-dried three neck flask containing NI 6 (241 mg, 0.955 mmol) and MAN 6.3 (515 mg, 1.43 mmol) was added dry triethylamine (25 mL) and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (25 mg, 10 mol %), CuI (18 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (67 mg, 10

mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 18 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O (100 mL) and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield **6** as a yellow solid (421 mg, 0.792 mmol, 82.9 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.66 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.69 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.25 – 4.16 (m, 4H), 2.02 – 1.93 (m, 2H), 1.80 – 1.70 (m, 2H), 1.65 – 1.55 (m, 2H), 1.49 – 1.28 (m, 10H), 0.94 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 164.00, 156.76, 134.33, 132.69, 132.57, 131.72, 130.66, 128.49, 128.38, 127.94, 127.53, 126.10, 125.83, 125.77, 123.23, 122.88, 121.88, 111.74, 104.60, 98.44, 90.01, 68.68, 40.74, 31.76, 31.73, 29.30, 28.25, 26.98, 26.08, 22.79, 22.73, 14.23, 14.21. (CI, negative): Calc. for C<sub>36</sub>H<sub>37</sub>NO<sub>3</sub> [M]<sup>-</sup> 531.2773, found 531.2786.

**1-bromo-4-(heptyloxy)naphthalene (MAN 7.1):** To a solution of 4-bromo-1-naphthol (3.72 g, 16.7 mmol) in dry acetonitrile (80 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (6.9 g, 49.9 mmol) and 1-bromoheptane (3.4 mL, 21.7 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug which was then rinsed with DCM (500 mL). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography (100% hexanes) to yield **MAN 7.1** as a white solid (4.189 g, 13.0 mmol, 78.1% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.93 (p, *J* = 7.3, 6.5 Hz, 2H), 1.56 (p, *J* = 7.2 Hz, 2H), 1.47 – 1.30 (m, 6H), 0.93 (t, *J* = 7.0 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.86, 132.59,

129.65, 127.80, 127.13, 126.95, 125.95, 122.67, 113.03, 105.38, 68.55, 31.95, 29.35, 29.24, 26.36, 22.78, 14.25. HRMS (CI, positive): Calc. for C<sub>17</sub>H<sub>21</sub>BrO [M]<sup>+</sup> 320.0776, found 320.0767.

4-(4-(heptyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 7.2): To a stirring solution of MAN 7.1 (3.692 g, 11.5 mmol) in triethylamine (88 mL) was added 2-methyl-3-butyn-2-ol (1.45 mL, 14.9 mmol) and Argon was bubbled through the solution for 10 min. After degassing the solution, CuI (110 mg, 5 mol %), PPh<sub>3</sub> (152 mg, 5 mol %), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (407 mg, 5 mol %) were added and the reaction was brought to 90°C and left for 23 hrs. The reaction was then filtered, washed with diethyl ether (100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H2O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and sat. NaCl (3 x 300 mL). The organic layer was then dried over  $Na_2SO_4$ , loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 7.2 as brown oil (1.815 mg, 5.59 mmol, 48.7% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.50 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.13 (t, J = 6.4 Hz, 2H), 2.23 (s, 1H),1.93 (p, J = 7.5, 6.6 Hz, 2H), 1.73 (s, 6H), 1.60 – 1.51 (m, 2H), 1.46 – 1.29 (m, 6H), 0.92 (t, J =6.6 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.58, 134.36, 131.24, 127.32, 125.89, 125.67, 125.60, 122.49, 112.14, 104.27, 97.13, 80.65, 68.42, 66.07, 31.94, 31.91, 29.34, 29.24, 26.34, 22.77, 14.23. HRMS (CI, positive): Calc. for C<sub>22</sub>H<sub>2802</sub> [M]<sup>+</sup> 324.2089, found 324.2085.

**1-ethynyl-4-(heptyloxy)naphthalene (MAN 7.3):** To a round bottom flask containing **MAN 7.2** (1.510 g, 4.65 mmol) was added finely ground KOH pellets (784 mg, 14 mmol) and toluene (36 mL). The reaction was then refluxed for 12 hrs and upon cooling the KOH was filtered, washed using DCM, and concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded **MAN 7.3** as an amber-brown oil (1.220 g, 4.58 mmol, 98.5% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 – 8.27 (m, 2H), 7.66 (d, *J* 

= 8.0 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 4.15 (t, J = 6.4 Hz, 2H), 3.38 (s, 1H), 1.98 – 1.89 (m, 2H), 1.61 – 1.51 (m, 2H), 1.45 – 1.29 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.97, 134.62, 132.14, 127.50, 125.94, 125.78, 125.58, 122.53, 111.60, 104.21, 82.33, 80.28, 68.48, 31.95, 29.33, 29.24, 26.35, 22.78, 14.24. HRMS (CI, positive): Calc. for C<sub>19</sub>H<sub>22</sub>O [M]<sup>+</sup> 266.1671, found 266.1670.

**6-bromo-2-heptyl-1H-benzo**[*de*]isoquinoline-1,3(2*H*)-dione (NI 7): To a solution of 4-bromo-1,8-naphthalic anhydride (1.0 g, 3.6 mmol) in ethanol (10 mL) was added 1-heptylamine (0.64 mL, 4.3 mmol). The vial was purged with Nitrogen and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered and washed with hot ethanol (50mL) to remove unwanted, insoluble by-products. To recrystallize the product, the filtrate was then heated and additional ethanol was added until the contents were completely dissolved. The flask was cooled to room temperature for 3 hours, before then being moved to the freezer, where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 7 as off-white needles (0.515 g, 1.38 mmol, 38.1% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.65 (d, *J* = 7.3 Hz, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.40 (d, *J* = 7.5 Hz, 2H), 1.46 – 1.26 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.75, 163.72, 133.33, 132.13, 131.33, 131.22, 130.77, 130.30, 129.15, 128.21, 123.33, 122.46, 40.78, 31.90, 29.17, 28.23, 27.23, 22.75, 14.22. HRMS (CI, negative): Calc. for C<sub>19</sub>H<sub>20</sub>BrNO<sub>2</sub> [M]<sup>-</sup> 373.0667, found 373.0668.

#### 2-heptyl-6-((4-(heptyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-

**dione (7):** To a solution of **NI** 7 (1.04 mg, 2.78 mmol) in dry triethylamine (75 mL) was added PPh<sub>3</sub> (57 mg, 5 mol %) and **MAN 7.3** (1.158 mg, 4.34 mmol). Argon was bubbled through the solution for 10 min. To this solution was added CuI (41 mg, 5 mol %), PPh<sub>3</sub> (57 mg, 5 mol%) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (152 mg, 5 mol %) and the reaction was heated to 90°C for 12 hrs. After

allowing the reaction to cool, the reaction was filtered to obtain the product which was rinsed with H<sub>2</sub>O and dried under vacuum. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded **7** as a yellow-orange solid (893 mg, 1.60 mmol, 57.4 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 7.3 Hz, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.25 – 4.16 (m, 4H), 1.98 (p, *J* = 7.6, 6.4 Hz, 2H), 1.75 (p, *J* = 7.7 Hz, 2H), 1.59 (p, *J* = 7.8, 7.3 Hz, 2H), 1.46 – 1.26 (m, 14H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 164.00, 156.76, 134.33, 132.69, 132.57, 131.72, 130.67, 128.49, 128.39, 127.93, 127.53, 126.10, 125.83, 125.77, 123.23, 122.89, 121.88, 111.74, 104.60, 98.44, 90.00, 68.69, 40.75, 31.96, 31.93, 29.34, 29.26, 29.22, 28.32, 27.28, 26.37, 22.80, 22.77, 14.26, 14.24.HRMS (CI, negative): Calc. for C<sub>38</sub>H<sub>41</sub>NO<sub>3</sub> [M]<sup>-</sup> 559.3086 , found 559.3094.

**1-bromo-4-(octyloxy)naphthalene (MAN 8.1):** To a solution of 4-bromo-1-naphthol (4.0 g, 17.9 mmol) in dry acetonitrile (100 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (7.42 g, 53.7 mmol) and 1-bromooctane (4.0 mL, 23.3 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug which was then rinsed with DCM (500 mL). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography (100% hexanes) to yield **MAN 8.1** as a white solid (4.2 g, 12.5 mmol, 70% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.52 (td, *J* = 7.6, 6.9, 1.2 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 1.92 (p, *J* = 7.3, 6.5 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.45 – 1.27 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.88, 132.60, 129.66, 127.82, 127.14, 126.97, 125.96, 122.68, 113.04, 105.41, 68.58, 31.98, 29.53, 29.41, 29.35, 26.40, 22.82, 14.26. HRMS (CI, positive): Calc. for C<sub>18</sub>H<sub>23</sub>BrO [M]<sup>+</sup> 334.0932, found 334.0923.

2-methyl-4-(4-(octyloxy)naphthalen-1-yl)but-3-yn-2-ol (MAN 8.2): To an oven-dried three neck flask containing MAN 8.1 (3.24g, 9.66 mmol) in triethylamine (78 mL) was added 2methyl-3-butyn-2-ol (1.42 mL, 14.6 mmol) and Nitrogen was bubbled through the solution for 10 min. The three-neck flask was then equipped with a solid addition funnel containing  $PPh_3$ (274 mg, 10 mol %), CuI (199 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (730 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir overnight. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether (2 x 100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and brine (3 x 300 mL). The organic layer was then dried over  $Na_2SO_4$ , loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 8.2 as a brown oil (1.23 g, 3.63 mmol, 35.0% yield).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.50 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.14 (t, J = 6.4 Hz, 2H), 2.11 (s, 1H),1.97 - 1.88 (m, 2H), 1.72 (s, 6H), 1.58 - 1.53 (m, 2H), 1.42 - 1.29 (m, 8H), 0.90 (t, J = 6.7 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.62, 134.37, 131.25, 127.34, 125.89, 125.70, 125.62, 122.51, 112.14, 104.28, 97.11, 80.67, 68.45, 66.10, 31.98, 31.93, 29.85, 29.53, 29.40, 29.35, 26.39, 22.82, 14.26. HRMS (CI, positive): Calc. for C<sub>23</sub>H<sub>30</sub>O<sub>2</sub> [M]<sup>+</sup> 338.2246, found 338.2244.

**1-ethynyl-4-(octyloxy)naphthalene (MAN 8.3):** To a round bottom flask containing **MAN 8.2** (0.693 g, 2.05 mmol) was added finely ground KOH pellets (345 mg, 6.15 mmol) and toluene (16 mL). The reaction was then refluxed for 12 hrs and upon cooling the KOH was filtered, washed using DCM, and concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded **MAN 8.3** as a brown oil (0.549 g, 1.96 mmol, 95.5% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 – 8.27 (m, 2H), 7.66 (d, *J* = 8.0

Hz, 1H), 7.59 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.51 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 4.15 (t, J = 6.4 Hz, 2H), 3.38 (s, 1H), 1.93 (p, J = 7.4, 6.6 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.45 – 1.28 (m, 8H), 0.90 (t, J = 6.7 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.98, 134.62, 132.14, 127.50, 125.94, 125.78, 125.58, 122.54, 111.60, 104.22, 82.33, 80.28, 68.49, 31.98, 29.53, 29.41, 29.32, 26.38, 22.82, 14.26. HRMS (CI, positive): Calc. for C<sub>20</sub>H<sub>24</sub>O [M]<sup>+</sup> 280.1827, found 280.1820.

**6-bromo-2-octyl-1***H***-benzo**[*de*]**isoquinoline-1,3(2***H***)-dione (NI 8):** To a solution of 4-bromo-1,8-naphthalic anhydride (3.0 g, 10.8 mmol) in ethanol (30 mL) was added 1-octylamine (2.50 mL, 15.1 mmol). The vial was purged with Nitrogen and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered and washed with hot ethanol (50mL) to remove unwanted, insoluble by-products. To recrystallize the product, the filtrate was then heated and additional ethanol was added until the contents were completely dissolved. The flask was cooled to room temperature for 3 hours, before then being moved to the freezer, where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 8 as pale-yellow needles (2.346 g, 6.05 mmol, 56% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.65 (d, *J* = 7.2 Hz, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.40 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.74, 163.72, 133.32, 132.13, 131.33, 131.22, 130.76, 130.30, 129.15, 128.20, 123.32, 122.46, 40.78, 31.96, 29.47, 29.36, 28.23, 27.28, 22.78, 14.23. HRMS (CI, negative): Calc. for C<sub>20</sub>H<sub>22</sub>BrNO<sub>2</sub> [M]<sup>-</sup> 387.0834 , found 387.0826.

#### 2-octyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(8): To an oven-dried three neck flask containing NI 8 (296 mg, 0.76 mmol) and MAN 8.3 (165 mg, 0.59 mmol) was added dry triethylamine (15 mL) and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition

funnel containing PPh<sub>3</sub> (16 mg, 10 mol %), CuI (11 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (42 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for xx hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) yielded **8** as a yellow solid (241 mg, 0.41 mmol, 69.7 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 (d, *J* = 7.2 Hz, 1H), 8.67 (d, *J* = 7.2 Hz, 1H), 8.59 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.25 – 4.16 (m, 4H), 1.97 (p, *J* = 7.8, 6.7 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.59 (p, *J* = 7.5 Hz, 2H), 1.49 – 1.22 (m, 18H), 0.94 – 0.85 (m, 6H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 164.00, 156.76, 134.33, 132.69, 132.57, 131.72, 130.67, 128.49, 128.39, 127.93, 127.53, 126.09, 125.83, 125.77, 123.23, 122.89, 121.88, 111.73, 104.60, 98.44, 90.01, 68.69, 40.75, 31.99, 29.54, 29.52, 29.42, 29.39, 29.33, 28.32, 27.33, 26.40, 22.83, 22.80, 14.27, 14.25. HRMS (CI, negative): Calc. for C<sub>40</sub>H<sub>45</sub>NO<sub>3</sub> [M]<sup>-</sup> 587.3399, found 587.3413.

**1-bromo-4-(nonyloxy)naphthalene (MAN 9.1)**: To a solution of 4-bromo-1-naphthol (1.94 g, 8.7 mmol) in dry acetonitrile (51 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (3.6 g, 26. mmol) and 1-bromononane (2.16 mL, 11.3 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (~100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug which was then rinsed with DCM till the filtrate was colorless (~500 mL). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography (100% hexanes) to yield **MAN 9.1** as a white solid (2.32 g, 6.6 mmol, 77% yield). <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.32 (ddd, *J* = 8.4, 1.4, 0.7 Hz, 1H), 8.17 (ddd, *J* = 8.4, 1.3, 0.6 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.53 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.10 (t, *J* = 6.4 Hz, 2H), 1.93 (p, *J* = 8.0, 6.8, 6.6 Hz, 2H), 1.56 (p, *J* = 7.4, 6.8 Hz, 2H), 1.47 – 1.25 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, cdcl<sub>3</sub>)  $\delta$ 

154.85, 132.59, 129.65, 127.80, 127.12, 126.96, 125.94, 122.67, 113.02, 105.37, 68.54, 32.04, 29.71, 29.57, 29.43, 29.34, 26.38, 22.84, 14.27. (CI, positive): Calc. for  $C_{19}H_{25}OBr [M]^+$  348.1089, found 348.1088.

2-methyl-4-(4-(nonyloxy)naphthalen-1-yl)but-3-yn-2-ol (MAN 9.2): To a stirring solution of MAN 9.1 (1.81 g, 5.2 mmol) in triethylamine (40 mL) was added 2-methyl-3-butyn-2-ol (0.71 mL, 7.25 mmol) and Argon was bubbled through the solution for 10 min. After degassing the solution, CuI (49.5 mg, 5 mol %), PPh<sub>3</sub> (68.2 mg, 5 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (182 mg, 5 mol %) were added and the reaction was brought to 90 °C and left for 20 hrs. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether (2 x 100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and brine (3 x 300 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 9.2 as a brown oil (0.707 g, 2.01 mmol, 38.6% yield). <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.30 (ddd, J = 8.3, 1.5, 0.8 Hz, 1H), 8.23 (ddd, J = 8.3, 1.4, 0.7 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.50 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.12 (t, J = 6.4 Hz, 2H), 2.23 (s, 1H), 1.92 (p, J = 7.6, 7.0, 6.5, 6.5 Hz, 2H), 1.73 (s, 6H), 1.60 – 1.52 (m, 2H), 1.43 – 1.25 (m, 10H), 0.90 (t, J = 6.7 Hz, 3H). <sup>13</sup>C NMR  $(101 \text{ MHz}, \text{ cdcl}_3) \delta 155.51, 134.33, 131.21, 127.28, 125.87, 125.63, 125.56, 122.46, 112.13,$ 104.23, 97.16, 80.60, 77.48, 77.16, 76.84, 68.36, 66.01, 53.52, 32.00, 31.88, 29.66, 29.54, 29.39, 29.29, 26.34, 22.80, 14.23. (CI, positive): Calc. for C<sub>24</sub>H<sub>32</sub>O<sub>2</sub> [M]<sup>+</sup> 352.2402, found 352.2399.

**1-ethynyl-4-(nonyloxy)naphthalene (MAN 9.3)**: To a round bottom flask containing **MAN 9.2** (0.555 g, 1.6 mmol) was added finely ground KOH (0.265 g, 4.8 mmol) and toluene (12.3 mL). The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being

concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded **MAN 9.3** as a brown oil (0.357 g, 1.21 mmol, 77.0% yield). 1H NMR (400 MHz, cdcl3)  $\delta$  8.41 – 8.33 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.64 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.56 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.12 (t, J = 6.4 Hz, 2H), 3.44 (s, 1H), 1.94 (p, J = 7.9, 7.3, 6.6, 6.6 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.48 – 1.30 (m, 10H), 0.96 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, cdcl3)  $\delta$  155.90, 134.59, 132.11, 127.45, 125.92, 125.73, 125.54, 122.52, 111.58, 104.14, 82.32, 80.30, 68.38, 32.03, 29.70, 29.56, 29.43, 29.29, 26.35, 22.84, 14.27. (CI, positive): Calc. for C21H26O [M]+ 294.1984, found 294.1981.

**6-bromo-2-nonyl-1H-benzo[de]isoquinoline-1,3(2H)-dione** (**NI 9**): To a solution of 4-bromo-1,8-naphthalic anhydride (2.15 g, 7.8 mmol) in ethanol (21.5 mL) was added n-nonylamine (1.7 mL, 9.3 mmol). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 9 as yellow-white needles (2.463 g, 6.12 mmol, 78.9% yield). 1H NMR (400 MHz, cdcl3)  $\delta$  8.64 (dt, J = 7.3, 1.1 Hz, 1H), 8.54 (dt, J = 8.5, 1.2 Hz, 1H), 8.39 (dd, J = 7.8, 1.0 Hz, 1H), 8.02 (dd, J = 7.8, 1.0 Hz, 1H), 7.83 (ddd, J = 8.4, 7.3, 0.8 Hz, 1H), 4.15 (t, J = 7.5 Hz, 2H), 1.71 (p, J = 7.5 Hz, 2H), 1.45 – 1.22 (m, 12H), 0.86 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3)  $\delta$  163.76, 163.74, 133.34, 132.15, 131.34, 131.23, 130.79, 130.31, 129.17, 128.22, 123.34, 122.48, 40.79, 32.00, 29.65, 29.51, 29.41, 28.24, 27.28, 22.81, 14.25. (CI, positive): Calc. for C<sub>21</sub>H<sub>24</sub>BrNO<sub>2</sub> [M]<sup>+</sup> 401.0990, found 401.0996.

2-nonyl-6-((4-(nonyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (9): To an oven-dried three neck flask containing NI 9 (718 mg, 1.8 mmol) and MAN 9.3 (350 mg, 1.2 mmol) was added dry triethylamine (30 mL) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh3 (16 mg, 5 mol %), CuI (11 mg, 5 mol %) and PdCl2(PPh3)2 (42 mg, 5 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 17 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H2O and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield 9 as an orange-yellow solid (569 mg, 0.92 mmol, 77.7 % yield). 1H NMR (400 MHz, cdcl3)  $\delta$ 8.82 (dd, J = 8.4, 1.2 Hz, 1H), 8.63 (dd, J = 7.3, 1.2 Hz, 1H), 8.55 (d, J = 7.7 Hz, 1H), 8.40 (dt, J = 8.3, 0.9 Hz, 1H), 8.35 (dt, J = 8.2, 1.0 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.86 - 7.80 (m, 2H), 7.67 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.57 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 4.23 – 4.14 (m, 4H), 1.96 (dt, J = 14.2, 6.5 Hz, 2H), 1.74 (p, J = 7.5 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.47 – 1.25 (m, 22H), 0.94 – 0.84 (m, 6H). 13C NMR (101 MHz, cdcl3) δ 164.19, 163.92, 156.73, 134.29, 132.60, 132.55, 131.64, 130.60, 128.44, 128.32, 127.90, 127.46, 126.06, 125.80, 125.74, 123.19, 122.87, 121.83, 111.73, 104.58, 98.43, 90.03, 68.68, 40.73, 32.04, 32.02, 29.71, 29.68, 29.58, 29.55, 29.43, 29.34, 28.31, 27.34, 26.40, 22.84, 22.82, 14.26. (CI, positive): Calc. for C42H49NO3 [M]+ 615.3712, found 615.3721.

**1-bromo-4-(decyloxy)naphthalene (MAN 10.1)**: To a solution of 4-bromo-1-naphthol (4.00 g, 17.9 mmol) in dry acetonitrile (100 mL) was added dry  $K_2CO_3$  (7.42 g, 53.7 mmol) and 1-bromodecane (4.82 mL, 23.3 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (~100mL) and the  $K_2CO_3$  removed using a celite plug which was then rinsed with DCM till the filtrate was colorless (~500 mL). The crude solution was then adsorbed onto silica, which was

then subjected to column chromatography (100% hexanes) to yield **MAN 10.1** as an oily white solid (3.62 g, 9.96 mmol, 56% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (dd, J = 8.4, 1.3 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 4.11 (t, J = 6.4 Hz, 2H), 1.93 (p, J = 7.7, 7.3, 6.7, 6.4 Hz, 2H), 1.56 (p, J = 7.8, 7.3 Hz, 2H), 1.43 – 1.27 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.87, 132.60, 129.66, 127.81, 127.14, 126.97, 125.95, 122.68, 113.04, 105.40, 68.57, 32.06, 29.74, 29.72, 29.56, 29.48, 29.34, 26.39, 22.84, 14.27. (CI, positive): Calc. for C<sub>20</sub>H<sub>27</sub>BrO [M]<sup>+</sup> 362.1245, found 362.1240.

4-(4-(decyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 10.2): To a stirring solution of MAN 10.1 (2.50 g, 6.9 mmol) in triethylamine (53 mL) was added 2-methyl-3-butyn-2-ol (0.95 mL, 9.7 mmol) and Argon was bubbled through the solution for 10 min. After degassing the solution, CuI (131 mg, 10 mol %), PPh<sub>3</sub> (181 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (484 mg, 10 mol %) were added and the reaction was brought to 90 °C and left for 23 hrs. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether (2 x 100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and brine (3 x 300 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50%) DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 10.2 as a brown oil (1.085 g, 2.96 mmol, 42.8% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.60 - 7.54 (m, 2H), 7.50 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.14 (t, J = 6.4 Hz, 2H), 2.08 (s, 1H), 1.93 (dt, J = 14.6, 6.6 Hz, 2H), 1.72 (s, 6H), 1.62 – 1.50 (m, 2H), 1.42 - 1.26 (m, 12H), 0.88 (t, J = 7.1, 6.6 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 155.63, 134.39, 131.25, 127.34, 125.90, 125.70, 122.52, 112.01, 104.30, 97.12, 80.68, 68.47, 66.11, 32.06, 31.93, 29.86, 29.74, 29.72, 29.57, 29.48, 29.35, 26.39, 22.83, 14.26. (CI, positive): Calc. for C<sub>25</sub>H<sub>34</sub>O<sub>2</sub> [M]<sup>+</sup> 366.2559, found 366.2572.

**1-(decyloxy)-4-ethynylnaphthalene** (MAN 10.3): To a round bottom flask containing MAN **10.2** (1.00 g, 2.7 mmol) was added finely ground KOH (0.459 g, 8.2 mmol) and toluene (21 mL). The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded MAN 10.3 as a brown solid (0.813 g, 2.64 mmol, 96.6% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 – 8.29 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 3.39 (s, 1H), 1.93 (dt, *J* = 14.4, 6.7 Hz, 2H), 1.56 (p, *J* = 7.2 Hz, 2H), 1.43 – 1.26 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.97, 134.62, 132.13, 127.49, 125.94, 125.77, 125.58, 122.54, 111.60, 104.21, 82.33, 80.28, 68.47, 32.06, 29.74, 29.72, 29.56, 29.48, 29.32, 26.37, 22.84, 14.27. (CI, positive): Calc. for C<sub>22</sub>H<sub>28</sub>O [M]<sup>+</sup> 308.2140, found 308.2133.

**6-bromo-2-decyl-1***H***-benzo**[*de*]**isoquinoline-1,3(2***H***)-dione** (**NI 10**): To a solution of 4-bromo-1,8-naphthalic anhydride (2.150 g, 7.76 mmol) in ethanol (33 mL) was added n-decylamine (2.00 mL, 9.90 mmol). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give **NI 10** as fluffy yellow needles (2.386 g, 5.73 mmol, 73.9% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.65 (d, *J* = 7.4 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.84 (dd, *J* = 8.5, 7.3 Hz, 1H), 4.16 (t, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.45 – 1.22 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.76, 163.73, 133.33,

132.14, 131.34, 131.23, 130.78, 130.31, 129.16, 128.21, 123.34, 122.48, 40.79, 32.03, 29.70, 29.51, 29.44, 28.23, 27.28, 22.82, 14.26. (CI, positive): Calc. for C<sub>22</sub>H<sub>26</sub>BrNO<sub>2</sub> [M]<sup>+</sup> 415.1147, found 415.1135.

# 2-decyl-6-((4-(decyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(10): To an oven-dried three neck flask containing NI 10 (572 mg, 1.37 mmol) and MAN 10.3 (305 mg, 0.989 mmol) was added dry triethylamine (33 mL) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (26 mg, 10 mol %), CuI (19 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 21 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield 10 as a yellow-orange solid (564 mg, 0.876 mmol, 89 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.87 (dd, J = 8.3, 1.3 Hz, 1H), 8.67 (dd, J = 7.2, 1.2 Hz, 1H), 8.60 (d, J = 7.6 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.38 (dd, J = 8.4, 1.1 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.69 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.58 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 4.25 -4.16 (m, 4H), 1.97 (p, J = 6.6 Hz, 2H), 1.75 (dt, J = 15.3, 7.6 Hz, 2H), 1.59 (p, J = 7.4 Hz, 2H), 1.46 - 1.24 (m, 26H), 0.92 - 0.85 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.25, 163.99, 156.76, 134.34, 132.68, 132.57, 131.71, 130.66, 128.49, 128.39, 127.93, 127.52, 126.09, 125.83, 125.79, 123.24, 122.89, 121.89, 111.75, 104.61, 98.44, 90.01, 68.70, 40.75, 32.07, 32.05, 29.75, 29.73, 29.57, 29.55, 29.49, 29.46, 29.33, 28.32, 27.33, 26.40, 22.84, 14.27. (CI, Negative) Calc. for C<sub>44</sub>H<sub>53</sub>NO<sub>3</sub> [M<sup>-</sup>] 643.4025, found 643.4024.

1-bromo-4-(dodecyl)naphthalene (MAN 12.1): To a solution of 4-bromo-1-naphthol (2.00 g, 8.97mmol) in dry acetonitrile (70 mL) was added dry K<sub>2</sub>CO<sub>3</sub> (3.27 g, 26.9 mmol) and 1-

bromododecane (2.80 mL, 11.7 mmol) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM (~100mL) and the K<sub>2</sub>CO<sub>3</sub> removed using a celite plug which was then rinsed with DCM till the filtrate was colorless (~500 mL). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography (100% hexanes) to yield **MAN 12.1** as a white solid (3.10 g, 7.92 mmol, 88.3% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.92 (p, *J* = 6.8 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.43 – 1.24 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.89, 132.62, 129.66, 127.82, 127.16, 126.98, 125.96, 122.68, 113.05, 105.42, 68.59, 32.07, 29.82, 29.80, 29.76, 29.74, 29.56, 29.50, 29.35, 26.39, 22.84, 14.27. (APCI, positive): Calc. for C<sub>22</sub>H<sub>31</sub>BrO [M+H]<sup>+</sup> 391.1631, found 391.1643.

**4-(4-(dodecyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol** (MAN 12.2): To a stirring solution of MAN 12.1 (1.70 g, 4.34 mmol) in triethylamine (77 mL) was added 2-methyl-3-butyn-2-ol (0.55 mL, 5.6 mmol) and Argon was bubbled through the solution for 10 min. After degassing the solution, CuI (83 mg, 10 mol %), PPh<sub>3</sub> (106 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (316 mg, 10 mol %) were added and the reaction was brought to 90 °C and left for 16 hrs. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether (2 x 100 mL) and concentrated by rotary evaporation. DCM was then added (300 mL) and the organic solution was washed with H<sub>2</sub>O (3 x 300mL), 1N HCl (3 x 300mL), H<sub>2</sub>O (3 x 300mL) and brine (3 x 300 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50%/50% DCM/Hexanes) and concentrated by rotary evaporation to yield **MAN 12.2** as a brown oil (0.583 g, 1.48 mmol, 34.0% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, *J* = 8.7 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.50 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 2.10 (s, 1H), 1.93 (p, *J* = 7.7, 7.2, 6.6, 6.4 Hz, 2H), 1.72 (s, 6H), 1.59 – 1.52 (m, 2H), 1.43 – 1.25 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 

155.62, 134.37, 131.25, 127.34, 125.90, 125.69, 125.63, 122.51, 112.14, 104.28, 97.11, 80.67, 68.45, 66.10, 32.07, 31.93, 29.85, 29.82, 29.80, 29.76, 29.74, 29.57, 29.50, 29.35, 26.38, 22.84, 14.27. (ESI, positive): Calc. for C<sub>27</sub>H<sub>38</sub>O<sub>2</sub> [M+Na]<sup>+</sup> 417.2764, found 417.2764.

**1-(dodecyloxy)-4-ethynylnaphthalene** (MAN 12.3): To a round bottom flask containing MAN **12.2** (0.300 g, 0.760 mmol) was added finely ground KOH (0.127 g, 2.28 mmol) and toluene (6.3 mL). The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM a colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography (50%/50% DCM/Hexanes) yielded MAN 12.3 as a brown oil (0.214 g, 0.636 mmol, 83.7% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 – 8.27 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.59 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.38 (s, 0H), 1.93 (dt, *J* = 14.4, 6.7 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.42 – 1.25 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.99, 134.64, 132.14, 127.50, 125.96, 125.79, 125.61, 122.55, 111.63, 104.23, 82.34, 80.27, 68.50, 32.08, 29.86, 29.82, 29.80, 29.77, 29.74, 29.56, 29.51, 29.33, 26.38, 22.84, 14.27. (CI, positive): Calc. for C<sub>42</sub>H<sub>32</sub> [M]<sup>+</sup> 336.2453, found 336.24540

**6-bromo-2-dodecyl-1***H***-benzo**[*de*]**isoquinoline-1,3(2***H***)-dione** (**NI 12**): To a solution of 4bromo-1,8-naphthalic anhydride (2.00 g, 7.22 mmol) in ethanol (30 mL) was added ndodecylamine (1.74 g, 9.4 mmol). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 12 as an off-white powder (1.92 g, 4.32 mmol, 59.8% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.66 (dd, J = 7.3, 1.2 Hz, 1H), 8.57 (dd, J = 8.5, 1.2 Hz, 1H), 8.42 (d, J = 7.9 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.85 (dd, J = 8.5, 7.2 Hz, 1H), 4.16 (t, J = 7.7 Hz, 2H), 1.72 (p, J = 7.5 Hz, 2H), 1.46 – 1.22 (m, 19H), 0.88 (t, J = 6.9 Hz, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.79, 163.77, 133.36, 132.16, 131.36, 131.25, 130.82, 130.32, 129.21, 128.23, 123.38, 122.52, 40.80, 32.07, 29.79, 29.77, 29.75, 29.70, 29.52, 29.50, 28.25, 27.28, 22.84, 14.26. (ESI, positive): Calc. for C<sub>24</sub>H<sub>30</sub>BrNO<sub>2</sub> [M+Na]<sup>+</sup> 466.1352, found 466.1352.

#### 2-dodecyl-6-((4-(dodecyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-

dione (12): To an oven-dried three neck flask containing NI 12 (423 mg, 0.951 mmol) and MAN **12.3** (214 mg, 0.634 mmol) was added dry triethylamine (63 mL) and Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (17 mg, 10 mol %), CuI (12 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (45 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 24 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O (50 mL) and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) yielded 12 as an orange solid (294 mg, 0.420 mmol, 66.2% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.87 (dd, J = 8.3, 1.2 Hz, 1H), 8.67 (dd, J = 7.3, 1.2 Hz, 1H), 8.59 (d, J = 7.6 Hz, 1H), 8.44 (d, J = 8.3)Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.69 (ddd, J = 7.7 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.80 ( 8.3, 6.8, 1.4 Hz, 1H), 7.58 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 4.25 – 4.15 (m, 4H), 1.97 (dt, J = 14.4, 6.6 Hz, 2H), 1.75 (p, J = 7.5 Hz, 2H), 1.59 (p, J = 7.3 Hz, 2H), 1.47 – 1.24 (m, 34H), 0.88 (td, J = 6.9, 3.5 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.22, 163.96, 156.73, 134.29, 132.64, 132.56, 131.68, 131.66, 130.63, 128.46, 128.33, 127.91, 127.48, 126.07, 125.80, 125.73, 123.18, 122.87, 121.82, 111.71, 104.58, 98.43, 90.01, 68.67, 40.73, 32.07, 29.82, 29.80, 29.78, 29.77, 29.75, 29.72, 29.57, 29.55, 29.50, 29.32, 28.30, 27.33, 26.39, 22.84, 14.27. (ESI, positive): Calc. for C<sub>48</sub>H<sub>61</sub>NO<sub>3</sub> [M+Na]<sup>+</sup> 722.4544, found 722.4557.

6-((4-(hexyloxy)naphthalen-1-yl)ethynyl)-2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (M6N8): To an oven-dried three neck flask containing NI 8 (174 mg, 0.449 mmol) and MAN 6.3 (136 mg, 0.539 mmol) was added dry triethylamine (10 mL) and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (5.9 mg, 5 mol %), CuI (4.3 mg, 5 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (15.8 mg, 5 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 14 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield M6N8 as a bright yellow-orange solid (232 mg, 0.414 mmol, 92.3%) yield). <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.85 (dd, J = 8.4, 1.2 Hz, 1H), 8.64 (dd, J = 7.3, 1.2 Hz, 1H), 8.57 (d, J = 7.6 Hz, 1H), 8.42 (ddd, J = 8.3, 1.3, 0.7 Hz, 1H), 8.35 (ddd, J = 8.3, 1.4, 0.7 Hz, 1H),8.02 (d, J = 7.6 Hz, 1H), 7.90 - 7.78 (m, 2H), 7.67 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.56 (ddd, J = 7.6 Hz, 1H),8.2, 6.8, 1.3 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 4.24 - 4.11 (m, 4H), 1.96 (p, J = 7.4 Hz, 2H), 1.73 (p, J = 7.5 Hz, 2H), 1.58 (p, J = 7.4 Hz, 2H), 1.45 – 1.23 (m, 14H), 0.93 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.22, 163.96, 156.74, 134.31, 132.64, 132.56, 131.68, 130.63, 128.46, 128.35, 127.91, 127.49, 126.08, 125.81, 125.76, 123.21, 122.87, 121.85, 111.74, 104.59, 98.43, 90.02, 68.68, 40.74, 31.98, 31.76, 29.51, 29.39, 29.30, 28.31, 27.33, 26.07, 22.80, 22.78, 14.24, 14.20. (CI, Negative) Calc. for C<sub>38</sub>H<sub>41</sub>NO<sub>3</sub> [M<sup>-</sup>] 559.3086, found 559.3107.

# 2-hexyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (M8N6): To an oven-dried three neck flask containing NI 6 (139 mg, 0.386 mmol) and MAN 8.3 (130 mg, 0.464 mmol) was added dry triethylamine (10 mL) and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid

addition funnel containing PPh<sub>3</sub> (5.0 mg, 5 mol %), CuI (3.7 mg, 5 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (13.3 mg, 5 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 95°C and left to stir for 16 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O (50 mL) and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield M8N6 as an orange-yellow solid (201 mg, 0.359 mmol, 93.1% yield). <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.87 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 7.3 Hz, 1H), 8.59 (d, J = 7.6 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.26 – 4.13 (m, 4H), 1.97 (p, J = 6.8 Hz, 2H), 1.75 (p, J = 7.5 Hz, 2H), 1.59 (p, J = 7.3 Hz, 2H), 1.49 – 1.29 (m, 14H), 0.93 - 0.87 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 164.00, 156.77, 134.34, 132.69, 132.57, 131.72, 130.67, 128.50, 128.40, 127.94, 127.53, 126.10, 125.84, 125.79, 123.25, 122.90, 121.90, 111.75, 104.62, 98.45, 90.01, 68.70, 40.74, 31.99, 31.73, 29.54, 29.41, 29.33, 28.26, 26.98, 26.40, 22.83, 22.73, 14.26, 14.22. (CI, negative): Calc. for C<sub>38</sub>H<sub>41</sub>NO<sub>3</sub> [M]<sup>+</sup> 599.3086, found 599.3083

**6-((4-(decyloxy)naphthalen-1-yl)ethynyl)-2-octyl-1***H***-benzo**[*de*]isoquinoline-1,3(2*H*)-dione (M10N8): To an oven-dried three neck flask containing NI 8 (296 mg, 0.76 mmol) and MAN 10.3 (181 mg, 0.59 mmol) was added dry triethylamine (15 mL) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (16 mg, 10 mol %), CuI (11 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (42 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 17 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O (50 mL) and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield **M10N8** as a yellow-orange solid (254 mg, 0.412 mmol, 70.3% yield). <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.85 (dd, J = 8.3, 1.2 Hz, 1H), 8.65 (dd, J = 7.3, 1.2 Hz, 1H), 8.58 (d, J = 7.7 Hz, 1H), 8.46 – 8.33 (m, 2H), 8.03 (dd, J = 7.8, 0.7 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.68 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.57 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 4.25 – 4.11 (m, 4H), 2.03 – 1.91 (m, 2H), 1.81 – 1.67 (m, 2H), 1.65 – 1.53 (m, 2H), 1.47 – 1.25 (m, 22H), 0.93 – 0.83 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 164.00, 156.77, 134.34, 132.68, 132.57, 131.72, 130.66, 128.49, 128.39, 127.93, 127.52, 126.09, 125.83, 125.79, 123.24, 122.89, 121.89, 111.75, 104.61, 98.45, 90.01, 68.70, 40.75, 32.07, 31.99, 29.75, 29.73, 29.57, 29.51, 29.49, 29.39, 29.33, 28.32, 27.34, 26.40, 22.84, 22.80, 14.27, 14.24. (CI, negative): Calc. for C<sub>42</sub>H<sub>49</sub>NO<sub>3</sub> [M]<sup>+</sup> 615.3712, found 615.3726.

#### 2-decyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(M8N10) :To an oven-dried three neck flask containing NI 10 (316 mg, 0.76 mmol) and MAN 8.3 (163 mg, 0.58 mmol) was added dry triethylamine (15 mL) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh<sub>3</sub> (16 mg, 10 mol %), CuI (11 mg, 10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (42 mg, 10 mol %). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to 90°C and left to stir for 21 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H<sub>2</sub>O (50 mL) and dried under vacuum. Purification of the crude product via column chromatography (50%/50% DCM/Hexanes) to yield M8N10 as a yellow-orange solid (271 mg, 0.440 mmol, 75.7% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.86 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 7.2 Hz, 1H), 8.58 (d, *J* = 7.6 Hz, 1H), 8.43 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.20 (dt, *J* = 14.5, 7.0 Hz, 4H), 1.97 (p, *J* = 6.7 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.59 (p, *J* = 7.4 Hz, 2H), 1.48 – 1.25 (m, 22H), 0.89 (dt, *J* = 14.3, 6.7 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.25, 163.98, 156.76, 134.33,

132.67, 132.56, 131.70, 130.65, 128.48, 128.38, 127.93, 127.51, 126.09, 125.83, 125.78, 123.23, 122.89, 121.88, 111.74, 104.61, 98.44, 90.01, 68.70, 40.75, 32.05, 31.99, 29.72, 29.55, 29.46, 29.41, 29.33, 28.32, 27.33, 26.40, 22.83, 14.26. (CI, negative): Calc. for  $C_{42}H_{49}NO_3$  [M]<sup>+</sup> 615.3712, found 615.3709.

# CHAPTER 3

# Stimuli-Responsive Properties and Self-Assembly of Monoalkoxynaphthalene-Naphthalimide Donor-Acceptor Dyads<sup>1</sup>

# **3.1 CHAPTER SUMMARY**

# **3.1.1 Introduction**

Previous comparative spectroscopic and structural characterizations led to the conclusion that dyad stimuli-responsive properties were the result of polymorphic conformational switching. However, no direct structural comparison could be made between yellow crystals grown from solution and thermally generated yellow solids in 1,4-monoalkynaphthalene-naphthalimide donor-acceptor dyads. Further, previous work showed that the thermochromic transitions did not significantly change the surface morphology despite dramatic structural reorganization.

Enabled by a detailed understanding of dyad packing and the photophysical origins for differences in solid-state color as described in Chapter 2, investigations into the stimuliresponsive properties of dyads materials in the solid-state were carried out. The thermochromic orange-to-yellow transition was viewed as the most unique stimuli-responsive behavior in our dyad system, as the overall morphology of the crystals did not change following the application of a stimulus, unlike the case when orange crystals materials were mechanically sheared. Further, microscopic observations during heating allowed for the most convenient characterization of both initiation and propagation of the transition process, especially compared to the yellow-to-

<sup>&</sup>lt;sup>1</sup> This chapter was adapted in part from the published article: Wight, C. D.; Xiao, Q.; Wagner, H. R.; Hernandez, E. A.; Lynch, V. M.; Iverson, B. L., Mechanistic Analysis of Solid-State Colorimetric Switching: Monoalkoxynaphthalene-Naphthalimide Donor–Acceptor Dyads. *J. Am. Chem. Soc.* **2020**, 142 (41), 17630-17643. CDW designed and conducted experiments and wrote the manuscript with BLI.
orange transition that occurs in the presence of solvent vapor. Thus, characterization of the stimuli-responsive properties in the dyad materials was focused on characterizing the thermochromic orange-to-yellow transition.

Detailed optical, spectroscopic, thermal, and structural characterizations of thermally generated polymorphs were pursued in order to determine the structure of the yellow stimuliproduced polymorph. Following fundamental investigations into the structure, quantitative investigations into material changes after thermal conversion were explored. Analysis of asymmetric stimuli responsive properties was completed using analogous characterization methods. Finally, the ability to tune the stimuli-responsive properties of the system (e.g. transition temperature) were explored.

#### **3.1.2 Scientific Questions**

After investigating the polymorphic abilities of dyads in Chapter 2, the work described here sought to answer key questions related to the stimuli-responsive behavior of dyad materials, by trying to answer both fundamental and also specific, application-based questions. Specifically: *What is the structure of the thermally-generated polymorph? How will differences in side chain identity influence stimuli responsive properties? What is the role of side-chain length on stimuli-induced transition properties (e.g. orange to yellow transition temperature)? Can the stimuli-responsive properties be tuned? What micro- and/or nanoscopic changes occur to dyad materials following thermally induced orange-to-yellow changes? What will the introduction of asymmetric side chains do to the stimuli-responsive properties?* 

# 3.1.3 Approach

In order to answer the questions defined above, comprehensive optical, spectroscopic, and structural analyses were completed on orange materials, the thermally generated materials derived from them, as well as asymmetric derivatives that were heated. Characterization of the dynamic transition process was utilized heating polarized optical microscopy (POM), differential scanning calorimetry (DSC), in situ heating X-ray diffraction (XRD). Optical profilometry and non-contact atomic force microscopy (AFM) measurements were made in order to quantify surface and morphological changes following thermal conversion. Solid-state absorbance and emission measurements were made to provide spectroscopic comparisons to known dyad crystals. Grazing-incidence wide-angle X-ray scattering (GIWAXS) and well in situ heating single-crystal XRD experiments were employed in order to further elucidate the structure of the yellow material.

#### 3.1.4 Results

All symmetric, head-to-head packed orange polymorphs in the study showed the same orange-to-yellow thermochromic and mechanochromic behavior, as well as the same yellow-to-orange solvatochromic behavior previously reported for **8**.<sup>64</sup> The thermochromic orange-to-yellow crystal-to-mesophase transition was repeatedly observed to move as a transition wavefront through orange crystals, adopting a characteristic angle relative to the long axis of the crystal. In symmetric orange dyad crystals, the orange-to-yellow transition temperatures and transition enthalpies were not clearly correlated with side-chain length, however, these transition parameters were found to be reproducibly influenced by crystal size.

All symmetric yellow head-to-tail packed dyad crystals and two of the four asymmetric dyad yellow crystals, M6N8 (yellow, head-to-tail) and M8N6 (gold, head-to-head) were found to have a single thermally induced melting transition without a color change. The other two asymmetric derivatives with the longest side chains, M8N10 (orange-red, head-to-head) and M10N8 (yellow-orange, head-to-head), were found to have two thermally induced transitions. Further, of these asymmetric derivatives with the longest with the longest side chains, only M8N10 had an

orange-to-yellow color change, M10N8 had an observable but colorless transition prior to melting.

Formed from the heating of symmetric dyad orange crystals, thermally generated yellow material was found to have similar solid-state packing as yellow crystals grown from solution based on spectroscopic and structural characterization. Microscopic morphology of dyad materials was confirmed to not change significantly following heating, although for the first time nanoscopic surface changes were seen to accompany the thermal transitions.

## **3.2 RESULTS**

#### 3.2.1 Stimuli-Responsive Behavior

Consistent with previous reports,<sup>63, 64</sup> and as discussed in chapter 2, many dyads in this study could crystalize as orange ('**O**', or '**o**') or yellow ('**Y**' or '**y**') polymorphs. When symmetric orange crystals of **6**, **7**, **8**, **9**, **10**, and **12** referred to here as **60**, **70**, **80**, **90**, **100**, and **120**, respectively, are heated beyond 100°C, the orange crystals transition to a soft-crystalline yellow material that persists indefinitely upon cooling. Reversal back to the orange crystalline phase occurs in less than 24 hours when exposed to DCM vapor in a fuming chamber.<sup>64</sup> Further, all aforementioned symmetric orange dyad crystals were seen to be mechanochromic displaying an orange to yellow transition when a shearing force was applied.

When heated, **1bo** crystals do not form a yellow material, and directly sublime at 284°C. The two longer asymmetric dyad derivatives, **M8N10** (orange-red) and **M10N8** (yellow-orange) were seen to undergo thermally induced transitions: **M8N10** had an orange to yellow transition, while **M10N8** had an observable, yet colorless, transition prior to subsequent melting. Of the asymmetric derivatives, only **M8N10** showed mechanochromic behavior, with a transition to a yellow material when a shearing force was applied.

# **3.2.2** Symmetric Dyad Stimuli-Responsive Properties and Thermochromic Orange-to-Yellow Transition

## 3.2.2.1 Optical Characterization: Polarized Optical Microscopy

Color Switching Moves Most Quickly as a Wavefront Through the Crystal. When symmetric orange dyad crystals are heated, they transform to a yellow material (designated as 'Y\*' or 'y\*' in the following discussion) prior to melting. Examination of this thermochromic orange-to-yellow conversion under a POM equipped with a heating stage revealed that thermally generated yellow material retains the overall microscopic morphology of the starting orange crystal (Figure 3.1 & 3.2, Movie 3.1 & 3.2). Details regarding heating POM experiments, including equipment used, heating protocols, and data acquisition parameters, can be found in section 3.5.1.

Numerous heating experiments of orange crystals under a POM verified that the thermochromic transition proceeds as one or more wavefronts moving through the orange crystal. It is assumed that a structural transition is occurring at the orange-yellow wavefront interface. The transition generally is observed to start at a crystal edge or a small crack/defect in the crystals.

While the overall crystal morphology is retained following thermal conversion, molecules within the thermally generated material have various degrees of freedom that will be described in the sections that follow. Thus, this thermal conversion is not a single-crystal to single-crystal transition; it is best characterized as a crystal-to-mesophase transition, where the yellow material ( $Y^*$ ) is characterized as a soft crystalline mesophase.



Figure 3.1 Visualized under a microscope equipped with a heating stage, a single **70** orange crystal is heated at 2°C min<sup>-1</sup> to form a yellow material, **7y**\*, that persists indefinitely after cooling. Adapted with permission from Ref<sup>66</sup>. Copyright 2020 American Chemical Society.

In Figure 3.1, there are a series of POM images showing a single **70** crystal being heated at a heating rate of  $2^{\circ}$ C min<sup>-1</sup> to form a yellow mesophase, **7y**\* (see Movie 3.1). As temperature increases, a series of relatively fast moving wavefronts can be seen moving down the length of the crystal, and as the wave passes, the color of the crystal changes to some extent. When viewed from above, a single point in the crystal may have multiple wavefronts pass through, presumably at different layers within the thickness of the crystal. Slower moving waves can also be seen moving up from the bottom of the long axis of the crystal. Between the fifth and sixth image in Figure 3.1, the bottom of the crystal is seen to go out of focus: the bottom of the crystal bent slightly out of the field of view, and this bending movement was noted to correlate with the movement of the faster, downward moving wave.

To gain additional insight into changes that occur during the transition, heating experiments were carried out under cross polarized conditions. Shown in Figure 3.2 (Movie 3.2), a large ( $\sim$ 1 mm long) single **60** crystal is heated to the corresponding **6y**\*.



Figure 3.2 A single **60** crystal is heated under a cross polarized microscope at 5°C min<sup>-1</sup> to form **6y**\*. Bottom: Cartoon depiction of thermally induced changes occurring during the **60** to **6y**\* transition in the corresponding images above with the wavefront speed shown in white [ $\mu$ m sec<sup>-1</sup>] and the angle relative to the indicated crystal long axis shown in blue. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

Similar to the thermal conversion of **70** shown in Figure 3.1, the thermochromic conversion of **60** to **6y**\* proceeds following a series of wavefronts that move through the crystal

without visibly disrupting the overall morphology of the crystal. The fastest moving orange-toyellow wavefronts proceed parallel to the long axis of the crystal (see Movie 3.2).

To better visualize how the transition moves through **60** in Figure 3.2, a cartoon depiction of thermally induced changes occurring during the **60** to **6y**\* transition is shown below each image. The yellow coloring denotes complete transition to the yellow form through all layers of the crystal. Inside the cartoon in white, arrows show the direction of wavefront movement and adjacent values representing the speed of the wavefront in  $\mu$ m sec<sup>-1</sup>. The angle of the wavefront relative to the indicated long axis of the crystal is shown in blue.

Shown in Figure 3.2, the widest and fastest moving of these wavefronts move at speeds on the order of 12  $\mu$ m s<sup>-1</sup> and are generally diagonal in nature, exhibiting an average angle of 38 ± 4° relative to the long edge of the crystal. When viewed from above the crystal, horizontal wavefronts are also seen that move parallel to either the long or short axis of the crystal, and proceed slower through the crystal with speeds on the order of 0.2 – 0.5  $\mu$ m s<sup>-1</sup>. Importantly, the slower horizontal waves have been observed to turn, and as the angle becomes more pronounced the wavefront speed also increases. Note the lower portion of the **60** crystal in Figure 3.2. In images 2-4, the transition can be seen moving perpendicular to the long axis of the crystal. In the fifth image, two different wavefront speeds are shown, indicating the wave is beginning to adopt an angle that becomes pronounced in the sixth and seventh crystal images.

As the wavefront passes, the surface features and overall dimensions of the material only change slightly. For the **60** crystal shown in Figure 3.2 after heating from orange to yellow the average dimensions of the crystal grew 2.04  $\mu$ m (0.21%) in length, 2.05  $\mu$ m (1.1%) in width, and 0.21  $\mu$ m (2.8%) in height, all while maintaining similar microscopic features.

In thicker crystals, multiple wavefronts are generally seen, apparently caused by multiple wavefronts moving through different horizontal layers within the crystal. Thicker crystals exhibited more of these waves. Thinner crystals appear to have only one or a few transition layers. Thicker crystals were also noted to deform or bend less during the thermal transition as compared to thinner crystals, as previously noted for the **70** crystal shown in Figure 3.1.

# 3.2.2.2 Spectroscopic Characterization: UV/vis and Fluorescence

Steady state absorbance and fluorescence measurements of thermally generated yellow material were made in an identical fashion to measurements of crystalline samples previously described (see sections 2.3.5.2 and 2.6.4). A comparison of solid-state absorbance and emission spectra between the **O**, **Y**, and **Y**\* forms for **6**, **7**, and **8**, respectively, is shown in Figure 3.3, and a summary of absorbance ( $\lambda_{abs-Max}$ ) and emission maxima ( $\lambda_{em-max}$ ) is present in Table 3.1. Spectroscopic measurements of **9y**\*, **10y**\*, and **12y**\* are not shown, as yellow crystals for those derivatives could never be grown and thus compared.

In general, Y and Y\* have closely matching absorption and emission spectra for each of the three derivatives. For 7 and 8, Y\* emission profiles have a small bathochromic shift compared to their Y counterparts, while  $6y^*$  shows a small hypsochromic shift in comparison to 6y (Figure 3.3).



Figure 3.3 Solid-state absorbance and emission comparing orange (O) and yellow (Y) crystals grown in solution to thermally produced yellow (Y\*) derivatives of 6 (top), 7 (middle), and 8 (bottom). Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

Compound	λ <sub>abs-max</sub> (nm)	$\lambda_{em-max} (nm)$
6y	392	569
7y	390	554
<b>8</b> y	395	554
6y*	393	561
7y*	392	566
8y*	392	563

 Table 3.1
 Solid-state absorbance and emission parameters for dyad derivatives.

Orange thin films generated from vapor annealing (see section 2.3.4) showed similar behavior to orange crystals. Heating of orange thin films resulted in a blue-shift in both absorbance and emission profiles, as shown in the top of Figure 3.4. Emission maxima is 613 nm for  $7o_{Thin \ Film}$  and 562 nm for  $7y^*_{Thin \ Film}$ , compared to 617 nm and 566nm for 7o and  $7y^*$ , respectively. Heating of 7o and 10o thin films at temperatures ranging from 105-120°C for 25-120 seconds resulted in the thermal conversion to a yellow film, as shown in the bottom of Figure 3.4. Similar to the heating of 1bo crystals, no visible change was seen for thin films of 1bo when heated at 150°C for 10 minutes.



Figure 3.4 Absorbance and emission and side by side comparison of a 70 thin film (left) and a 7y\* thin film (right). 7y\* thin films were generated from heating 70 thin films for 2 minutes at 120°C. Adapted with permission from Ref<sup>66</sup>. Copyright 2020 American Chemical Society.

# 3.2.2.3 Thermal Characterization: Differential Scanning Calorimetry

**DSC Thermal Transition Characterization – Experimental Setup.** Differential scanning calorimetry (DSC) was used in order to quantify thermally induced phase transitions. Shown in Figure 3.5 are two successive DSC heating-cooling cycles, starting with representative

symmetric orange (**70**) and yellow (**6y**) crystals. In each of the two cycles, the temperature is ramped up at a rate of  $5^{\circ}$ C min<sup>-1</sup> from  $40^{\circ}$ C to  $200^{\circ}$ C, held at  $200^{\circ}$ C for 5 minutes, cooled at  $5^{\circ}$ C min<sup>-1</sup> to  $40^{\circ}$ C, followed by a 5 minute hold at  $40^{\circ}$ C to end the first heating-cooling cycle. This cycle is then repeated a second time in order to provide information about the material that forms when cooled from the isotropic melt (Iso).



Figure 3.5 Representative DSC measurements for symmetric orange (**O**) and yellow (**Y**) crystals in successive heating-cooling cycles. Values near peaks show the corresponding peak temperature (°C), bracketed values represent the integrated transition enthalpy [kJ mol<sup>-1</sup>] for thermal transitions during the first heating-cooling cycle.

For the initial heating of **70** (trace shown as a solid black line), two endothermic peaks are seen during initial heating, corresponding to the observed thermal transition of **70** to **7y**\*, and the subsequent melting of **7y**\* to the isotropic phase. The **70** to **7y**\* transition has a peak temperature of 107.7°C with an integrated transition enthalpy of 42.2 kJ mol<sup>-1</sup>, and the **7y**\* to isotropic transition occurs at 140.9°C with a transition enthalpy of 23.6 kJ mol<sup>-1</sup>. Subsequent cooling from the isotropic phase generates a collection of non-resolvable exothermic peaks, with a peak temperature of  $125.7^{\circ}$ C and transition enthalpy of 23.8 kJ mol<sup>-1</sup>. Immediate reheating of this same, initially orange, material in a second identical heating-cooling cycle shows a change in thermal properties compared to the starting sample. Most notably, a single endothermic peak is seen in the second heating cycle that coincides with the initial **7y**\* to isotropic transition. This peak also has a nearly identical peak temperature of  $141.0^{\circ}$ C and a transition enthalpy of 22.5 kJ mol<sup>-1</sup>. The strong similarity in endothermic peaks near  $141^{\circ}$ C for both heating cycles is indicative that the material formed from cooling the isotropic phase is structurally similar to **7y**\*.

In contrast to the heating of **70**, the heating of a typical yellow derivative shows only one large endothermic peak in the first heating cycle (Figure 3.5). A single large endothermic peak at  $150.2^{\circ}$ C with a transition enthalpy of 26.3 kJ mol<sup>-1</sup> corresponds to POM observations for the melting of **6y** to the isotropic phase. Cooling of this isotropic phase shows a single exothermic cooling peak with a peak temperature of  $124.4^{\circ}$ C and a transition enthalpy of  $24.2 \text{ kJ mol}^{-1}$ . This exothermic cooling peak is in line with POM observations of **60** showing a single crystallization event when the isotropic phase solidifies into a yellow material. During subsequent reheating in the second heating cycle, a single endothermic peak is seen at a slightly lower temperature, with a lower peak temperature of  $147.1^{\circ}$ C and a smaller transition enthalpy of  $23.2 \text{ kJ mol}^{-1}$ . A consistent decrease in endothermic peak temperature and transition enthalpy in the second heating cycle of **Y** crystals may indicate that the yellow material formed from the cooling of the isotropic phase has less structural integrity compared to the yellow crystalline starting material,

while also having some general structural similarities. A reasonable conclusion is that some structural differences exist between **Y** and **Y**\* forms.

It is useful to note that in some yellow crystals, a second, small endothermic peak was occasionally seen during the initial heating. Note the small peak in the first heating cycle of **6y** with a peak temperature of 127.5°C and a transition enthalpy of 2.6 kJ mol<sup>-1</sup>, roughly an order of magnitude smaller than all other phase transitions enthalpies observed. This peak may correlate to fast moving often colorless transitions occasionally seen in POM experiments that could be observed using polarizers, but often not observed under brightfield, non-polarized conditions. This relatively small peak that did not cause observable microscopic changes is attributed to relatively small molecular movements within the crystal prior to melting.

Thermal Transition Characterization – Symmetric Dyad Crystals. DSC was used to characterize the orange-to-yellow transition for **60**, **70**, **80**, **90**, **100**, and **120**. A comparison of two successive DSC heating-cooling cycles for all orange crystals is shown in Figure 3.6, with respective peak temperatures and transition enthalpies shown. Overall, the DSC traces of each derivative show two endothermic peaks corresponding to the **O** to **Y**\* phase transition and the subsequent melting of **Y**\* to the isotropic phase (Figure 3.6).

Cooling from the isotropic phase generates a yellow material that is believed to be structurally similar to thermally generated  $Y^*$ , as shown by successive heating-and-cooling cycles (Figure 3.6). Heating of the yellow material that solidified from cooling of the isotropic phase shows an endothermic transition with nearly identical peak temperatures and transition enthalpies, shown inside the dashed boxes in Figure 3.6.



Figure 3.6. DSC heating and cooling experiments for all orange crystals (rates of 5°C min<sup>-1</sup>) shows the presence of two endothermic transitions for all orange crystals during the first heating-cooling cycle (solid line) and one endothermic peak during the second (dashed line). Values near or within peaks show the corresponding peak temperature (°C), bracketed values represent integrated transition enthalpy [kJ mol<sup>-1</sup>] for thermal transitions during the first heating-cooling cycle. Values inside dashed boxes represent the corresponding values for peaks in the second heating cycle.

Several unique features of these transitions should be noted. Most importantly, once heated to  $\mathbf{Y}^*$ , this form persists indefinitely for each derivative, even when cooled extremely slowly. For example, when **70** was heated to produce  $\mathbf{7y}^*$ , the  $\mathbf{7y}^*$  form persisted even when cooled at the slowest obtainable rate of  $0.1^\circ$ C min<sup>-1</sup>. Further, holding orange crystals at temperatures slightly below the transition temperature for extended periods was not seen to result in significant thermally induced conversion of **0** to  $\mathbf{Y}^*$ . Note the transition temperature range of 100.9-115.3°C for the conversion of **70** to  $\mathbf{7y}^*$  shown in Figure 3.6. When **70** crystals were heated to  $94^\circ$ C (rate at  $2^\circ$ C min<sup>-1</sup>) and held at that temperature for 4 hours, additional heating after the four hour isotherm showed two endothermic transitions, with the first transition having an integrated transition enthalpy of 37.0 kJ mol<sup>-1</sup>. While slightly less than the previously reported transition enthalpy for **70** to  $\mathbf{7y}^*$  (42.2 kJ mol<sup>-1</sup>, Figure 3.6), the presence of the thermal transition indicates that orange material was present to a significant extent following the prolonged heating at  $94^\circ$ C, or at the very least, that prolonged heating did not result in the same extent of structural reorganization that accompanies the **0** to **Y**\* conversion.

A comparison of transition onset and peak temperatures, as well as transition enthalpies for all orange and yellow crystals, is provided in Table 3.2. In general, when the respective orange crystals of similar size are heated for the different derivatives, the longer the side chains, the larger the enthalpy of transition for the **O** to **Y**\* conversion. In addition, similarly-sized yellow crystals grown from derivatives with longer side chains melt to the isotropic phase with increasing enthalpies of transition ranging from 24.10 to 34.69 kJ mol<sup>-1</sup> for **6y-8y**, respectively (Table 3.2). Importantly, compared to the grown yellow crystals (**Y**), thermally generated **Y**\* melts to the isotopic phase with less energy as shown by comparatively lower transition enthalpies for longer chain derivatives **7** and **8**. In contrast, thermally generated **6y**\* has a larger transition enthalpy when heated to the isotropic phase compared to the same transition for **6y**.

	$0 \rightarrow Y^*$			Y* → Iso		
	Onset Temp (°C)	Peak Temp (°C)	Transition Enthalpy (kJ mol <sup>-1</sup> )	Onset Temp (°C)	Peak Temp (°C)	Transition Enthalpy (kJ mol <sup>-1</sup> )
60Larger Crystals	97.17	105.24	32.24	147.50	148.94	28.78
<b>60</b> Smaller Crystals	98.94	110.43	35.10	147.23	149.31	31.11
70	100.86	107.7	42.16	138.20	140.91	23.61
80	97.03	99.78	53.12	133.83	136.72	27.07
90	104.07	108.68	56.10	132.82	135.04	26.75
10o	103.87	105.90	55.18	125.53	130.56	21.53
120	105.90	107.81	69.97	124.37	1274.07	26.93

	$Y \rightarrow Iso$			
	Onset Temp (°C)	Peak Temp (°C)	Transition Enthalpy (kJ mol <sup>-1</sup> )	
6y	145.45	150.27	24.10	
7y	126.62	142.75	32.90	
8y	141.56	144.35	34.69	

Table 3.2 Summary of symmetric dyad phase transitions measured by DSC at a heating rate of 5°C min<sup>-1</sup> for all samples. "O" represents Orange crystals grown from solution, "Y\*" represents thermally generated yellow material from heating orange crystals (O), "Iso" represents the isotropic phase, and "Y" represents yellow crystals grown from solution.

However, care must be taken when interpreting the differences between derivatives, as we observed that crystal size influences the transition temperature and transition enthalpies measured for both the **O** to **Y** transition and the **Y**\* to the isotropic phase transition. For example, as shown in Figure 3.7, larger **60** crystals ( $60_{Larger}$ ) transformed to **Y**\* at higher temperatures, with larger enthalpies of transition, compared to smaller **60** crystals ( $60_{smaller}$ ). For comparison, **70** is also shown in Figure 3.7, and the peak temperature for the **O** to **Y**\* transition in **70** is noted to fall between differently sized **60** crystals. Melting of **6y**\* to the isotropic phase followed the same size dependent trend. The **60** crystals used in DSC experiments were significantly larger than the **6y** crystals used, and as such, the thermally generated **6y**\* crystals were significantly larger than 6y (as overall morphology of crystals was seen to be retained when transitioning from **O** to **Y**<sup>\*</sup>, see section 3.3.2.1).



Figure 3.7 Crystal size dependence in thermal transitions of orange crystals. Larger 60 crystals (60<sub>Larger</sub>) are seen to transition from orange-to-yellow at higher temperatures and require more energy than smaller 60 crystals (60<sub>Smaller</sub>). Heated at 5°C min<sup>-1</sup>, DSC curves show orange crystals (O) being thermally converted to a yellow material (Y\*) prior to melting to the isotropic phase (Iso). Values near peaks show the corresponding peak temperature (°C), bracketed values represent integrated transition enthalpy [kJ mol<sup>-1</sup>]. Adapted with permission from Ref.<sup>66</sup> Copyright 2020 American Chemical Society.

## 3.2.2.4 Morphological Characterization: Optical Profilometry

**Crystal Size Changes Following Heating.** Microscopic observation of the thermal transition of orange crystals to the soft crystalline mesophase saw overall retention of crystal shape following heating (Figure 3.1 & 3.2, Movie 3.1 & 3.2). However, small changes to crystal dimensions were observed in numerous heating experiments. Accurately quantifying these small changes using a POM proved difficult due to the small size of uniform crystals combined with POM imaging limitations (e.g. image resolution, depth of field limitations). Quantitative measurements of crystal size changes were investigated with optical profilometry in order to circumvent the aforementioned limitations. Details regarding equipment, sample preparation, measurement, and data analysis can be found in section 3.5.5.

The calculated density of **7o** and both **7y** polymorphs, as determined from single-crystal structures, are 1.25 and 1.22 g cm<sup>-3</sup>, respectively (Table 2.1 & 2.2). Based on the differences in density of **7o** and either **7y** polymorph, a hypothetical single-crystal-to-single-crystal transition from the more dense **7o** to the less dense **7y** would theoretically cause an increase in volume of  $\sim 2.5\%$  (see Theoretical  $\Delta$ Volume **7o**  $\rightarrow$  **7y**/**7y**', Table 3.3). In contrast, the **6o** polymorph is slightly less dense than both **6y** polymorphs, and so a conversion of **6o** to either **6y** polymorph would result in a theoretical decrease in crystal size of  $\sim 0.2\%$  (see Theoretical  $\Delta$ Volume **6o**  $\rightarrow$  **6y/6y'**, Table 3.3).

Optical profilometer measurements of individual **O** crystals before and after heating to **Y**\* were used to quantify volume changes after the transition in crystals of **6** and **7** (Table 3.3). Crystals of **70** adsorbed onto a silicon substrate showed a  $4.4 \pm 0.5\%$  increase in crystal volume after heating **70** crystals to **7y**\* similar to that expected based on **7y** crystal structures. In comparison, crystals of **6** showed a  $3 \pm 1\%$  increase in size.

Dyad Crystal	O <sub>Volume</sub> (µm <sup>3</sup> )	Y* <sub>Volume</sub> (µm <sup>3</sup> )	$\Delta$ Volume from O to Y* (%)
6	148,831	154,043	3.5%
6	133,792	138,275	3.4%
6	416,397	434,147	4.3%
6	188,562	190,711	1.1%
		Average $\Delta$ Volume <b>60</b> $\rightarrow$ <b>6</b> y*	+3 ± 1 %
		Theoretical $\Delta$ Volume <b>60</b> $\rightarrow$ <b>6y</b>	-0.32%
		Theoretical $\Delta$ Volume <b>60</b> $\rightarrow$ <b>6y</b> '	-0.08%
7	2,887	3,018	4.6%
7	1,025	1,074	4.7%
7	627	651	3.8%
		Average $\Delta$ Volume 70 $\rightarrow$ 7y*	$+4.4 \pm 0.5\%$
		Theoretical $\Delta$ Volume 70 $\rightarrow$ 7y	+2.25%
		Theoretical $\Delta$ Volume 70 $\rightarrow$ 7y'	+2.61%

Table 3.3 Optical profilometry volume measurements of individual crystals following the thermal conversion from **O** to **Y**\* with the corresponding percent change in volume, as measured by optical profilometry. "Theoretical  $\Delta$ Volume" is the calculated percent change in volume expected for the given transformation, based on the density determined from the single-crystal structures (see Table 2.1 & 2.2). Adapted with permission from Ref<sup>66</sup>. Copyright 2020 American Chemical Society.

While optical profilometry provided an easy way to quantify volume changes in crystals, the technique had two major pitfalls. Profilometry measurements were made using a focused 404 nm laser that would quickly scan the crystal surface. When the laser intensity was too high, as was often required for measuring smaller samples, the laser would 'write' in the surface as it scanned and measured the crystal, and the crystal surface was noticeable changed during the measurement process, as shown in Figure 3.8. While the surface changes were not observed to cause significant morphological change, it was anticipated that these surface changes were local surface melting or transformations of  $\mathbf{O}$  to  $\mathbf{Y}^*$  that could decrease accuracy of volume measurements.



Figure 3.8 Laser based optical profilometry measurements can transform the crystal, but also reveal morphological changes on the sub-micrometer scale that cannot be resolved, shown as the dark region indicated by the arrow in the lower panel.

A second major challenge occurred when trying to make volume measurements on glass or quartz substrates. The instrument would inconsistently and often inaccurately determine the location of the glass substrate relative to the sample, a result of the transparent nature of the substrate and how the instrument determines the three dimensional location of individual components within the viewing frame. Transparent substrates were frequently seen to have oscillating variations in the baseline, with amplitudes as large as 2  $\mu$ m. This deviation made the accurate measurement of small crystals on transparent substrates impossible. For example, the **70** crystal shown in Figure 3.1 has dimensions of a typical small orange dyad crystal, and has an estimated height relative to substrate of ~8  $\mu$ m. Because baseline variations on transparent substrates were on the same order as crystal dimensions, crystals used in transmission POM measurements (e.g. Figure 3.1 & 3.2) were not included in volume change measurements shown in Table 3.3.

Despite the limitations related to quantitative measurements of crystals on glass slides, measuring crystal dimensions on transparent substrates could be achieved when the relevant dimensions were easily distinguished from the substrate. Shown in Figure 3.8, the large **60** crystal previously shown in Figure 3.2 possesses distinct crystal faces that allow for individual crystal dimensions to be measured (e.g., average length profile of **60** and corresponding **6y**\* at the top of the crystal are 957.93 and 959.97  $\mu$ m, respectively). As noted previously, after heating the **60** crystal shown in Figure 3.8 (and Figure 3.2) average dimensions of the crystal grew 2.04  $\mu$ m (0.21%) in length, 2.05  $\mu$ m (1.1%) in width, and 0.21  $\mu$ m (2.8%) in height

Optical profilometry measurements allowed for micrometer scale measurement resolution, enabling accurate measurements of specific crystal dimensions and, when on the appropriate substrate, volume. These measurements further verified the POM observations that indicated changes in crystal dimensions were on the order of 1% and revealed that, while on average, individual dimensions changed little, specific regions of crystals can have larger than average changes. The arrow shown in the bottom left of Figure 3.8 indicates a region that was seen to develop rough surface features and the loss of previously protruding features following heating. Quantification of these sub-micron surface changes was not resolved using profilometry due to resolution limits, and alternative methods of nanometer scale surface characterization were explored.

#### 3.2.2.5 Topological Characterization: Atomic Force Microscopy

Quantifying Nanoscopic Changes – Atomic Force Microscopy (AFM). Nanometer scale morphological changes accompanying the thermal conversion of **O** to **Y**\* were investigated using non-contract AFM. Non-contact AFM imaging of a single **70** orange crystal found on a **70** polycrystalline thin film reveals clean, sharp edges on an isolated single-crystals formed from the

fuming of a thin film of 7 (Figure 3.9). Thermal conversion of this single crystal to  $7y^*$  and subsequent imaging shows the general crystalline shape is maintained following conversion, while the surface has nanoscopic feature changes including the formation of numerous ridges/steps. Shown alongside each AFM image is an optical micrograph at the indicated magnification that highlights the resolution achieved by AFM, especially in comparison to microscope-based measurements.



Figure 3.9 Non-contact AFM generated 3D profiles of the same crystal before and after heating, showing retention of overall shape with nanoscopic surface changes. Top: AFM image of 70 crystal before heating, right: optical micrograph of corresponding 70 crystal. Bottom: Image of the same crystal following thermal conversion to 7y\*, right: optical micrograph of corresponding 7y\* crystal. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

Additional polycrystalline thin films were imaged to further characterize and resolve morphological changes following thermal conversion. Imaging of **70** thin films proved

challenging because of nearly vertical crystal boundaries with large step heights in most crystals. For example, the **70** crystal shown in Figure 3.10 had a step height of ~40 nm, while the adjacent crystals shown in the corresponding micrograph had step heights of over 500 nm. Film edges near the edge of the substrate were observed to have crystals with the smallest step heights, yet were challenging to image due to the presence of dust and other debris that would move with the AFM tip. The ideal location for imaging was found to be small inverted 'islands' within the film, as shown in Figure 3.10 (film shown previously in Figure 2.23). These crater like regions within the film are surrounded on all side by crystals, which are thought to minimize the amount of debris that collects near crystals within these crater-like depressions. Further, multiple crystals with step heights of less than 100 nm are often observed in these regions. Larger step heights can be imaged, although scans must be significantly slowed to enable the AFM tip to traverse large vertical boundary to remain in non-contact mode. While orange crystals were structured and not measurably changed when imaged in separate contact mode imaging experiments, samples of soft crystalline **7y\*** were seen to have altered surface features following contact-mode measurements.

Multiple different regions, defined and shown in Figure 3.10, were imaged before and after heating. Three different sub-regions, named region "A", "B", and "C", were identified and imaged within a 400  $\mu$ m<sup>2</sup> area, referred to as the "20 $\mu$ m AFM Region". Each of the three sub-regions had distinct morphological features and were chosen in order to investigate how different crystalline features change following heating, and each of these regions will be described individually.



Figure 3.10 Protected regions within thin films show ideal properties for AFM imaging, with minimal step heights and protection from dust. Top: Optical micrographs of **70** and the regions imaged by AFM, shown in Figures 3.11 & 3.12. Bottom: AFM images of a 20 μm AFM region for **70** (left) and **7y\*** (right). These images show the 4 areas that were imaged using non-contact AFM for both **70** and **7y\*** show in Figure 3.11 & 3.12. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.



Figure 3.11 AFM images for **70** and their thermally generated **7y**\* counterparts. Side-by-side non-contact AFM generated 3D profiles comparing **70** (left) and **7y**\* (right) for the region specified above each image and defined in Figure 3.10. Arrows point to the same location on each film by referencing the indicated surface features. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society. Shown in Figure 3.11 are comparisons of **70** (left) and **7y**\* (right) forms for the 20  $\mu$ m AFM region, Region A, and Region B. Note that surface features (e.g. dust specs, etches in quartz) can be seen in both **O** and **Y**\* images. Direct comparisons of the same location can be made before and after heating by referencing surface features (e.g., bumps, etches in the quartz) that were seen to not change their relative locations before and after heating.

Initial comparison of the 20  $\mu$ m region shown in the top of Figure 3.11 reveals several general morphological similarities between the two polymorphs. In both cases, most long crystal edges are intact and traverse the same path. Moreover, in general, features that were raised in the **O** form are raised to a similar extent in the **Y**\* form. However, sharp edges and clearly defined crystal boundaries seen between individual crystal domains in the bottom of the **7o** 20  $\mu$ m region are no longer differentiable in the **7y**\* image.

The arrow shown in Region A of both 70 and 7y\* (Figure 3.11) is in the same location in each image, based on identifying and overlapping distinct surface features. The arrow in 70 Region A points to a tall, fin-like feature, that extends 30 nm above the rest of the crystal, with a width of ~175 nm. After heating, the general shape of Region A remains the same, with noticeable changes to smaller surface ridges. The fin-like feature was seen to shrink 15 nm in height while increasing in width. Additional smaller steps are noted to emerge in the same location as the fin following the heating.

Indicated by the arrow in **70** Region B (Figure 3.11) is a ~110 nm gap between two individual crystals, with the gap being between the middle segment of one crystal and the terminal segment of another. Following heating, the terminal gap between the two crystals is no longer separated, and the previously point-like crystal terminus is seen to have retracted and are seen to be more rounded, with general changes to surface features similar to those previously noted.

The most resolved imaging was seen in the 4  $\mu$ m<sup>2</sup> Region C, as shown in Figure 3.12. Non-contact AFM measurements of **70** in Region C indicated the presence of lamellar structures with a step height of ~1.3 nm (green profile, Figure 3.13) roughly the height of the aromatic core in the dyad molecule (1.36 nm). The general dimensions and lamellar structure are maintained following heating, however, nanoscopic changes to the shape of individual layers were observed (Figure 3.12). The differences in layer shapes after heating are interpreted to indicate that the layers underwent structural transitions somewhat independently from each other. Step height profiles passing through the same spatial location on the substrate, as indicated by the reference circles, are shown for **70** (blue trace) and **7y**\* (black trace). Comparison of the profiles reveal that significant reorganization took place at that location, where five identifiable layers in **70** (green trace) were later seen to have only two layers in **7y**\* (gold trace). While the location of individual layers changes, a detailed comparison of each AFM image shows 10 recognizable layers in each image at similar heights above the surface. The general morphology of the layers changed from longer, narrow to shorter and wider layers with discontinuities. In contrast to the layers in **70** with frequent step changes, layers observed in **7y**\* were seen to have rounded edges, and noted to more frequently 'flow' down with changes in step height, having significantly more curvature than the sharper edges seen in **70**.

Taken together, non-contact AFM imaging of 70 and  $7y^*$  support previous imaging findings that show retention in much of the original crystalline boundaries and overall morphology following thermal conversion. However, AFM has uniquely shown that while there is, at least to a small extent, change occurring between individual layers, the overall lamellar structure is retained following thermal conversion.



Figure 3.12 Non-contact 3D AFM image of single 7 crystal before and after heating showing nanoscopic surface changes following heating. Top left: 3D image of a single 70 crystal. Top right: Step-height profile of the blue trace (top) and the inset green trace (bottom) in the adjacent 70 AFM image. Bottom left: 3D image of the same region above, after conversion to 7y\*. Bottom right: Step-height profile of the black trace (top) and the inset yellow trace (bottom) in the adjacent 7y\* AFM image. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

## 3.2.2.6 Structural Characterization: Molecular Orientation

To explain the molecular movements that take place during the heating process, an understanding of the molecular orientation in each polymorph is necessary. As discussed in Chapter 2, dyad crystals were found to have a preferred orientation within crystals, with the long axis of all crystals shown to correspond to the direction of aromatic stacking (see section 2.3.3.5). The two smaller crystal dimensions were made from either interactions between columns, or interactions between adjacent side chain layers, and this dimensional preference varied with different derivatives and crystals (see Figure 2.20, section 2.3.3.5).

Using grazing-incidence wide-angle X-ray scattering (GIWAXS), preferred orientation of **70** thin films was previously shown (see Figure 2.22f, section 2.3.4) to have a dominant orientation preference for the long crystallographic axis (010) to be normal to the quartz substrate. The combination of GIWAXS scattering data and non-contact AFM indicate **70** thin films formed a bilayer type, lamellar structure with alternating alkyl and aromatic layers parallel to the substrate, similar to the preferred orientation seen in orange crystals (see Figure 2.6). Thus, dyad molecules in **70** thin films are oriented as shown in Figure 3.14, with the crystal long axis made from stacked dyad cores, and the height of the crystal made from stacks of dyad layers. These measurements confirm that individual layers of **70** imaged in AFM experiments (Figure 3.12) were individual layers of dyad molecules.



Figure 3.13 Preferred orientation of **70** in polycrystalline thin films as determined by GIWAXS measurements.

In agreement with the thermochromic conversion of a single crystal of 70 to  $7y^*$ , heating of a 70 polycrystalline thin film generated the corresponding  $7y^*$  thin film as confirmed by spectroscopic measurements previously described (see Figure 3.4). GIWAXS measurements of the thermally generated  $7y^*$  thin film reveals that the structure of  $7y^*$  is not crystalline following thermal conversion, but is best described as a soft- or liquid-crystalline mesophase (Figure 3.15).

Shown in Figure 3.14 is a comparison of GIWAXS scattering data for 7o and  $7y^*$  thin films. Inside each diffraction pattern, white circles show the calculated diffraction spots<sup>143</sup> (transmission) and corresponding Miller indices based on lattice parameters from single-crystal structure data for 7o (top) and 7y (bottom), with preferred orientation where the crystallographic long axis is perpendicular to the substrate.



Figure 3.14 GIWAXS scattering pattern for thin films of 7 on a quartz substrate before and after heating. Top: Scattering of 70 polycrystalline thin film. Bottom: Scattering of 7y\* thin film produced from heating the 70 thin film shown above. White circles show the calculated diffraction spots (transmission) and corresponding Miller indices based on lattice parameters from single-crystal structure data for 70 (top) and 7y (bottom). Data collected at room temperature. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

The lower panel of Figure 3.14 shows scattering of the  $7y^*$  thin film with in-plane (e.g. directly above the center of the beam) diffractions that correspond to the (200) crystallographic axis perpendicular to the substrate. Note that by convention, the long crystallographic axis is defined as the b-axis (010) for 70, whereas the long axis is the a-axis (100) in 7y; the c-axis (001)

represents the packing of columns in both structures. The other diffuse diffraction spots seen in the  $7y^*$  scattering data match the expected location calculated<sup>143</sup> for the (20-2) and (40-2) crystallographic planes of 7y. As shown in Figure 3.15, the (20-2) and (40-2) planes pass through columns of the aromatic cores and observed scattering in these locations is interpreted to represent periodic order within columns. Other (*h0l*) planes, including the partially inverted (202) and (402) planes also reflect columnar ordering in the crystal. Taken together, this structural data reveals that the  $7y^*$  thin film has the same lamellar structure as 7o, and that there is periodic order within columns of dyads. This columnar order seen in  $7y^*$  is taken to indicate a significant reorganization of intercolumnar geometry following heating: columns packed roughly perpendicular about the dyad long axis in 7o (see Figure 2.5) reorganized to become roughly parallel about the long axis, while adopting a short axis rotation, as seen in yellow crystals of 7 (see Figure 2.11).

An increase in amorphous scattering at larger scattering angles in  $7y^*$  thin films, as well as more diffuse diffraction spots indicates that some disorder is present in  $7y^*$ . In-plane scattering from  $7y^*$  thin films in the (*h*00) plane occurs at a smaller scattering angle than would occur for 7y based on calculated diffraction spots from the 7y crystal structure. This smaller observed scattering angle of the (*h*00) planes in the  $7y^*$  thin film is indicative of a slightly larger (~3Å) lamellar spacing in  $7y^*$  as compared to 7y and can be partially attributed to positive thermal expansion.<sup>114</sup>

Yellow crystals of symmetric dyads were previously shown to have segregated side chains (see Figure 2.12), and so the increase in increase in lamellar spacing seen following heating of **7o** to **7y**\* is believed to reflect the fact that the interdigitated side chains in **7o** (see Figure 2.6) became segregated during the transition to **7y**\*, possible to a larger extent than in **7y**. The overall correspondence between calculated diffraction patterns of **7y** and observed scattering of **7y**\* reflect similar packing motifs between the two species, and the proposed molecular packing for **7y**\* is shown in Figure 3.15.



Figure 3.15 The proposed molecular packing of 7y\* is believed to be similar to that of 7y, with a lamellar structure and some columnar and intercolumnar order, however 7y\* lacks long range crystalline order seen in 7y. The proposed 7y\* structure shown is the single-crystal structure of 7y, with select 7y crystallographic planes shown in green.

One final addition must be noted for the proposed structure of  $7y^*$  that has not been addressed and is not accounted for in Figure 3.15: a variable tilt in lamellae of  $7y^*$  observed in several different X-ray scattering experiments. In one experiment, a single 70 crystal was heated to the corresponding  $7y^*$  form. Following conversion, a WAXS transmission experiment was performed in an end-on geometry, as shown at the top of Figure 3.16. In this geometry, the crystal was oriented such that the incoming X-ray beam will run parallel to, and through, the long axis of the crystal. The diffraction from this  $7y^*$  sample is shown in Figure 3.16. Shown in the raw detector image and the polar transformation are equally spaced rings, that correspond to the (*h*00) planes formed from lamellar packing. Specific planes are indicated in the polar transformed diffraction pattern shown on the right hand side of the figure that has been corrected to take the Ewald sphere into account. Diffraction from the (h00) planes in circular rings is an indication that multiple sets of equally spaced crystallographic planes are oriented in variable angles relative to the substrate.<sup>144</sup> The strongest scattering, represented by the darkest color, is seen in-plane and is taken to indicate that the dominant orientation of lamellae are oriented parallel to the substrate. The lower intensity scattering seen moving away from in-plane scattering is taken to indicate that lamellae oriented parallel to the substrate are the most common orientation of crystalline lamellae present. Other peaks observed are derived from ordering between lamellae, most notably a diffraction peak with spacing of 4.3Å (q = 1.47 Å<sup>-1</sup>) is seen, corresponding to spacing of crystalline packing in alkyl side chains.<sup>101</sup> The presence of this peak supports the notion that some side chains are packed in the solid-state, however, other measurements observed variable extents of alkane packing, and as such, **7y**\* is believed to have a mix of ordered, crystalline and disordered alkyl side chains across the sample.


Figure 3.16 End on transmission WAXS measurement of **7y**\* following the heating of a single **7o** crystal shows scattering from lamellar packing with orientations in all directions, as seen by the circular diffraction rings. The strongest intensity scattering is seen inplane, originating from lamellae oriented parallel to the substrate. Data collected at room temperature.

### 3.2.2.7 Structural Characterization: In Situ Heating X-ray Diffraction

**Structural Changes During Polymorphic Transitions in Polycrystalline Samples.** In an effort to elucidate the structural changes that accompany the real-time transition from **O** to **Y**, in-situ heating X-ray diffraction (XRD) experiments were conducted. While typical real time experiments are done using more intense synchrotron radiation sources, large crystals were found to diffract well from lab X-ray sources to gather structural information in short exposures (e.g. 9-30 seconds).

Numerous attempts to induce a single-crystal-to-single-crystal transition in crystals of **60** and **70** were unsuccessful, as variable orientations were seen for individual crystallographic planes, similar to that seen in Figure 3.16. In these attempted single-crystal-to-single-crystal experiments, the crystal was heated with a stream of hot nitrogen gas. The soft crystal was noted to physically deform with movement of the goniometer in the gas stream, and these deformations consistently resulted in loss of all diffraction spots. In order to circumvent these limitations, new experimental methods were devised to keep the crystal in place during heating and X-ray exposure.

The overall experimental setup for in situ heating XRD experiments is shown in Figure 3.17. A single orange crystal is placed in sandwiched between two thin, 5-7 $\mu$ m, mica sheets, and placed on a stationary heating stage in line with an X-ray source. Using this set up, numerous **60** and **70** crystals were heated while short transmission X-ray exposures (e.g. 30 seconds) were taken during heating in order to understand structural changes to crystals as they undergo the **0** to **Y**\* polymorphic transition. Shown in the bottom of Figure 3.17 is the **70** crystal over the beamline before, and the **7y**\* soft-crystalline mesophase seen after heating, and again, the microscopic morphology of the crystal is noted to not change following heating.



Figure 3.17 Heating XRD experimental setup and single crystal of 70 shown before and after in situ heating to generate 7y\*. Top left: Optical micrograph of initial 70 crystal. Top Right: Macroscopic perspective of 70 on the heating stage shown in the bottom left. Bottom let: Optical micrograph of 70 crystal on top of heating stage mounted over the X-ray transmission hole. Crystal is held in place two pieces of mica sheets. Bottom right: Optical micrograph of 7y\* on heating stage directly following heating XRD-experiment.

The cross section of the X-ray beam is much larger than all transition wavefronts seen visualized by POM, meaning that these exposures are more of a bulk measurement that includes the **O** to **Y**\* transition wavefront, as well as regions of growing **Y**\* and shrinking **O**. Despite these challenges, these measurements support the hypothesis that the transition from **O** to **Y**\* proceed through an amorphous transition state.<sup>69</sup>

Shown in Figure 3.18 are the 2D and 1D diffraction patterns showing the changes that accompanied the **7o** to **7y**\* transition of the crystal shown in Figure 3.17. In the experiment, the crystal is heated from room temperature to 95°C at 5°C min<sup>-1</sup>, then ramped at 2°C min<sup>-1</sup> to 120°C and held at 120°C for 2 minutes before ramping 10°C min<sup>-1</sup> to 90°C, at which time the final exposure (1200 seconds) was captured. During heating beyond 95°C, 30 second exposures were collected, and the time and temperature at the start of each exposure are embedded within the 2D scattering patterns shown in Figure 3.18. Time, t = 0 s, was defined to start with the initiation of heating from 95°C.

As **70** is heated, the few spots that satisfy the Bragg condition are seen to weaken in intensity before disappearing. Quickly following the gradual disappearance of **70** diffraction spots, diffraction spots from **7y**\* appear in rapid succession, with scattering from **7y**\* lamellar spacing being observed before scattering from dyad stacks (Figure 3.18). The emergence of a low angle peak at  $3.38^{\circ}$  two-theta (blue traces) correspond to lamellar spacing from the (200) plane that appears before other (*h*00) planes, and before the planes near  $12.2^{\circ}$  and  $13.7^{\circ}$  two-theta (green traces). The peak seen at  $12.20^{\circ}$  is attributed to columnar order in **7y**\* and can be assigned to the (202) plane. The peak observed at  $13.74^{\circ}$  is attributed to the overlap of the (800) and (402) planes, the latter of which also represents columnar order. Note the spots seen in the bottom of the 2D diffraction patterns are attributed to diffraction caused by the mica sheets used to hold the crystal in place.



Figure 3.18 In situ heating XRD of the **70** crystal shown in Figure 3.17 as it is heated to generate **7y**\*, shows the emergence of new diffraction patterns. Bottom: 1D traces from transformed 2D diffraction patterns shown above.

### 3.2.3 Asymmetric Dyad Stimuli-Responsive Properties

**Optical Changes.** The two shorter asymmetric derivatives **M6N8** (yellow) and **M8N6** (gold) did not have any observable optical transitions when heated prior to melting. Only the two longer asymmetric dyad derivatives, **M8N10** (orange-red) and **M10N8** (yellow-orange) were seen to undergo thermally induced transitions. Orange-red **M8N10** had an orange-red-to-yellow transition that was observed to initiate all around the crystal edge and move towards the interior, creating small pixelated domains throughout the transformed yellow material. In contrast, **M10N8** (yellow-orange) had an observable, yet colorless, transition prior to subsequent melting. Following heating, the thermally generated mesophase persists once cooled back to room temperature. Of the asymmetric derivatives, only **M8N10** (orange-red) showed mechanochromic behavior, with a transition to a soft liquid-crystalline like yellow material when a shearing force was applied.

Thermal Transition Characterization – Asymmetric Dyad Crystals. Shown in Figure 3.8 are successive heating-cooling DSC measurements for asymmetric dyad derivatives. Peak transition temperatures and enthalpies of transition for these four derivatives are provided within Figure 3.20 and in Table 3.4. Interestingly, the existence of two endothermic transitions was seen not seen to correlate with head-to-head stacking geometry, but did occur in the two longer side chain derivatives. As noted in section 2.3.3.3, M8N6 (gold) M10N8 (yellow-orange) had similar head-to-head stacking geometries, M6N8 (yellow) was shown to have head-to-tail stacking geometry, and while no crystal structure was solved for M8N10 (orange-red), it is believed to have packing similar to **90** and thus pack in a head-to-head geometry (see Figure 2.18).

The two shorter derivatives, **M8N6** (gold, head-to-head) and **M6N8** (yellow, head-totail), are seen to have a single endothermic peak in the first heating that corresponds to POM observations for direct melting to the isotropic phase. Subsequent cooling of the isotropic phase generates a solid that, when reheated, has a lower transition temperature compared to each initial crystalline sample (Figure 3.20). In contrast, the two longer asymmetric derivatives, **M10N8** (yellow-orange, head-to-head) and **M8N10** (orange-red, head-to-head), are seen to have two endothermic transitions, at 102.3° and 107.1°, respectively, before melting to the isotropic phase. The integrated enthalpy of transition was different for both derivatives, with measured transition enthalpies of 16.2 and 48.0 kJ mol<sup>-1</sup> for **M10N8** (yellow-orange) and **M8N10**, respectively. In contrast, a smaller difference was observed for the transition enthalpy corresponding to melting to the isotropic phase, with transition enthalpies of 19.8 and 25.5 kJ mol<sup>-1</sup> for **M10N8** (yellow-orange) and **M8N10** (orange-red), respectively.

In comparison to the two transitions seen in orange symmetric crystals (Figure 3.6 and Table 3.2), **M10N8** (yellow-orange) had the smallest transition enthalpy of all crystalline to mesophase transitions measured. In contrast, **M8N10** (orange-red), had a crystal to mesophase transition enthalpy of 48.0 kJ mol<sup>-1</sup>, most comparable to the transition enthalpy measured for the conversion of **80** to **8y**\* (53.1 kJ mol<sup>-1</sup>), and less than its constitutional isomer, **90**, with a transition enthalpy of 56.1 kJ mol<sup>-1</sup>.

In comparison to the crystal-to-isotropic transition seen in yellow symmetric crystals (Figure 3.5, Table 3.2), head-to-head stacked **M8N6** (gold) was seen to have the largest transition enthalpy measured (42.2 kJ mol<sup>-1</sup>), for derivatives with a single thermal transition. The largest symmetric yellow crystal-to-isotropic transition was shown to be in **8**y, with transition temperature of 144.4°C and a transition enthalpy of 34.7 kJ mol<sup>-1</sup>. However, as discussed in section 3.2.2.3, crystal size was seen to influence transition temperatures and transition enthalpies. The larger three dimensional growth of **M8N6** compared to symmetric yellow crystals (Figure 2.2) hinders meaningful thermodynamic comparisons between head-to-head and head-to-tail polymorphs that display a single thermal transition. Comparison of head-to-tail stacked **M6N8** and its constitutional isomer **7y** and **7y'** reveal similar transition temperatures and enthalpies (see Table 3.2) between the three derivatives with similar packing geometries (see Figure 2.19). However, the parallel intercolumnar relationship between **M6N8** (Figure 2.15)

resembles that of 6y/6y', in contrast to the 49° short-axis rotation seen between dyads in adjacent columns of 7y/7y' (Figure 2.11).



Figure 3.19 Successive DSC heating and cooling experiments for all asymmetric dyad crystals shows the presence of two endothermic transitions for longer M10N8 (yelloworange) and M8N10 (orange-red) derivatives, while only a single transition is seen for shorter derivatives. Values near peaks show the corresponding peak temperature (°C), bracketed values represent integrated transition enthalpy [kJ mol<sup>-1</sup>].

	Lower Temperature Transition, if Present			Higher Temperature Transition		
Sample	Onset Temp (°C)	Peak Temp (°C)	Transition Enthalpy (kJ mol <sup>-1</sup> )	Onset Temp (°C)	Peak Temp (°C)	Transition Enthalpy (kJ mol <sup>-1</sup> )
M6N8	-	-	-	137.76	142.44	30.93
M8N10	102.08	107.08	47.98	128.01	132.32	25.53
M8N6	-	-	-	140.26	143.66	42.23
M10N8	100.71	102.30	16.24	122.70	127.80	19.81

Table 3.4Summary of asymmetric dyad phase transitions measured by DSC at a heating rate<br/>of 5°C min<sup>-1</sup> for all samples.

### 3.2.4 Self-Assembly From Isotropic Cooling

Previously, all orange symmetric dyads were shown to have the same general properties when heated, regardless of side chain length: initial thermal conversion into a yellow softcrystalline mesophase, and continued heating would result in melting to the isotropic phase. Shown in Figure 3.6 is an alkyl chain length dependent behavior for dyads when cooled from the isotropic phase, exhibiting differences in the patterns of exothermic cooling peaks.

When shorter derivatives 6, 7, and 8 were cooled from the isotropic phase, exothermic peaks were seen that cannot be individually resolved (e.g. the signal does not return completely to baseline). In contrast, cooling from the isotropic phase of derivatives 9, 10, and 12 show two distinct exothermic peaks (or sets of peaks). Investigation of this phenomenon using a heating stage equipped POM shows optical differences are observed when 7 and 9 are cooled at 5°C min<sup>-1</sup> from the isotropic phase.

Shown in Figure 3.20 is the cooling of 7 from the isotropic phase at 1°C min<sup>-1</sup> when viewed under cross polarized and brightfield conditions in separate, successive cooling experiments. The phase transition from the isotropic melt occurs over a period of 171-181 seconds in the two experiments, and is seen to follow the classical nucleation and growth crystallization pathways. The initial appearance and growth of the long rectangular domains resembles the smectic bâtonnets,<sup>149</sup> suggesting a single transition from isotropic to a smectic, soft crystalline mesophase.



Figure 3.20 Self-assembly of 7 when cooled from the isotropic phase at 5°C min<sup>-1</sup> as viewed under cross polarized and brightfield conditions shows the initial formation of long rectangular bâtonnet like solids, indicative of an Iso-Sm like transition.

In contrast to 7, and in agreement with two exothermic peaks seen in DSC (Figure 3.6) cooling of **9** from the isotropic phase at 1°C min<sup>-1</sup> shows the emergence of two distinct molecular species (Figure 3.21). Initial cooling from the isotropic phase generates small, randomly dispersed anisotropic circles that resemble fan-shaped focal conic domains (FCD), a well-known

smectic A defect, once cooled below 139.6°C. The number and size of these FCDs were seen to increase as the sample was further cooled to 134.1°C. Holding the temperature at this point was noted to not change the optical characteristics. The presence of concentric rings, four extinction brushes in the shape of a cross with a central hedgehog point defect are indicative of smectic phase under hybrid anchoring conditions.<sup>150-152</sup> The emergence of FCD reflect the self-assembly of **9** into domains that have overall orientational order, with the dyads likely assembling within large cylindrical columns with the long axis of dyads oriented radially.

Continued cooling at a rate of 1°C min<sup>-1</sup> shows no further changes until the second transition temperature of 121.4°C, ~1,100 seconds after the FCDs were observed. Once this lower transition temperature is reached, a relatively fast moving transition wave is seen to move through the remaining isotropic melt over a period of 10-15 seconds. The wave initiates near the edge of the isotropic melt, and moves radially outward, creating a series of concentric ridge-like rings in the material. Movement of this transition wave was seen to move through previously self-assembled FCD. As shown by the last three brightfield images, the FCDs were still visible after the wave-like transition. Further characterization of this solid using optical profilometry reveals the focal conic holes are still intact after the fast wave-like transition (Figure S3). Combined, the emergence of FCD and wave-like transition suggests **9** underwent an isotropic-smectic to a smectic, soft crystalline mesophase. transition.



Figure 3.21 Self-assembly of **9** when cooled from the isotropic phase at 5°C min<sup>-1</sup> viewed under cross polarized and brightfield conditions, showing the formation of two different phases over different timescales, initial formation of focal conic disc-like domains at higher temperatures before the movement of a faster wave like transition.

# **3.3 DISCUSSION**

# 3.3.1 Self-Assembly From the Isotropic Melt

During cooling from the isotropic phase, varying extents of self-assembly are observed for different derivatives as a function of temperature. In the isotropic melt, the side-chain movements keep dyad molecules separated and prevents any anisotropic ordering. Upon cooling, the first molecular associations to occur are expected to be aromatic interactions between dyad cores, associating to form columnar stacks, while flexible alkyl side remain fluid, as previously seen in mixtures of DAN and NDI.<sup>60, 61</sup> Once below a side chain dependent threshold temperature, it is thought that the attractive interactions between dyad cores can overcome thermal motion within side chains, thus nucleating columnar growth. Above this threshold temperature, interactions between dyad cores in nucleation processes are overcome by thermal motion of the side chains, while below the threshold temperature, growth from templated columns is likely. Continued cooling would be expected to reduce side-chain flexibility until they solidify into the final soft crystalline mesophase.

However, these two distinct self-assembly processes are not observed in all derivatives, and variations in side-chain length were correlated with different optical characteristics during the cooling process, as shown in Figure 3.20 and 3.21. Because shorter side-chains have less degree of freedom, **7** is expected to be able to nucleate successful columnar growth at higher temperatures compared to **9**, as was observed (onset for **7** 148.5°C, for **9** 139.6°C, Figure 3.20 & 3.21). The two-step, discrete self-assembly process observed in **9** is taken as an indication that once columnar stacks form, there is still significant side chain mobility, as seen by observed smectic A FCDs. Subsequent observable changes were only seen with additional cooling below a second transition temperature, at which point a fast moving wave-like transition moved through the sample. Once cooled past the second transition temperature, side chains in **9** are no longer able to remain fluid, and freeze out in a rapid nucleation and growth type process, as seen by the fast moving wave-like transition.

In contrast to 9, it is thought that the shorter side chains in 7 do not have enough thermal motion to maintain fluidity once assembled into columns. Thus, heptyl side chains become ordered as columns are formed, leading to the multidimensional growth observed in Figure 3.21, in a single self-assembly process. This postulated mechanism is further supported by the trends seen when all derivatives are cooled from the isotropic phase, as measured by DSC (Figure 3.6). Shorter derivatives 6 and 7 have a single exothermic transition, whereas derivatives 8, 9, 10, and 12 have two discrete exothermic transitions. These longer derivatives are also seen to have a final transition at successively lower temperatures, attributed to increasing thermal disorder in

derivatives with longer side that impede the complete self-assembly process until thermal motion can no longer overcome associations between side chains.

# **3.4 CONCLUSIONS**

In summary, all symmetric orange dyads investigated were found to have thermochromic, transitions upon heating, with orange crystals transforming into a yellow material. The structure of the yellow material was determined to be a soft crystalline mesophase based on spectroscopic, structural, and thermal characterization methods. The thermally produced soft crystalline mesophase was shown to have similar molecular packing to yellow symmetric crystals grown from solution: head-to-tail dyad packing, columnar and intercolumnar order, with segregated side chains, yet differing from yellow crystals by having a decrease in long range order, a mix of order and disorder in side chains, and variably tilted lamellae.

When heated, **1bo** crystals were found to directly sublime, and the two shorter asymmetric derivatives were seen to melt directly to the isotropic phase. The two longer asymmetric dyad derivatives, **M8N10** (orange-red) and **M10N8** (yellow-orange) were seen to undergo thermally induced transitions prior to melting, and only **M8N10** had a thermochromic transition.

Visualized by POM, this thermochromic transition was seen to move as a wavefront through orange crystals. Repeatable observations revealed the fastest transitions move down the long axis of the crystal, and are observed to move at a 38° angle, on average, relative to the long axis. Thermal analysis with DSC revealed that the orange-to-yellow transition temperature is influenced by crystal size in addition to side chain length, and a thus the tunability of the system is multivariable in nature. Micro- and nanoscopic measurements of crystals before and after heating confirm POM observations that the overall morphology of the material does not significantly change following the transition. A slightly larger change in crystal volume

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following heating, compared to theoretical changes based on single-crystal structures, supports the proposed structure of the soft crystalline mesophase. High resolution AFM imaging of orange and yellow materials revealed a lamellar structure, with general retention of layers following transition, providing support for a transition mechanism operating largely within individual layers. Our proposed molecular mechanism(s) by which dyad packing switches from head-tohead to head-to-tail during the orange-to-yellow transition must account for the observed altered columnar and side chain packing. Further, any proposed mechanism must explain why the transition wavefront was seen to move at an angle, and how different layers within the crystal transition.

### **3.5 EXPERIMENTAL**

### 3.5.1 Heating Microscopy

The heating microscopy experiments were carried out on a Zeiss Axio Scope A.1 microscope equipped with a Linkam LTS420 thermal stage with either a 10x N-Acroplan or 20x N-Acroplan objective, with the ability to image under linear polarized, cross polarized, or unpolarized light. The chamber was closed during the experiment. The heating was controlled by Linkam add-on in the ZEN Core. Micrographs were taken every second (1 fps) during the heating interval from 100°C to 120°C. Time and temperature for each frame were determined by the Linkam software.

Protocol for heating of **70** to **7y**\* in Movie 3.1 and Figure 3.1 using 20x N-Acroplan objective: Heating from room temperature (RT) to 90°C at 20°C min<sup>-1</sup>, then 10°C min<sup>-1</sup> to 100°C. The crystal was held at 100°C for 30 seconds, then heated at 2°C min<sup>-1</sup> to 120°C, and directly was cooled to RT at a rate of 10°C min<sup>-1</sup>.

Protocol for heating of **60** to **6y**\* in Movie 3.2 and Figure 3.2 using 10x N-Acroplan: Heating from room temperature to 90°C at 20°C min<sup>-1</sup>, then 10°C min<sup>-1</sup> to 100°C. The crystal was held at 100°C for 30 seconds, then heated at 5°C min<sup>-1</sup> to 120°C, held at 120°C for 1min, then cooled to RT at 10°C min<sup>-1</sup>. In the lower panel of Figure 3.2, wavefront speed was calculated as the distance the wave traveled perpendicular to the closest crystal long axes between the three frames (three seconds) before and three frames after the given frame.

### 3.5.2 Grazing-Incidence Wide Angle X-ray Scattering and Wide-Angle X-ray Scattering

Two-dimensional wide-angle X-ray scattering (WAXS) measurements and Grazing-Incidence Wide Angle X-ray Scattering (GIWAXS) were made using a SAXSLabs Ganesha and analyzed using SAXSGUI and GIXSGUI<sup>3</sup>. The SAXSLAB Ganesha has a Cu K $\alpha$  radiation source ( $\lambda = 1.5418$  Å) with a Pilatus 300 detector (pixel size 0.172 x 0. 172 mm). Sample detector distance for wide angle measurements was 140.8143 mm, 3 aperture GIWAXS mode, all horizontal and vertical guards set to 0.7mm. Heating experiments inside were performed using a Linkam heating stage. Crystals were sandwiched between two thin Mica sheets (10 mm Mica Windows for Sandwich Cell (5-7 micron thick), SAXSLABS U.S., Inc.), on top of the Linkam stage and held in place with two 'lollipop' holders (see top right of Figure 3.17)

### 3.5.3 Atomic Force Microscopy

Non-Contact Atomic Force Microscopy (AFM) measurements were made on Park Scientific Instruments XE-100 and analyzed using Gwyiddon<sup>153</sup>. Following thermal conversion, the material was allowed to rest at room temperature for two days prior to subsequent imaging.

### 3.5.4 Thin Film Preparation

Thin films were made via physical vapor deposition (AMOD Thermal Deposition System, Ångstrom Engineering Inc.) onto quartz substrates. Vapor annealing of thin films were done in sealed fuming chambers with volumes of DCM between 700  $\mu$ L and 2.0 mL to generate the orange form.

### **3.5.5 Optical Profilometry**

Crystal size was quantitatively determined using a Keyence VK-X1100 Optical Profilometer and analyzed using VK-X1Series MultiFileAnalyzer software. To measure the change in crystal volume, orange crystals were adsorbed onto a cleaned silicon wafer by placing a single **60** or **70** crystal onto the wafer and dispensing 1 $\mu$ L of cold methanol next to the crystal using an Eppendorf autopipette before gently moving the crystal into the methanol. Cold methanol was shown to not dissolve the crystals while allowing crystals to evenly adhere onto the surface as the small volume evaporated. After adsorption, crystals were left at room

temperature for at least 24 hours before  $O_{Volume}$  was measured. O crystals were next heated at 120°C for 2 minutes, and then measured again to determine  $Y*_{Volume}$ . Volume was determined using Keyence VK-X Series MultiFileAnalyzer software following flattening of the substrate baseline and defining the boundary of the crystal. Silicon wafers were viewed as instrumental to volumetric analyses, as they consistently had a flat baseline measurement, in contrast to glass substrates which yielded inconsistent baseline measurements.

### 3.5.6 Information on Supplementary Movies 3.1 – 3.2

**Movie 3.1**. Movie of the heating of **70** to **7y**\* as viewed under a 20x objective equipped POM with a heating stage. Images acquired at 1 fps and stitched together to generate the following movie. Heating program: room temperature (RT) to 90°C at 20°C min<sup>-1</sup>, then 10°C min<sup>-1</sup> to 100°C. The crystal was held at 100°C for 30 seconds, then heated at 2°C min<sup>-1</sup> to 120°C, then directly was cooled to RT at a rate of 10°C min<sup>-1</sup>.

**Movie 3.2.** Movie of the heating of **60** to **6y**\* as viewed under a 10x objective equipped cross polarized POM with a heating stage. Images acquired at 1 fps and stitched together to generate the following movie. Heating from room temperature to 90°C at 20°C min<sup>-1</sup>, then 10°C min<sup>-1</sup> to 100°C. The crystal was held at 100°C for 30 seconds, then underwent 5°C min<sup>-1</sup> to 120°C, held at 120°C for 1 min, then cooled to RT at 10°C min<sup>-1</sup>.

# **CHAPTER 4**

# Mechanistic Analysis of Polymorphic Switching in Monoalkoxynaphthalene-Naphthalimide Donor-Acceptor Dyads<sup>1</sup>

# 4.1 CHAPTER SUMMARY

# **4.1.1 Introduction**

In chapter 3, thermally induced polymorphic switching was described in both symmetric and asymmetric dyad derivatives. Heating of symmetric dyad orange crystals (head-to-head packing, orthogonal columns about the long molecular axis, and interdigitated side chains) were shown to form a yellow soft-crystalline mesophase (head-to-tail packing, parallel columns about the long molecular axis, and segregated side chains) that persists indefinitely after heating and in the absence of organic solvent vapor. Transitions were observed to start on crystal borders and defects, initially proceeding as slow moving transition waves that that formed dark, "pixelated" regions. In symmetric dyad orange crystals, a size dependency in transition temperature was observed, and transition wavefronts were repeatably observed to move 1-2 orders of magnitude faster than the slower transitions, always observed to be moving down the long axis of the crystal at 38° angle on average. In asymmetric dyad derivatives, a variety of different thermally induced behaviors were observed. In longer asymmetric derivatives, both thermochromic and colorless transitions were observed, yet in both cases, no angled wavefront transition behavior was

<sup>&</sup>lt;sup>1</sup> This chapter was adapted in part from the published article: Wight, C. D.; Xiao, Q.; Wagner, H. R.; Hernandez, E. A.; Lynch, V. M.; Iverson, B. L., Mechanistic Analysis of Solid-State Colorimetric Switching: Monoalkoxynaphthalene-Naphthalimide Donor–Acceptor Dyads. *J. Am. Chem. Soc.* **2020**, 142 (41), 17630-17643. CDW designed and conducted experiments and wrote the manuscript with BLI.

observed, and transitions were seen to proceed in all directions at similar rates and form similar "pixelated" regions. Unique to asymmetric dyads, two dyads with the same features (head-to-head, columns orthogonal about the short molecular axis, mix of segregated and interdigitated side chains) showed diverging behavior, with one having a crystal-to-mesophase transition, and the other melting directly to the isotropic phase with the only apparent difference being side chain length. Key questions related to the mechanism and thermodynamics of the transformation remain.

# 4.1.2 Goals

This chapter seeks to answer: What is the molecular mechanism for the orange-to-yellow transition in orange crystals of symmetric dyads? Why does the transition consistently move at an angle in orange crystals of symmetric dyads? Why does crystal size affect the transition? Why do thermally induced transitions in asymmetric dyads not move at an angle? Why are some asymmetric dyad crystal-to-mesophase transitions thermochromic, and others do not have a color change? What is the thermodynamic basis for the transition, and how does the crystal remain intact during the transition and not melt? Why does the transition not reverse when cooled down to room temperature? What are the "pixelated" regions observed in asymmetric dyad crystals, and at the start of symmetric transitions before the emergence of an angled wavefront?

### 4.1.3 Results

Herein we report the first molecular-level mechanistic picture of the polymorphic transition that describes the molecular level movements that take place in thermochromic transition of symmetric MAN-NI dyads, as well as the thermochromic and colorless (or color neutral) transitions of asymmetric MAN-NI dyads. In contrast to previously reported

polymorphic systems with alkyl chains,<sup>83, 116, 118, 119</sup> the stimuli-induced thermochromic transition of symmetric MAN-NI dyads proceeded without altering the microscopic morphology of the original crystal while simultaneously exhibiting a dramatic visible color change in symmetric derivatives. Comprehensive standard and in situ heating XRD, grazing-incidence wide-angle Xray scattering (GIWAXS), non-contact atomic force microscopy (AFM), polarized optical microscopy (POM), spectroscopy, and differential scanning calorimetry (DSC) analyses were used to develop a full picture of the polymorphic switching process. Our analysis revealed that the MAN-NI dyads appear to be the first example of a polymorphic system involving a nucleation and growth mechanism that converts to a faster cooperative mechanism *during* a transition. The transition critically depends upon a complex interplay between the overall layered structure of the starting crystal, the thermodynamics of the two different polymorphs, and similar densities of the interconverting polymorphs.

## **4.2 DISCUSSION**

### **4.2.1** Aliphatic Layer Packing Differences.

In all polymorphs except **1bo**, dyads assemble to create an alternating bilayer type structure, with alternating alkyl and aromatic layers (Figure 4.1). However, the nature of alkyl chain packing differs markedly between the symmetric **O**, symmetric **Y**, and asymmetric polymorphs. Crystal structures of all head-to-head **O** polymorphs have alkyl chains in predominantly anti-staggered conformations, with side chains from adjacent layers interdigitating, forming a close-packed 'cork' and 'bottle' like structure (Figure 4.1, Figure 2.6). Alkyl side chains in head-to-tail **Y** crystals show more disorder and adopt mixtures of staggered-anti and gauche conformations and have segregated (i.e. not interdigitated) side chains (Figure 4.1, Figure 2.12). Disorder in **Y** side chains is seen by larger thermal displacement ellipsoids associated with side chains of **Y** crystals and multiple site occupancies for some alkyl chain atoms in **6y**, **7y**, and **7y'** (Figure 2.8, Table 2.2).

Importantly, in **O** crystals, the orientation of the dyad cores *alternates* in adjacent columns as shown in Figure 4.1. In other words, if a given aromatic stack in an **O** crystal has the NI units of the dyads oriented "up" in the crystal, both adjacent columns within the same layer will have the NI units oriented "down", and *vice versa*.



Figure 4.1 Crystal structures of 70 and 7y highlight the differences in all three packing dimensions, when viewed from two orthogonal perspectives. Top: Crystal structure of 70 showing head-to-head aromatic stacking geometry, perpendicular columns relative to the long axis of the dyad aromatic core, and interdigitated side chains. Bottom: Crystal structure of 7y showing head-to-tail dyad stacking geometry, adjacent columns tilted 49° relative to the short axis of the aromatic dyad core, and segregated side chains. Previously, 7y\* was shown to have the same three dimensions of packing as 7y, with the major difference being lack of long range crystalline order.

The nearly perpendicular relationship between columns in all **O** crystals appear to be stabilized through a combination of favorable side-chain packing and electrostatic interactions between the most polarized bonds in the dyads, namely the imide carbonyl C-O bonds and the C-H bonds of alkoxy O-CH<sub>2</sub> groups of the MAN units as shown by dashed green lines in Figure 4.2a (section 2.4.1). These proposed C-H···O non-conventional hydrogen bonds create a zig-zag

network of connected dyads in the same layer of the crystal, and as seen in Figure 4.2b, the molecules linked in this way trace out an angle between  $37 - 38^{\circ}$ , relative to the long axis of the aromatic stacks, in **60**, **70**, and **80**.



Figure 4.2 (a) Single-crystal structure of 70 illustrating intermolecular C-H…O hydrogen bonds (dashed green lines) between adjacent columns. Terminal side-chain atoms removed for clarity. (b) Cartoon depiction of typical orange crystal dimensions with preferred orientation: crystal long-axis is made from dyads stacked in columns, while the height of the crystal is made from alternating aromatic and alkyl layers. Projecting out of the cartoon is the 70 crystal structure as viewed from each unique crystal face, with H-atoms omitted on the line structures for clarity. Shown in space filling mode, six dyad molecules connected through the intercolumnar C-H…O hydrogen bonding network shown in a). Top Right in magenta: When viewed from above the crystal, this intermolecular H-bonding network creates an angle relative to the long axis of the crystal of 37.5° in 70 (shown in magenta), and 37.2° in 60. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

Asymmetric head-to-head packed **M10N8** (yellow-orange crystals) and **M8N6** (gold crystals) have unique alkyl layer packing, possessing a mix of interdigitated and segregated sidechain packing (Figure 4.3, Figure 2.16). Segregated NI side chains seen in Figure 4.3b decrease the interaction between adjacent layers in both derivatives, however a second subtle effect also decreases stability between layers. Unique to these two asymmetric derivatives is a *hybrid alkyl/aromatic* sublayer bordering both sides of each alkyl layer. Highlighted in Figure 4.3a, this hybrid sublayer contains alkyl and aromatic components across columns. This sublayer results in a decrease in the width of respective aromatic and the alkyl layers due to the staggered nature of asymmetric dyad packing.



Figure 4.3 a) Packing of asymmetric **M10N8** (yellow-orange crystals) and **M8N6** (gold crystals) is characterized by head-to-head packing, adjacent columns rotated roughly orthogonal about the short axis of the dyad aromatic core, and a mixture of interdigitated and segregated side chains that result in hybrid alkyl and aromatic containing sublayers. b) Similar side chain packing in both derivatives, with a mix of interdigitated and segregated side chain packing between layers. Crystal structures shown as displacement ellipsoids set to the 50% probability level with hydrogen atoms omitted for clarity.

## 4.2.2 Orientations of Dyad Molecules in Crystals

Through a combination of transmission and GIWAXS experiments, done on both single and polycrystalline samples, as well as prediction of crystal morphology using Bravais, Friedel, Donnay, and Harker (BFDH) calculations from single-crystal data, the orientation of dyad molecules in each polymorph was determined (Figure 4.4a, section 2.3.3.5). In all dyad crystals, the long axis of the crystal is made from dyad aromatic stacking.

A schematic for orange dyad crystal packing is shown in Figure 4.4b. Orange crystals of symmetric dyads (**60**, **70**, **80**, **90**, **100**, and **120**) are structurally analogous to a nice lasagna, with the relatively thick "noodle" layers comprised of highly ordered, closely packed alkyl side chains from adjacent layers, interdigitated in a 'cork' and 'bottle' fashion (Figures 2.4-2.7). The "meat/cheese/sauce" layers have the head-to-head aromatic dyad units stacked with the direction of stacking parallel to the long axis of the crystal (Figure 4.2 & 4.4).



Figure 4.4. Comparison of 70 and 7y. (a) Cartoon illustrating preferred orientation, with alkyl and aromatic layers parallel to the substrate. Crystal structure of 70 showing head-to-head dyad core stacking geometry, perpendicular columns relative to the long axis of the dyad aromatic core, and interdigitated side chains (b) Schematic of 70 packing. (c) Cartoon illustrating preferred orientation of Y crystals, with aromatic layers parallel to the substrate. Crystal structure of 7y showing head-to-tail dyad core stacking geometry, adjacent columns tilted 49° relative to the short axis of the dyad aromatic core, and segregated side chains. Select crystallographic planes of 7y seen in 7y\* are shown in green. (d) Schematic of 7y packing. Adapted with permission from Ref <sup>66</sup>. Copyright 2020 American Chemical Society.

The yellow material is also structured like a molecular lasagna (Figure 4.3d), but with important differences compared to the orange polymorph. In the yellow polymorph, the alkyl chains show more disorder, have a larger proportion of gauche conformations, and are no longer interdigitated between layers (Figure 4.3c & 4.1). Similar to the orange material, however, the head-to-tail stacked aromatic dyad units of the yellow material are also stacked with the direction of stacking parallel to the long axis of the crystal.

As discussed in chapter 3, the general features of yellow material produced in various ways are consistent, especially with respect to dyad head-to-tail packing geometries, yet specific differences are present. Yellow crystals grown directly from solution (**Y**) exhibit a high level of short- and long-range order as indicated from single-crystal structures. On the other hand, thermally generated yellow material derived from orange crystals (**Y**\*) is best described as a soft-crystalline mesophase owing to long-range disorder and multiple variably oriented crystalline domains not seen in yellow crystals grown from solution (section 3.2.2.6).

### 4.2.3 Transition Moves Through the Orange Crystal as a Wavefront

When heated, we always observed the crystal-to-mesophase transition starting on the crystal boundary, or at a crystal defect, with the majority of a given orange-to-yellow transition sweeping along the long axis of the crystal (direction of stacking) as a wavefront, and different individual layers moving at slightly different rates (Figure 3.1 & 3.2, Movie 3.1 & 3.2). The wavefronts from each end meet in the interior of the solid to complete the conversion of the entire crystal. Using in situ heating transmission XRD, we could not detect any crystalline intermediate states during the transition process. In agreement with many proposed polymorphic transition mechanisms,<sup>69, 86</sup> we believe the transition wavefront represents an amorphous, fluid-like transition state between **O** and **Y**\* that enables the conformational switching from **O** to **Y**\* at this wavefront interface. Interestingly, the fastest wavefronts move at an approximately  $38 \pm$ 

4° angle relative to the crystal long axis in what behaves like a highly cooperative or concerted process.

#### 4.2.4 Structural Transition "Trigger"

So, what triggers the structural transition from the orange to the yellow polymorph prior to symmetric dyad crystals melting entirely? We propose that upon heating of the orange crystal, the structural transition "trigger" involves the local melting of the interdigitated alkyl chain layer, likely initiating through rotational isomerization of the alkyl side chains. Conformational isomerization of alkyl side chains would break the 'cork' and 'bottle' interaction between interdigitated side chains, resulting in an increase in disorder in the alkyl chain layer. This increase in disorder would allow for some translational movement within the alkyl chain layer, analogous to the fluidity exhibited within biological membranes. This flexibility and fluidity enables translational and/or rotational motion that has been seen in other alkyl chain containing polymorphic materials.<sup>83, 116, 118, 119</sup> The proposed triggering event, initiated by local melting of alkyl layers, does not disrupt the overall crystal morphology, apparently still held together by the stacked aromatics in between fluid alkyl layers as well as being confined by layers that have already transitioned, or are still in their orange crystalline form.

Importantly, we are assuming that the fluidity in alkyl side chains does allow the dyad molecules to move laterally within the layers of the material, to at least a limited extent. Even with fluidity in the alkyl chain layer, how do all of the molecules reorganize from head-to-head (**O**) to head-to-tail ( $\mathbf{Y}^*$ ) as the wavefront passes through the material without disrupting the overall crystal morphology? With the single exception of **1bo**, all symmetric dyad polymorphs have lamellar structures with consistent phase separation of alkyl and aromatic layers. A vertical "flip" of a single dyad within an **O** stack would convert the head-to-head packing into the head-to-tail packing seen in **Y**\*. However, this vertical "flip" of the molecules is highly improbable as the phase separation would be lost during a "flipping" transition. The lowest energy transition

pathway that maintains the microscopic morphology of the crystal is thus expected to maintain this bilayer structure, with the majority of the reorganization happening within 2D dyad layers.

The head-to-head to head-to-tail stacking reorganization *can* readily occur with a limited *lateral* motion between adjacent layers of the dyads. Note in the structure of the orange material in Figure 4.1, the polarities of the adjacent head-to-head stacks of the dyads are exactly inverted with respect to each other in alternating fashion. Meaning, that if a given dyad molecule moves laterally into either adjacent stack in the solid, it will essentially be switching from the head-to-head orientation in its own stack to a head-to-tail orientation in the adjacent stack!

### 4.2.5 Both Faster and Slower Wavefronts are Seen in Orange Crystals of Symmetric Dyads

Slower transition wavefronts move in variable directions, however all share the same feature that they begin at an edge or crack and propagate away from regions that have already transitioned. The slowest transition wavefronts in symmetric crystals move parallel to horizontal crystal boundaries (Figure 3.2) while the fastest wavefronts move at an angle (Movie 3.1 & 3.2).

Analogous to growth of a new crystalline phase from a liquid phase, most phase transitions are believed to begin through initiation mechanisms that, in general, resemble nucleation and growth processes of crystals from solution.<sup>69, 82</sup> Initiation of all thermal transitions and the subsequent propagation of the slower transition wavefronts are believed to operate through these nucleation and growth mechanism. A crystal edge provides opportunity for dyad translational movement that does not exist in the packed crystal interior.<sup>69</sup> Local melting of the alkyl chain layer allows for mobility within layers, and lateral motion within layers can allow for conformational sampling through translational movements without disrupting the crystal morphology. Conformational sampling on the crystal edges leads to nucleation of  $\mathbf{Y}^*$  that then templates subsequent  $\mathbf{Y}^*$  growth within the same layer. As multiple nucleation sites can emerge at different locations around a single crystal, and nucleation sights can have differences in orientation, multiple transitions across a single crystal give rise to numerous soft, polycrystalline

**Y**\* domains, and contributes to the observation that no SCSC transition was observed, despite numerous attempts. The darker "pixelated" region that makes up the majority of **Y**\* in the first four images shown Figure 3.2 is attributed to these soft polycrystalline domains with variable orientations that formed from a nucleation and growth mechanism, the major transition observed at the start of transitions, and next to crystal edges and cracks, when dyads are not confined in all three crystallographic dimensions.

### 4.2.6 Why Do the Fastest Wavefronts Move at an Angle in Orange Crystals?

Interestingly, the fastest wavefronts move at an angle, and slower moving wavefronts speed up as an angled wavefront emerges. Because these fastest wavefronts move in a single direction through the crystal at speeds 1 - 2 orders of magnitude faster than the slower wavefronts, the molecular rearrangements resulting in the transition along the wavefront are likely to be more or less concerted. A reasonable mechanistic hypothesis for the orange to yellow transition also needs to explain the observed  $38 \pm 4^{\circ}$  angle of the transition wavefront relative to the long axis of the crystal, noting that this angle is the same as the proposed strongest intermolecular interaction between adjacent aromatic stacks in orange crystals, the proposed C-H…O hydrogen bonds (see Figure 4.2). We therefore propose that once one of the molecules in the C-H-O hydrogen bonding network moves, the hydrogen bond to an adjacent molecule is disrupted. The loss of this hydrogen bond, that we believe stabilizes the geometry between columns, results in increased motion of the adjacent molecule, enabling its movement, and the disruption of the hydrogen bond to its adjacent molecule, and so on right down the entire 38° line of hydrogen bonded molecules at the wavefront. This wavefront then moves down the crystal long axis, with a cooperative motion that turns the perpendicular dyad stacks parallel through a concerted "push", where successive dyads turn like individual pages when quickly flipping through a book. To the best of our knowledge, the observation of both thermally induced transition mechanisms operating in tandem and the switch from a nucleation and growth

mechanism on crystal edges to a cooperative mechanism in the crystal interior during a transition has not previously been reported.

#### 4.2.7 Thermodynamic Balancing Act

DSC measurements confirmed that the orange material is the more stable at room temperature (and below) presumably because of the combination of a reasonably stable head-tohead stacking geometry, along with maximum van der Waals interactions between the perfectly ordered and close-packed staggered-anti, interdigitated alkyl chains. In the yellow form, stabilized by slightly more favorable electrostatic interactions on the periphery of the aromatic units, the presumably more stable head-to-tail stacking geometry is present, but the alkyl chains are no longer all staggered-anti, highly ordered, close-packed, or interdigitated. Importantly, modeling indicates that for geometric reasons, the dyad molecules cannot assemble in the more stable head-to-tail aromatic stacking orientation of the yellow solid and simultaneously accommodate the close-packed, staggered-anti, interdigitated alkyl chain layer seen in the orange crystal. The bottom line is that there is an energetic and structural trade-off between the two forms; more stable side chain packing but less stable aromatic stacking geometry in the orange form, yet more stable aromatic stacking geometry with less favorable alkyl chain packing in the yellow form. Affecting this balance, *there is a dominating influence of entropy so that temperature becomes determinant of stability*.

As mentioned above, the more highly ordered orange material is more stable at lower temperature because of larger surface area of contact and therefore an *overall* increased van der Waals attraction between adjacent molecules. However, at higher temperature, where  $\Delta S$ becomes more dominant, the yellow material is now more stable because of the more robust aromatic stacking geometry accompanied by a decrease in overall order (so an increase in intrinsic  $\Delta S$ ) of the alkyl chains. Serendipitously, the temperature at which the yellow form

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becomes more stable than the orange form occurs for our dyad derivatives before the melting temperature of either the orange or the yellow material is reached.

Significantly, once the transition wavefront has gone through the heated crystal, cooling the solid does not bring back the orange material because the alkyl chains do not have the opportunity to repack, and so the material stays yellow. On the other hand, adding organic solvent vapor allows the surface alkyl chains to reorder at room temperature, regenerating the orange material *only at the solid-air surface*. Once reorganized on the surface back to the orange structure, the reorganization is propagated through the entire solid in a functional, or possibly mechanistic, reverse of the process observed upon heating.

### 4.2.8 Additional Evidence for Colorimetric Switching Mechanism

One expected consequence of the proposed mechanism is that each layer reorganizes more or less independently. As the alkyl bilayer becomes more fluid, associations between molecules in different layers are lost. In other words, once alkyl chains are no longer interdigitated, the proposed mechanism would predict that lateral diffusion of dyads and realignment to give head-to-tail stacking can occur at different rates in adjacent layers. Close inspection using optical analysis of extremely thin crystals undergoing the orange-to-yellow transition indicated that indeed the lower layers, closer to the heated surface, transitioned to yellow first, apparently independently from layers farther from the heated surface, that soon followed.

Side chain packing is expected to be critical for propagating the transition through the height of the crystal (e.g. through dyad layers). Local melting of a single alkyl layer disrupts stabilizing interactions in the adjacent aromatic layer, likely resulting in melting of the alkyl layer on the other side of this aromatic layer. Propagation of this disruption of alkyl-aromatic-alkyl layers can thus be expected to enable the transition to proceed through dyad layers within

the crystal, in an analogous fashion to how cooperative transitions were previously described to propagate between columns.

The proposed mechanism would predict that the number of molecules in each layer would remain the same before and after the orange to yellow transition, but the morphology of each layer might change slightly as the molecules can diffuse laterally to some extent. Such minor changes in layer morphology, while maintaining overall layer volume, was indeed seen in the high-resolution AFM images of Figure 3.12. Further, similar densities of orange and yellow polymorphs support the small volume changes measured before and after heating (section 3.2.2.4).

Non-contact AFM of 7y\* thin films observed the presence of more curved lamellae compared to 70 (Figure 3.12) and WAXS characterization of 7y\* generated from a heating single 70 crystal observed diffractions from lamellae with variable orientations (Figure 3.17). The presence of more curved lamellae in 7y\* thin films is an expected consequence for exposed surface layers that are observed to have significant morphological changes following heating which likely influence transitions in other adjacent, surface layers not confined in three dimensions (Figure 3.12). As discussed previously (section 4.2.4), multiple nucleation sites for Y\* were observed to form at various crystal edges/defects, and seen to give rise to multiple different transition wavefronts within individual crystals (Figure 3.2). Thus, individual O to Y\* transition waves propagating from differently oriented Y\* nucleate lamellar growth with variable orientations, giving rise to variably orientated lamellae observed in non-contact AFM and WAXS experiments. The initiation of the transition in multiple individual locations provides a fitting explanation for why for why no single-crystal-to-single-crystal (SCSC) transition was observed. Further, it is known that SCSC transitions are often limited to small or nanocrystals<sup>69</sup> and are often composed of rigid molecules that lack flexible alkyl chain substituents.<sup>97, 99, 108, 110,</sup> 131, 136

Methyl dyad 1 was synthesized before our detailed transition model was developed. Upon prolonged heating, crystals of dyad 1 remain bright orange and do not undergo a thermally
induced phase transition prior to sublimation (284°C). In light of the proposed mechanism, this is as predicted. The methyl groups of **1** do not form a highly ordered, interdigitated alky chain bilayer (Figure 2.13), so there can be no triggering of a transition that would allow lateral motion of dyads in the solid state, as required in the other derivatives as the orange-to-yellow transition is triggered.

**Crystal Size Dependent Transitions.** In Chapter 3, the orange to yellow transition temperature was noted to have a dependence on size, where larger crystals transition at higher temperatures compared to smaller crystals (Figure 3.7). Physical size has been shown to influence the phase transition temperatures in a number of materials, most commonly nanomaterials including nanocrystals<sup>154, 155</sup> and nanorods,<sup>156</sup> and more recently in perovskites.<sup>157</sup> In these systems, a size dependence results from differences in surface energy and internal energy of each different crystal phase.<sup>156</sup> Fewer reports exist for size-dependent transitions in organic, small molecule systems, however size-dependent differences in the glass transition temperatures of polymer films have been reported.<sup>158</sup> The observation that larger crystals require more energy to transition, as measured by larger transition enthalpies, and the size-dependent variation in transition temperature supports the cooperative nature of the transition mechanism. On the other hand, it is possible that larger crystals, with a smaller surface area to volume ratio, had relatively fewer defects to nucleate growth of the new **Y**\* phase, and so kinetic effects cannot be definitively ruled out.

# 4.2.9 Asymmetric Dyad Materials

Asymmetric, head-to-head stacked **M10N8** (yellow-orange crystals) and **M8N6** (gold crystals) have the same preferred orientation features seen in symmetric dyad orange and yellow materials previously, with the long molecular axis being made of stacked aromatic dyad cores, and the height of crystals being made from alternating alkyl and aromatic sublayers (Figure 4.5). Both **M10N8** (yellow-orange) and **M8N6** (gold) have the structure of a molecular lasagna,

however, it deviates from the pristine molecular lasagnas of orange and yellow derivatives previously described. The formation of a hybrid alkyl and aromatic sublayer is better represented by an authentic lasagna, with intrusions between "noodle" and "meat/cheese/sauce" layers. On the molecular level, this intrusion manifests itself by the presence of alkyl and aromatic components within a defined region parallel to the substrate, highlighted in Figure 4.5.



Figure 4.5 Head-to-head stacked asymmetric **M10N8** (yellow-orange crystals) and **M8N6** (gold crystals) have preferred orientation with the same dimensional features orange and yellow crystals of symmetric dyads, but have a unique combination of interdigitated and segregated side chain packing that results in a hybrid alkyl and aromatic sublayer highlighted in beige.

Like orange crystals of symmetric dyads, asymmetric **M10N8** (yellow-orange) and **M8N6** (gold) are also seen to have a similar non-conventional C-H…O hydrogen bonds stabilizing adjacent columns, with an important difference resulting from adjacent columns being rotated roughly 90° about the short dyad molecular axis. In contrast to the hydrogen bonded

network in orange crystals that trace out a ~38° angle when viewed from above (Figure 4.2), the network of hydrogen bonds that link individual **M10N8** (yellow-orange) and **M8N6** (gold) dyads between adjacent columns trace out a line roughly perpendicular to the long axis of the crystal when viewed from above.

In an analogous manner, head-to-head stacked asymmetric dyads **M10N8** (yelloworange) and **M8N6** (gold) have the structural requirements believed to enable the head-to-head to head-to-tail polymorphic transition seen in orange crystals of symmetric dyads (Figure 4.3). Comparison of symmetric dyad orange (Figure 4.1) and yellow-orange **M10N8** (Figure 4.3) crystal structures shows the similar existence of separate alkyl and aromatic layers, and adjacent columns with inverted polarities, such that head-to-head to head-to-tail switching could occur with limited lateral movement of dyads into adjacent columns. The two most significant differences seen between symmetric dyad orange crystals and asymmetric **M10N8** (yelloworange) and **M8N6** (gold) is a different intercolumnar geometry, and the presence of a hybrid alkyl/aromatic layer previously noted to decrease the overall width of the alkyl layer in asymmetric derivatives. The difference in column geometry between head-to-head symmetric and asymmetric dyad crystals would still allow for the head-to-head to head-to-tail intralayer switching in asymmetric crystals, and would require a smaller extent of columnar reorganization, and analogous local melting of the asymmetric alkyl layers.

Single-crystal structures of **M8N6** (gold) and **M10N8** (yellow-orange) reveal head-tohead stacking geometries with a dominant short-axis offset (Figure 2.17). This short-axis offset is in contrast to the dominant long-axis offset seen in orange crystals of symmetric dyads, which was previously shown to result in significant orbital overlap. This overlap was shown to be the photophysical basis for the red shift seen in orange crystals in the solid-state (section 2.4.3) and noted to be sensitive to small changes in molecular slip. While no single-crystal structure was solved, indexing of the **M8N10** (orange-red) PXRD pattern revealed similar packing to **90**, and the similar orange-red color and observed red shift is consistent with head-to-head packing similar to in symmetric dyads that form orange crystals.

While the three aforementioned asymmetric derivatives had head-to-head stacking, only M8N10 (orange-red) was seen to go through a thermochromic orange-red-to-yellow color change upon heating, which is as predicted based on proposed packing. However, the transition was observed to move through crystals from initiation locations all over the crystal surface, with no discernable cooperative movements observed in the thermochromic transition, and wavefronts proceeding parallel to all crystal dimensions at similar rates (section 3.2.3). With similar packing to orange crystals, the polymorphic switching in M8N10 is expected to occur through the same mechanism as seen in orange crystals, with local melting of the alkyl layer followed by conformational switching from head-to-head to head-to-tail, resulting in the observed orange-toyellow color change. As discussed previously (section 2.3.3.3), it is likely that variation in M8N10 side chain packing prevents the formation of the hydrogen bonding network seen in orange crystals, yet, the side chains still pack and allow for local melting of the alkyl layer. Observed transitions that initiate and propagate with no observed cooperative transition behavior is believed reflect the absence of long-range hydrogen bonded network previously shown to give rise to the cooperative transitions in orange crystals, but could also reflect differences in alkyl layer dynamics caused by packing of asymmetric side chains. Taken together, the thermochromic transition in M8N10 (orange-red-to-yellow) follows the same nucleation and growth transition pathway observed in orange crystals, yet differences in side chain packing compared to orange crystals prevent a cooperative thermochromic transition in M8N10.

In contrast to **M8N10** (orange-red), the two other head-to-head packed asymmetric derivatives **M10N8** (yellow-orange) and **M8N6** (gold) had no clearly observable thermochromic transition prior to melting. Interestingly, despite having the same aromatic and side chain geometry, the same combination of interdigitated and segregated side chain packing, and the same hybrid alkyl/aromatic layer (Figure 4.3 & 2.17), only **M10N8** (yellow-orange) was seen to have two thermal transitions; **M8N6** (gold) melted directly to the isotropic phase when heated (Figure 3.19).

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Why then does M10N8 have a thermal phase transition prior to melting, while M8N6 (gold) directly melts to the isotropic phase when heated? M10N8 (yellow-orange) was observed to have a colorless transition prior to melting, optically similar to the progression of the thermal transition seen in M8N10 (orange-red), with no discernable cooperative movements accompanying the formation of numerous "pixelated" regions. Further, M10N8 (yellow-orange) was found to have the lowest transition enthalpy for all crystal-to-mesophase transitions measured, with a measured enthalpy of 16.2 kJ mol<sup>-1</sup> (Table 3.4), roughly half that of the next smallest crystal-to-mesophase transition measured (60, 32.2 kJ mol<sup>-1</sup>, Table 3.2). The smallest crystal-to-mesophase transition enthalpy measured in M10N8 (yellow-orange) may reflect weaker interactions between side chains that are already partially segregated, and/or may reflect the smaller structural reorganization that would accompany a crystal-to-mesophase transition following a similar mechanism seen in orange crystals, as columns in M10N8 are already parallel about the long axis (Figure 2.15). Both M10N8 (yellow-orange) and M8N6 (gold) are noted to have a hybrid alkyl/aromatic layer, previously noted to decrease the net overlap between alkyl chains from dyads adjacent layers (Figures 4.3 & 4.5). The major difference between the two results from the interactions between side chains of adjacent layers. The shorter side chains in M8N6 (gold) have less overlap between interdigitated side chains compared to longer side chains in M10N8 (yellow-orange). Thus, while both had similar head-to-head stacking, intercolumnar, and side chain orientations, there is a decrease in interactions between side chains of adjacent layers in M8N6 (gold) compared to M10N8 (yellow-orange).

The difference in behavior when **M10N8** (yellow-orange) and **M8N6** (gold) are heated is believed to reflect a critical requirement for side chain overlap between adjacent layers, where sufficient overlap is required to enable *local* melting between adjacent layers, thus allowing for polymorphic switching to occur. Direct melting of **M8N6** (gold) when heated can be attributed to a smaller overlap between side chains in adjacent layers that in turn prevents polymorphic switching to the corresponding mesophase at higher temperatures. During heating, thermal energy is thought to exceed the stabilizing interactions between **M8N6** (gold) side chains within individual alkyl layers, causing it to directly melt to the isotropic phase. In contrast, **M10N8** (yellow-orange) crystals, with a larger extent of side chain overlap tip the balance by having sufficient side chain overlap to allow for *local* melting of the alkyl layer, and thus enable conformational sampling and switching to a metastable head-to-tail mesophase at higher temperatures, without melting of the solid.

In contrast to the orthogonal relationship between dyad long axes in orange crystals, the orthogonal relationship about the dyad short axis in **M10N8** (yellow-orange) did not prevent a thermally induced crystal-to-mesophase transition. The colorless **M10N8** (yellow-orange) crystal-to-mesophase was observed to proceed by a nucleation and growth type mechanism without observed cooperative transition behavior or significant differences in transition rates along different crystalline axes. This observation, combined with previously discussed nucleation and growth transitions in **M8N10** (orange-red) further supports the role of side chain packing in enabling a cooperative transition.

Taken together, column orientation alone does not appear to dictate polymorphic switching behavior. In contrast, side chain packing appears to be the most critical factor in this stimuli-responsive transition, both enabling this dynamic process to occur, and also being critical for the emergence of observed cooperative transitions.

### **4.3 CONCLUSIONS**

**Symmetric Dyads.** In conclusion, symmetric dyad orange crystals adopt a lamellar, layered structure, alternating between a highly ordered, interdigitated alkyl chain layer and stacked aromatic dyad cores, with the stacks aligned along the long axis of the crystals. Upon heating, the transition initiates when the alkyl chain layers become disordered, allowing for some degree of lateral diffusion and conformational sampling for dyads at a crystal phase boundary and within their own layer. Moving to either adjacent stack in the same layer allows a dyad to exchange a head-to-head stacking geometry (orange form) for a head-to-tail stacking geometry

(yellow form). The transition often initiates as a nucleation and growth mechanism that can transform to a cooperative transition wavefront that propagates through the interior of the crystal. The fastest moving wavefronts have an approximately 38° angle with respect to the long axis of the crystal, corresponding to a C-H…O hydrogen bond network of dyad molecules in adjacent stacks of the orange crystals.

In all transitions, the driving force for the crystal-to-mesophase transition appears to be that at lower temperature, the more highly ordered head-to-head form is lower in energy due to maximized van der Waals contacts, while at higher temperature, less ordered head-to-tail packing with disordered side chains is lower in energy, dictated in part by the increased importance of entropy at higher temperature. Once formed, the disordered, head-to-tail form becomes kinetically trapped and will persist in the absence of solvent vapor. Remarkably, the crystal-to-mesophase transition is apparently triggered at a temperature that is very close to the temperature at which the head-to-head and head-to-tail forms exchange as the most stable form. Just as remarkably, the transition occurs at a temperature that is lower than the melting point of the original head-to-head, or final head-to-tail solid.

Asymmetric Dyads. In asymmetric dyads, crystals exhibiting head-to-head stacking geometry are observed to have both thermochromic and non-thermochromic crystal-to-mesophase, dependent on the initial dyad stacking geometry. In asymmetric dyads, transitions proceed exclusively through nucleation and growth pathways and are attributed to differences in side chain packing in asymmetric derivatives that prevent cooperative transitions seen in symmetric dyads. Side chain overlap between adjacent layers was shown to be the determinant factor for the emergence of polymorphic switching behavior in asymmetric dyads.

# **CHAPTER 5**

# Synthesis and Self-Assembly Properties of Symmetric and Asymmetric Perylene Diimides (PDIs) for Energy Conversion Applications

#### **5.1 CHAPTER SUMMARY**

# **5.1.1 Introduction**

Perylene diimides (PDIs) are widely used as dyes and pigments due to their electronic and structural properties: they strongly absorb light and have high photo and thermal stability. PDIs can also enable electronic energy conversion through spin allowed processes both in the solid-state and when interfaced with other materials (e.g. quantum dots). Theoretical calculations show that PDIs can be used for photon downconversion when certain slip stacking geometries are adopted. However, control over supramolecular assembly in PDI materials is not well understood. Deriving principles for the rational supramolecular assembly of PDI derivatives in the solid-state, with control over slip stacking geometry, is still a challenge despite a plethora of PDI crystal structures being reported. In addition, PDI derivatives have the potential to be useful for photon downconversion purposes, although synthetic challenges exist for making soluble PDI derivatives that can be interfaced with inorganic nanocrystals.

#### 5.1.2 Scientific Questions

This chapter seeks to answer: *How will varying substitutions on imide substituents* change solid-state packing of PDI derivatives? How will different regioisomeric substitution patterns affect solid-state PDI assemblies? Can solid-state packing of PDI derivatives be rationalized by modern aromatic interaction theory? Can general procedures allow for the synthesis and purification of asymmetric PDIs with variable carboxylic acid linkers?

# 5.1.3 Approach

In symmetric PDI derivatives, derivatives were synthesized using commercially available benzylic amines with different regioisomeric substitution patterns to explore the influence of substitution pattern and position on solid-state self-assembly of PDI derivatives. Crystals were grown and single crystal structures solved that allowed for structural evaluation. Asymmetric PDIs would be synthesized following established protocols, with a goal being to create general synthetic procedures for the synthesis of asymmetric PDIs with variable carboxylic acid linkers.

# 5.1.4 Results

Analysis of reported crystal structures provided insight on determinants of PDI selfassembly, and are in line with modern aromatic interaction theory. A strategy for the rational design of new PDI N-imide substituents allowing for access to new slip stacking geometries was developed following the analysis. Three new symmetric PDI derivatives were synthesized using regioisomers that allowed for evaluation of the design strategy, and single-crystal structures were solved. Regioisomeric substitutions were found to alter optical properties, where **2,6-difluoro-PDI** was found to form a red solid, and **3,5-difluoro-PDI** was found to form a black solid. Calculation of molecular slips verified the strategy as a means for accessing new symmetric PDIs for singlet fission materials. Characterization of symmetric PDIs is reported using low-resolution and high-resolution mass spectrometry, and reaction by-products and MS fragments are identified. Asymmetric PDIs were successfully synthesized and purified, and a generalizable purification procedure as well as strategies for working with notoriously insoluble PDIs is reported.

### **5.2 BACKGROUND**

#### 5.2.1 Structural Modifications and Self-Assembly of PDI Derivatives

Structurally similar to NDI, perylene-3,4,9,10-perylene tetracarboxylic acid diimides (PDIs) are a related diimide with a five-ring perylene core. The presence of a strongly polarizing diimides on the peri positions of the perylene core (Figure 5.1) allow for useful comparisons to be made between assemblies made from PDI and NDI derivatives. As such, many of the aromatic interactions discussed in chapter 1 will be useful for understanding and rationalizing the self-assembly and solid-state packing of PDI derivatives described in this chapter. Synthetic modifications of perylene diimides<sup>159-163</sup> can alter optical and energetic properties either through direct modifications of the perylene core that directly change energy of the frontier orbitals,<sup>164</sup> or through substitutions to the imide position<sup>121, 160</sup> that change how PDI derivatives pack in the solid-state<sup>165-167</sup> or self-assemble<sup>168-172</sup> in solution. Modifications to ortho<sup>164, 173, 174</sup> and bay<sup>175-177</sup> positions are well documented, with the latter known to cause twisting of PDI cores,<sup>178</sup> resulting in changes in optical and energy conversion properties.



Doesn't directly affect electronics of PDI Core

Figure 5.1 Positions where PDIs can be functionalized.<sup>159</sup>

Recent reports of bay substituted PDIs shows differences in self-assembly properties. In 2021, Shang and coworkers reported three different bay substituted PDI derivatives with different bay substitution patterns.<sup>179</sup> A single-crystal structure of a PDI derivative fluorinated on the 1- and 7-position of the perylene core are seen to pack in columns, and the strong C-F bond dipole (fluorine Pauling electronegativity is 4.0) is seen to either be localized behind an adjacent C-F bond, or position the fluorine atom above the imide carbonyl carbon. In both cases, the C-F bond can be thought of as contributing to the orientation of PDI self-assembly. Similar directing effects were shown with other polar, electron withdrawing groups. One derivative with a single cyano substitution on the bay position shows strong through space interactions between the electron withdrawing cyano group (group electronegativity of 3.3, scaled to be comparable to Pauling scale<sup>4</sup>) and the imide carbonyl carbon of the adjacent PDI core. A final derivative brominated on the 1- and 7-position of the perylene core are noted to have twisted aromatic cores, resulting from the steric clash between each bromine and the opposite bay hydrogen atom. This twisting clearly will affect both the energy of the frontier orbitals, as well as influence the

degree of wavefunction overlap that can exist between adjacent PDI cores when packed in the solid-state.

In 2020, Sharber and Thomas showed that regioisomeric changes to fluorinated benzene side chains (Figure 5.2) result in changes in self-assembly and gave rise to variations in optical and stimuli-responsive (mechanochromic) properties (Figure 9).<sup>180</sup> Importantly, simply by changing the fluorine substitution pattern on side chains between the three regioisomers shown in Figure 9, different solid-state packing was achieved and resulted in the observed differences in optical and stimuli-responsive properties.



Tetrafluoroinated Regioisomers

Figure 5.2 Regioisomeric substitution changes on tetrafluorinated benzene side chains enable differences in solid-state packing, resulting in different optical and stimuli-responsive that were attributed to the C-F and C-H bonds within the pendant side chains.<sup>180</sup>

#### **5.2.2 PDI for Energy Conversion Applications**

Singlet exciton fission is a photon down conversion process where a high energy excited state can be used to produce two separate, spin paired, electronically excited states. This process begins with the absorption of a photon by a molecule, resulting in the formation of an

electronically excited state. During this absorption process, spin is conserved, and thus the excitation results in a spin paired singlet excited state. Once excited, a number of different pathways are possible including fluorescence or radiationless internal conversion, where the excitation energy is lost as thermal energy.

In certain molecules, including polycyclic aromatics like tetracene<sup>181</sup> and pentacene,<sup>182</sup> the excited state energy can be efficiently transferred to adjacent molecules, and this process can favorable in the solid-state. Relaxation of the single spin-paired excited state can form two spin aligned triplet states when energy is conserved, namely when the triplet energies are half that of the singlet energy. Conservation of spin can be achieved when two molecules are involved, and thus this process can readily occur on faster time scales than could occur without flipping of spin, as in the case of intersystem crossing, typically a slow process in organic molecules.



Figure 5.3 The process for singlet fission can have both spin and energy conservation when two molecules are involved, and operate through successive electron and hole transfer. Reprinted with permission from Ref <sup>121</sup>. Copyright 2017 American Chemical Society.

Shown in Figure 5.3 is one of the postulated mechanisms showing how a two molecule, four electron system can create two spin aligned triplet excited states, following the excitation of one molecule to a spin paired, singlet excited state. The initial excitation on molecule "A" creates an electronically excited state when an electron is excited from the HOMO to the LUMO, with conservation of spin. This movement of the single electron creates a vacancy, or a 'hole' on

the HOMO of "A", and this electron and hole are then referred to as an exciton. The conservation of spin following the initial excitation is more specifically referred to as a singlet exciton. Transfer of the excited electron on "A" to the adjacent molecule "B" can create an ionic charge transfer state. This exciton is capable of migrating onto an adjacent molecule through an electron transfer process, when an electron is transferred from the HOMO of "B" to the LUMO of "A". The transfer of an electron with the opposite spin as the initially excited electron necessitates that this electron transferred must end up in a different orbital than the single electron in the HOMO of "A", as to not violate the Pauli exclusion principle. Energy can be conserved in this process when the initial excited state has double the energy of each triplet state. Thus, the generation of the two triplet excitons can form through processes that conserve energy and spin. Importantly, this process results in the creation of two different excited electronic states, yet only required a single electronic excitation.

Two major challenges for the application of this technology have proven to be the efficient absorption and production of triplet states and the efficient extraction of triplets once they are made. In 2013, Baldo and coworkers<sup>182</sup> showed that singlet fission in pentacene films could form solar cells with quantum efficiencies above 100%, showing that single photon absorption events can generate more than one charge carrier. While acenes are attractive because of their high charge-carrier mobility,<sup>183</sup> they are known to be more reactive with increasing the number of rings<sup>184</sup>, and are known to undergo [4+2] cycloadditions with oxygen<sup>185</sup> and this instability limits applications.

Perylene diimides (PDIs) appear to be valuable candidates for singlet fission applications.<sup>121, 186</sup> Since the 1950s, PDIs have found widespread use as dyes and pigments, especially in original automotive finishes,<sup>187</sup> in part because of their high thermal, oxidative, and photostable properties.<sup>172, 188</sup> Beyond being more chemically stable, PDI derivatives have larger molar absorption coefficients ( $\epsilon > 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ )<sup>121, 159, 174, 186</sup> compared to acene based organic dyes<sup>189, 190</sup> which could allow for the use of less material and the production of thinner films.

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In 2018, Roberts and coworkers<sup>121</sup> showed that the rate of singlet fission can be predicted based on Redfield theory calculations as a function of slip stacking geometry in a series of PDI derivatives. The strong dependence for singlet fission rate on slip stacking geometries of PDI films is shown in Figure 5.4. Changes in slip stacking geometry are known to change the excitonic structure of PDIs in the solid-state, as excitations are delocalized over multiple PDI molecules<sup>167</sup> where excited states are able to interact through short range orbital effects (e.g. HOMO-HOMO and LUMO-LUMO overlap), and longer range dipolar coupling mechanisms.<sup>141,</sup>



Figure 5.4 Singlet fission rate in PDI materials is seen to depend on the slip stacking geometry of adjacent dyads. Reprinted with permission from Ref. <sup>121</sup>. Copyright 2017 American Chemical Society.

Theoretical calculations predicted that expanding into new slip stacking geometries would enable more functional singlet fission materials when singlet fission rate is maximized while the rate of triplet decay is minimized, by for example changing the binding interaction of the spin correlated triplet pair. As tuning of the imide substituent has been shown to change the

solid-state packing of PDI derivatives,<sup>165, 166, 192</sup> PDI derivatives were sought that could expand into this unique slip-stacking space.

Photon upconversion is the functional the reverse process of singlet fission, the photon downconversion previously described. Typical organic molecules are not able to absorb light and generate an excited triplet state, as spin must be conserved, and the intersystem crossing that give rise to an excited triplet state is a slow process. As described previously, coupling of singlet excitons can give rise to triplet states, as in the case of PDIs in the solid state, with conservation of energy and spin.

Inorganic compounds are more effective at producing triplet states than many organics because of heavy atom effects that can induce strong spin-orbit coupling.<sup>193</sup> In this process, coupling of electron spin and orbital angular momentum enhances the rate of intersystem crossing, while conserving energy and angular momentum, and thus increases the rate of triplet formation.<sup>193, 194</sup>

It has also been shown that nanocrystal systems can sensitize (e.g., promote) the formation of triplet states. In some photon upconversion systems,<sup>190</sup> PbS nanocrystals have been shown to absorb lower energy photons (e.g. infrared), and generate excitons on nanocrystals. Following excitation, these nanocrystal systems can transfer multiple, lower energy triplets from nanocrystals to appended organic molecules (Figure 5.5) where lower energy excitons can be recombined, and result in the emission of a higher energy photon (e.g. visible).

Work by Roberts and coworkers<sup>190</sup> has characterized the triplet energy transfer to surface bound carboxylic acid functionalized TIPS-pentacene (6,13-bis-(triisopropylsilylethynyl)pentacene) ligands and showed the formation of intermediate triplet states localized on the nanocrystal surface, before being transferred to the acene derivative. This work highlighted the role the nanocrystal surface has in mediating energy transfer to appended ligands and the interactions between the nanocrystal and ligand as being influential for nanocrystal-based materials for photon upconversion purposes. For the same limitations

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previously highlighted in the acene family (e.g. stability) investigations into photon upconversion using PDI functionalized nanocrystals is a worthy endeavor.



Figure 5.5 Functionalization of nanocrystals with organic molecules (e.g. TIPS-pentacene) can allow for energy conversion where triplets formed on PbS nanocrystals can be transferred to pentacene derivatives and recombined. Reprinted with permission from Ref.<sup>190</sup> Copyright 2018 American Chemical Society.

# **5.3 RESULTS**

# 5.3.1 Literature Analysis of Symmetric PDI Crystal Packing

In order to rationally control the packing between PDI monomers in the solid-state to allow for maximal triplet exciton production while facilitating their extraction, an understanding of the non-covalent interactions that govern PDI packing is necessary. Following the established notion that substitution of the imide side chains<sup>195, 196</sup> and PDI core<sup>178, 197</sup> influences PDI packing, a survey of reported PDI crystal structures<sup>165, 166, 192</sup> was completed.

This search focused on PDI derivatives with various N-imide substituents, and without any core functionalization. Shown in Figure 5.6 is a plot of the slip stacking geometries seen in 23 reported PDI crystal structures, grouped based off of general characteristics side chain identity (e.g. aliphatic versus aromatic). Five of these crystal structures had two different slip stacking geometries, due to multiple packing orientations in the crystal, and both reported slip stacking geometries are shown in Figure 5.6.



Figure 5.6: Slip-stacking geometries for reported PDI crystal structures<sup>165, 166, 192</sup> shows the most variation in slip stacking comes from aromatic side chain-containing derivatives.

The largest variation in PDI slip stacking geometry is seen in derivatives with aromatic side chains, whereas many of aliphatic side chains display similar slip stacking geometries. Aliphatic chains with four or fewer carbons are seen to have a large variation in slip stacking.

Notably, there is clustering seen in longer aliphatic side chains possessing a  $\sim$ 3 Å long axis slip, and a shorter slip along the short axis (Figure 5.6 inset). The two aromatic derivatives seen with these stacking geometries have are pure hydrocarbons, being either a benzyl or m-xylenes side chain. It is worth pointing out that this  $\sim$ 3 Å long axis slip has a very similar geometry to that seen in the MAN-NI dyads described in chapters 2-4, which also contain an imide moiety. The outlier among aliphatic side chains has a long axis slip of 5.45Å and comes from a PDI with a branched sec-butyl side chain.



Figure 5.7 Reported PDI crystal structure with key intermolecular interactions shown.<sup>166</sup> a) PDI derivative with single-crystal structure shown in other panels. b) Distance between aromatic units of side-chain phenyl rings shown in green. c) Distance between H atoms and adjacent O atoms indicative of Hydrogen bonding that stabilize adjacent PDI columns. CCDC deposition number 1140280.

This survey identified the most relevant non-covalent interactions that should be manipulated in order to engineer new PDI derivatives that pack in predicted geometries. Analysis of published PDI crystal structures leads to the conclusion that aromatic side chains (Figure 5.6) and those capable of hydrogen bonding (Figure 5.7) allow for the greatest control over PDI packing morphologies in the solid-state. As shown in Figure 5.7, a methoxy benzyl side chain is seen to have aromatic interactions between adjacent benzyl side chains, and complementary hydrogen bonding between the methyl ethers.

#### 5.3.2 Design & Synthesis of Symmetric PDIs for Singlet Fission Purposes

As shown in Figure 5.7, the aromatic side chains play a role in PDI packing and in turn the slipped geometry adopted by the PDI cores. It is postulated that manipulation of the intermolecular interactions between aromatic side chains would influence the aromatic stacking geometry of the side chains, which would collectively influence the PDI cores stack relative to one another. In agreement with the aforementioned theory of aromatic interactions, we propose that substituting the 2,6 and/or 3,5 position of the phenyl ring with more electronegative halogen atoms should increase the strength of this side chain interaction, yet in different ways for different regioisomers. It is further proposed that changing the strength of side chain interactions would in turn change the geometries adopted by the PDI cores as the side chains intermolecular interactions vary. In addition, the size and electronegativity of the substituted atom (e.g., Cl vs. F) should also change the geometry adopted, as both steric and dipolar changes would result.

Aromatic N-imide substituents were previously shown to have the largest range in slip stacking geometries and thus were chosen to explore other PDI chemical space. Several additional criteria were added in order to simplify the process. Aniline based amines were avoided, as imide formation with anilines requires more forcing conditions and often producing lower yields. Further, aniline derived imides have an orthogonal relationship between the PDI cores and the aromatic rings of the aniline side chains, and coplanarity of these moieties is not seen due to the adjacent carbonyls. Benzyl amines and phenethyl amines would be explored, specifically those containing bonds that can direct the supramolecular assembly of PDIs, namely including strong bond dipoles in the form of fluorinated derivatives, and hydrogen bonding units like methoxy substituted derivatives. Further exploration of fluorinated derivatives would look at differences in assembly based on regioisomeric changes in fluorine substitution patterns (e.g. 2,6- versus 3,5-difluoro).

Guided by computational<sup>20, 27, 29-31</sup> and experimental<sup>34</sup> theory regarding aromatic interactions, PDI derivatives with benzyl sidechains were synthesized in one step following established synthetic protocols<sup>160</sup> using commercially available benzylic amines. Benzylic amines containing fluorines, chlorines, bromines, and methyl ethers were chosen based because of the strong influence they can exert on aromatic packing through hydrogen bonding and strong, through space dipolar interactions, as well as differences in steric size amongst the halogens. Each derivative was prepared on a 100 mg scale in a microwave reactor using the general procedure described in section 5.6.1. A general reaction scheme for symmetric PDI synthesis is shown below in Scheme 5.1.



Scheme 5.1 Example synthetic scheme for PDI synthesis, showing formation of the desired product and the undesired monoimide-monoanhydride by-product.

As symmetric PDI derivatives are sparingly soluble in organic solvents, purification of unreacted perylene dianhydride and the monoimide-monoanhydride adduct was achieved by stirring the crude reaction product in 10% KOH (aq.). Unreported results showed that anhydrides were saponified in these conditions within seconds at room temperature. However, due to the insoluble nature of PDI derivatives, samples were stirred for 2-12 hours and frequently agitated in order to try and saponify all unreacted anhydride. Filtration of the desired product and washing with copious amounts of water removed carboxylate byproducts, affording the final products as solids with colors ranging from black to red. Shown in the bottom of Figure 5.8, filtering of crude products for the **3,5-difluoro-PDI** yielded a red solid, while **2,6-difluoro-PDI** yielded a black solid.



Figure 5.8 Crystal growth of indicated PDI derivatives shows variations in 1- and 2dimensional growth with various N-substituted benzylamine side-chains. Crystals shown grown from slow cooling of a saturated nitrobenzene solution. Bottom: different difluorobenzylamine regioisomers are seen to give rise to different optical properties as solids following purification.

# 5.3.3 PDI Single-Crystal Growth and Single-Crystal X-ray Diffraction Structures

Growth of PDI crystals was attempted using vapor diffusion, sublimation, and slow cooling of concentrated PDI solutions. The only solvent that yielded X-ray quality PDI symmetric crystals came from slow cooling of PDI derivatives dissolved in hot nitrobenzene, insulated to allow for slow cooling over periods of 24-48 hours, and crystals formed from this method are shown in the top of Figure 5.8.

High-quality single-crystals suitable for X-ray diffraction analysis were obtained using a recently reported microspace in-air sublimation method.<sup>198</sup> In this method, crystals sublime at atmospheric pressure when heated on a hotplate at 350°C for periods of 1-5 days and are grown on a cleaned glass substrate ~100-200 µm above the sample. Only fluorinated PDI derivatives grew high quality single crystals by sublimation, and all fluorinated crystals were noted to be the largest crystals obtained and had the most structural integrity compared to other derivatives. Methoxy, and brominated derivatives sublimed but deposited as amorphous aggregates. Chlorinated derivatives were seen to grow 2-dimensional crystals, although the slightest manipulation resulted in bending of the crystal, after which time no diffraction could be observed.

Single crystal structures three different difluorinated PDI derivatives were obtained. A summary of crystallographic information for the three structures are provided in Table 5.1, and additional crystallographic information can be found in the Appendix. Interestingly, the three different crystals were found to have different space groups.

	PDI Crystal Structures		
	2,6-difluoro-PDI	3,5-difluoro-PDI	3,4-difluoro-PDI
a (Å)	4.89	28.58	6.73
b (Å)	29.95	4.38	7.69
c (Å)	9.24	22.10	13.51
a (deg)	90	90	80.06
β (deg)	105.04	103.684	85.94
γ (deg)	90	90	73.35
Volume [Å <sup>3</sup> ]	1,306	2,684	659
Space Group	P 1 2 <sub>1</sub> / <i>n</i> 1	C 1 2/c 1	P -1
Chemical Formula	$C_{38}H_{18}F_4N_2O_4\\$	$C_{38}H_{18}F_4N_2O_4\\$	$C_{38}H_{18}F_4N_2O_4\\$
MW [g mol <sup>-1</sup> ]	642.54	642.54	642.54
Density [g cm <sup>-3</sup> ]	1.634	1.590	1.619
Z	2	4	1
R (reflections) [%]	7.53	5.71	8.82
wR2 (reflections) [%]	22.05	15.22	24.23
Multiple Side Chain Occupancy	N/A	N/A	One benzyl ring has two site occupancies for all atoms bound to and in the ring; occupancy distribution 69:31

 Table 5.1
 Summary of crystallographic parameters for PDI single-crystal structures.

Calculation of slip stacking geometries for the three solved crystal structures shows a wide range of crystal slip stacking geometries that are achieved by the fluorinated side chain derivatives. Plotting of these slip stacking geometries alongside previous slip stacking geometry is shown in Figure 5.9, with abbreviations for each of the three structures inset. In order to make sense of the wide distribution seen in these three regioisomeric PDI derivatives, a closer inspection of each crystal structure is required.



Figure 5.9 Calculated slip stacking geometries of the three solved PDI crystal structures alongside previously shown slip stacking geometries (Figure 5.6).

Shown in Figure 5.10 are each of crystal structure shown as the single molecule making up the asymmetric unit. An angle can be defined that can describe the rotation seen in the benzylic side chain, where the angle is made from the intersection of the long axis of the PDI with a line that goes through the 2 and 6 carbons of each benzylic ring when viewed from above the PDI (shown in the top view of Figure 5.10). A similar angle is seen in benzylic side chains of the 2,6 and 3,5-difluoro derivatives, with a slightly larger torsion in the 2,6-derivative. The larger torsion in the 2,6 derivative may be due to an interesting electrostatic interaction between the fluorine and the carbonyl carbon, having a short measured distance of 3.099 Å. In comparison, the angle between the benzyl ring and the PDI long axis in the 3,4 derivative is ca. 90°. In order to understand the difference in these side chain orientations, packing must be taken into consideration.



Figure 5.10 Single-crystal structure of the three different PDI derivatives shows variable orientations of difluorobenzyl sidechains, with similarity seen in 2,6-difluoro-PDI and 3,5-difluoro-PDI. Multiple side chain occupancies shown in. Crystal structures shown as displacement ellipsoids set to the 50% probability level. Hydrogen atoms are omitted for clarity in some images. Note larger thermal ellipsoids in **3,5-difluoro-PDI** are a result of the 5.0.1 beamline set up at the ALS (Lawrence Berkeley National Laboratory) where the data was collected by Dr. Vince Lynch, and can be attributed to limitations to the detector distance that limit resolution capabilities.

Shown in Figure 5.11 are trimers for each of the crystal structures based on packing of adjacent side chains. The 5.69 Å long axis slip in the 3,4 derivative is clearly visible and results from the interdigitation of benzyl rings from adjacent PDI columns. The 3,4 derivative was seen to have a side chain in two site occupancies (details in Table 5.1) that can be seen in Figure 5.10, with slight rotational differences between the two conformations visible. The larger angle previously referenced in the 2,6 derivative is seen to result in the longer long axis slip (3.42 Å), compared to the 3,5 derivative (1.38 Å) and is attributed to the 2,6-difluoro substituents relative to the aromatic PDI cores, as well as interactions between adjacent side chains.



Figure 5.11 Single-crystal structures of trimers shown in space filling mode show how the different column morphologies that result across the three derivatives. Bottom: PDI derivatives stack in columns, view looking down sets of columns shows diversity of packing in various PDI derivatives.

Also shown in Figure 5.11 is the perspective when looking down on packed unit cells of each derivative. As expected for flat aromatic molecules, the PDI cores stack in columns, and the long axis of the crystals they form (Figure 5.8) is likely to be from this strong aromatic stacking interaction. It is interesting to note the different columnar orientations observed for each of the three derivatives.

## 5.3.4 Design and Synthesis of Asymmetric PDIs

A desire to covalently tether PDIs to lead-sulfide nanocrystal exists as described previously. In order to append PDIs to nanocrystals, a PDI should contain a carboxylic acid that can bind to the quantum dot surface. While symmetric, dicarboxylic acid PDI derivatives (e.g. Nsubstituted glycine on each side of the PDI) would be suitable for this purpose, their extremely poor solubility in organic solvents limits their efficacy, as they require dissolution to engage in a ligand exchange and bind to the nanocrystal surface.

While synthetic modifications can be made at the ortho and bay positions of PDIs, (see Figure 5.1) these substitutions are well known to influence the electronic properties of PDI cores. The synthesis of asymmetric PDIs has been reported for various purposes<sup>199</sup> including the study of interfacial electron transfer<sup>200</sup> and the self-assembly of PDI nanobelts.<sup>201</sup> Commonly in asymmetric PDI derivatives where solubility is desirable, "swallowtails"<sup>199</sup> are introduced that enhance solubility, enabling chromatographic separation as well as the solution based exchange of carboxylic acid functionalized PDI derivatives onto surfaces, including ITO (tin-doped indium oxide).<sup>200</sup>

Experimental protocols and characterizations for all asymmetric PDI derivatives can be found in section 5.6.2. Briefly, dihexyl amine was accessed in excellent yield from the reductive amination of dihexylketone, and used directly to make **PDI-Symmetric-Greasy**. Desymmetrization of the **PDI-Symmetric-Greasy** in KOH afforded the monoimide-monoanhydride (**MIMA**) that was reacted with each amino acid to afford the asymmetric PDI derivatives.

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Scheme 5.2 Synthetic scheme for the synthesis of asymmetric PDI derivatives.

#### **5.4 DISCUSSION**

# 5.4.1 Self-Assembly and Solid-State Packing of Symmetric PDI Derivatives

In the analysis of reported PDI crystal structures previously discussed, clustering of aliphatic PDI derivatives was shown (Figure 5.6) and is taken to reflect a small determinant influence of aliphatic side chain packing on PDI slip stacking geometry. In line with modern interaction theory introduced in chapter 1,<sup>20, 27, 29-31, 33</sup> the clustering can be rationalized as having slip stacking geometry determined simply by the polarized PDI carbonyl bonds. Since these aliphatic side chains do not have strong dipoles present, they have little influence on packing geometries adopted by aromatic PDI cores, and as such, all aliphatic PDI derivatives are driven to assemble in the same general slip stacking geometry. This is further supported by previous observations of other imide containing molecules with comparable ~3 Å long axis slips, detailed in chapter 2 (see Figure 2.19), and said to be the result of imide determinant self-stacking.

Fluorinated benzyl amine side chains yielded single crystal structures and were noted to be the easiest to grow and easy to characterize. Short packing distances between side chains and differences in crystal structure match expectations based on the assumption that strong bond dipoles will determine aromatic stacking geometry.

Shown in Figure 5.12 are calculated ESPs for the different difluorobenzyl amines used as the side chains in the three PDI crystal structures. As expected, the fluorine atoms are seen to create strong C-F bond dipoles, and nearby C-H bond dipoles are shown to have complementary electrostatic potentials. It is interesting to note the change in electrostatic potential of the benzylic methylene unit in between the two fluorines of 2,6 difluorobenzyl amine derivative, compared to the other derivatives.



Figure 5.12 Calculated ESPs for different benzyl amines show strong C-F and C-H dipoles (ωB97X-D, 6-311+G\*\*).

Analysis of these difluorobenzyl side chains can lead to predictions about how various side chains will pack when appended to PDI cores. Shown in Figure 5.13 is a perspective view of the **2,6-difluoro-PDI** crystal structure, with all short contacts measured, and categorized either based on the interaction type or the interaction geometry. As would be expected, the various C-H bond dipoles of the difluorobenzyl amine side chain make contacts to regions of high electron density, namely the carbonyl oxygen of adjacent PDI cores. On the other hand, fluorines are seen to make bidentate edge-to-face contacts with hydrogen atoms on the bay position of the PDI core, as well as having an interesting dipole interaction that aligns C-F dipoles opposite to one another in a face-to-face geometry (see 3.10Å contact in Figure 5.13).



Figure 5.13 Single-crystal structure of **2,6-difluoro-PDI** with intermolecular contacts showing all the short contacts to a single 2,6-difluorobenzylamine side chain in the solid-state. Contacts are classified as either the interaction geometry or the type of interaction.

A similar analysis for the **3,5-difluoro-PDI** derivative is shown in Figure 5.14, and while different individual contacts are observed, the same types of contacts are seen: C-H bonds interacting with imide carbonyl oxygens and fluorine atoms, and C-F bonds interacting with C-H bonds of other fluorinated side chains, as well as PDI hydrogens of the PDI core in a bidentate fashion.



Figure 5.14 Single-crystal structure of **3,5-difluoro-PDI** showing close contacts to one difluorobenzyl ring making contacts to adjacent C-H bonds of PDI cores, difluorobenzyl rings, as well as contacts from C-F and carbonyl C-O bonds.

An analysis of ESPs of the three different PDIs is shown in Figure 5.15 in order to make sense of the repeated observations of fluorine atoms interacting with hydrogens in the bay positions of PDI cores. Similar to ESPs calculated for naphthalimides shown in chapter 1 and 2, the strongly polarizing carbonyls are seen to compliment the positive electrostatic potential seen on the aromatic hydrogen atoms of the PDI core. It is interesting to note that the polarized bonds appear to be the carbonyls, and the C-H bonds of the PDI core, as oppose to the C-F bonds of the side chains. While the C-F bonds may not be as strong of bond dipoles compared to imide C-O bonds, they clearly are able to have a dramatic effect on the self-assembly of PDI derivatives in the solid-state, and warrant further investigations as a tool for manipulating the self-assembly and energy conversion properties seen in PDIs.



Figure 5.15 Calculated ESPs for the three indicated PDI derivates using conformations found in single-crystal structures reveal similarities in electrostatics of PDI cores, and significant differences in electrostatic potentials of the various side chains based off of fluorine substitution position.

# 5.4.2 Synthesis of Asymmetric PDI Derivatives

Notably, the introduction of "swallowtails" on PDI imide positions has helps improve the poor solubility seen in symmetric PDI derivatives. This is expected and in agreement with literature reports, where branching of the side chain is known to help prevent coplanar, face-to-face aggregation of PDI derivatives, due to the out of plane packing from the branched "swallowtails" (Scheme 5.2).<sup>159, 172</sup> Different synthetic routes have been reported for accessing asymmetric PDI derivatives,<sup>159</sup> yet the formation of the symmetric **PDI-Symmetric-Greasy** prior to desymmeterization was found to result in the easiest chromatographic purifications.

As such, asymmetric PDIs were synthesized following the method outlined in Scheme 5.2, and chromatographic separations after each step allowed for access to a pure final asymmetric PDI. While the dihexylamine helped improve solubility of PDI derivatives, the large aromatic core still hinders solubility and can result in incomplete chromatographic purification. Dry loading of crude reaction mixtures was observed to greatly improve the efficacy and ease of chromatographic separations. Column chromatography using a series of mobile phase gradients, detailed in section 5.6.2, were found to allow for effective separations of various byproducts in the final step, and allow access to pure asymmetric PDI products. Noteworthy, gradients of DCM with increasing polarity from the addition of acetone helped to slowly elute by products, yet not move the desired PDI starting material. PDIs were effectively mobilized with acetic acid, likely through hydrogen bonding to the carbonyls. The same use of acetic acid and DCM mixtures is also noted to effectively dissolve PDI derivatives and intermediates, allowing for easy removal from filter papers. To make working with derivatives easier, intermediates and final PDI products were freeze dried (lyophilized) from benzene, following previous reports.<sup>202</sup>

### 5.4.3 Characterization of PDI Derivatives

Poor solubility for symmetric benzylic side chain derivatives precluded characterization using NMR spectroscopy, and as such, the majority of the products were characterized using mass spectrometry (MS). Initial characterization and synthetic procedure optimization utilized Fourier-transform infrared spectroscopy (FTIR). Using FTIR, the starting material and product could be easily visualized from quick FTIR spectral analysis of the crude sample in the solid-state. Differentiation of the starting anhydride and the final imide product was seen based on changes to the carbonyl C=O stretching frequency,<sup>160, 203</sup> with the starting anhydride carbonyl having strong peaks at 1766 and 1730 cm<sup>-1</sup> while the final diimide product had observed peaks at 1690 and 1655 cm<sup>-1</sup> with no prominent peaks observed above 1700 cm<sup>-1</sup>.

A number of undesired masses were seen in low-resolution MS experiments, many of which are exemplified in Figure 5.16. The spectrum shown is that of the symmetrically substituted 3,5-difluoro-PDI, and the parent mass is observed as [M]<sup>-</sup> at 642 m/z. The other prominent peaks in the spectrum are attributed to fragments from the desired symmetrically substituted PDI product, the undesired monoimide-monoanhydride by-product, and interestingly, nucleophilic aromatic substitutions seen between fluorinated benzylic amine side chains. These structures of ions that are believed to give rise to several of these peaks are shown in Figure 5.17.


Figure 5.16 Low-resolution mass spectra for example PDI derivative (3,5-difluoro) shows the parent ion as [M]<sup>-</sup> at 642 m/z. Peaks at 405 and 517 are believed to result from fragmentation and 266 is believed to be a byproduct of side-chain reactions.



Figure 5.17 Potential structures that give rise to ions shown in Figure 5.16.

Fragmentation between the imide and the benzene ring, either the  $C_{Aromatic}$ - $C_{Benzylic}$  or  $C_{Benzylic}$ - $N_{Imide}$  bond is possible in chemical ionization (CI) methods, and would generate two different ions separated by 12 mass units. Interestingly, a feature seen during synthesis of fluorinated PDI derivatives was a prominent ion at 266 m/z with certain side chains. In the reaction conditions for PDI formation (165°C, 1 hr, base), nucleophilic aromatic substitution of one benzylic amine on another is a reasonable mechanism for the formation of the 266 m/z by product. This putative species is not removed during the standard aqueous workup procedure, but could be removed with acidic washing.

One final note on interpretation of PDI mass spectrum: the monoimide-monoanhydride byproduct and the fragmentation of the desired PDI product on the  $C_{Benzylic}-N_{Imide}$  bond are separated by a single mass unit. Note in Figure 5.18 the inclusion of a larger peak at 517 and a smaller at 516 m/z. The peak at 517 m/z correspond to the monoimide-monoanhydride byproduct with no <sup>13</sup>C atoms, while the peak at 518 corresponds to the byproduct with one <sup>13</sup>C atom. The peak at 516 is not from this byproduct; this peak is attributed to fragmentation of the desired PDI product along the  $C_{Benzylic}-N_{Imide}$  bond, initially forming the resonance stabilized benzylic fragment.



Figure 5.18 Low-resolution mass spectrum of 2,6-difluoro PDI following workup.

### **5.5 CONCLUSIONS**

An analysis of known PDI crystal structures revealed that, in line with modern aromatic interaction theory, N-substituted PDI crystals with aliphatic side chains that lack strong dipoles self-assemble with little variation in stacking geometry. As predicted by this theory, aromatic stacking geometry in these derivatives is determined by the interaction of strong dipoles, namely the imide C-O and C-H bond dipoles, and these interactions result in the consistent geometry observed across aliphatic side chain containing derivatives. Further along these lines, aromatic interactions were seen to influence the aromatic stacking geometry in the same analysis of reported structures. Thus, a design strategy for accessing new PDI slip stacking modes was put forth in line with modern aromatic theory. PDI slip stacking geometry was confirmed to be tightly influenced by aromatic interactions, and regioisomeric substitutions were found to allow access to a wide variety of slip stacking modes previously not observed. Taken together, this work showed that strong dipoles in aromatic side chains can be used as a design strategy for the self-assembly of PDIs for energy conversion purposes. Work in asymmetric PDI synthesis was successful, and two different asymmetric derivatives with varying carboxylic acid linkers were achieved, and a general synthetic and purification strategy to access these might allow structure activity relationships investigating the role of side chain length on PDI-nanocrystal assemblies for photon upconversion purposes to be carried out.

### **5.6 EXPERIMENTAL**

### 5.6.1 Symmetric PDI Synthesis

### **General Reaction For Symmetric PDI Derivatives:**

Adapted from ref. <sup>160</sup>. To a 10mL microwave tube with a stir-bar is added 100 mg (0.25 mmol) of perylene-3,4,9,10-tetracarboxylic dianhydride (PDA), 4 equivalents (1 mmol) of the benzylic amine, 5 mL DMF, and 50  $\mu$ L of triethylamine (TEA). The bright red microwave tube is then

briefly stirred and sonicated for 5 minutes to aid in dissolution of starting material. The reaction is then heated in a microwave reactor ( $T_{Max} = 165^{\circ}C$ , Power = 80W, Duration = 60 min, high stirring) until the protocol is finished, at which time the microwave vial was cooled prior to removal and noted to be significantly darker in color. The microwave vial is then emptied into an Erlenmeyer flask, and the microwave tube is rinsed with DMF (2 x 1 mL) and 10% aq. KOH (3 x 1 mL). An additional 50 mL of 10% aq. KOH is added to the reaction mixture and is stirred for 2 -12 hours at room temperature. The reaction mixture was then filtered and washed abundantly with water until the filtrate was colorless and the filtrate reached pH 7. The solid-product was then dried under vacuum to yield the corresponding symmetric perylene-3,4,9,10-tetracarboxylic diimide (PDI).

2,9-bis(2,6-difluorobenzyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone **(2,6-difluoro-PDI)**: HRMS (CI, Positive) Calc. for  $C_{38}H_{18}N_2O_4 F_4 [M^+]$  642.1203, found 642.1207.

2,9-bis(3,5-difluorobenzyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone **(3,5-difluoro-PDI)**: HRMS (CI, Positive) Calc. for  $C_{38}H_{18}N_2O_4$  F<sub>4</sub> [M<sup>+</sup>] 642.1203, found 642.1185.

2,9-bis(3,4-difluorobenzyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone **(3,4-difluoro-PDI)**: HRMS (CI, Negative) Calc. for  $C_{38}H_{18}N_2O_4$  F [M<sup>-</sup>] 642.1203, found 642.1201.

### 5.6.2 Asymmetric PDI Synthesis

**Tridecan-7-amine (dihexylamine)**: Adapted from Ref. <sup>200</sup> To an oven dried RBF with a stir bar is added tridecan-7-one (10.00 g, 50.42 mmol), ammonium acetate (38.88 g, 504 mmol) and NaBH<sub>3</sub>CN (2.20 g, 35.7 mmol) and was dissolved in dried methanol (108 mL). The reaction was monitored by GCMS, and upon completion after 24 hours, the reaction was quenched by the 10% aq. KOH to pH 12. The reaction mixture was then extracted with DCM (50 mL x 4). Organic fractions were then combined and washed with brine (100 mL x 2), dried with Na<sub>2</sub>SO<sub>4</sub>,

and reduced under vacuum to afford **tridecan-7-amine** as a clear oil (9.59 g, 48.1 mmol, 95.4% yield) that was used without further purification. Note: Caution must be taken when dealing with cyanide containing mixtures. Oxidation of the sodium cyanide salt in the aqueous layer following the reaction was done in an ice-cooled bath by the slow addition of bleach, following standard protocols.<sup>204</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.65 (dt, *J* = 7.3, 3.6 Hz, 1H), 1.39 – 1.20 (m, 20H), 1.08 (s, 2H), 0.87 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  51.36, 38.36, 32.02, 29.64, 26.29, 22.77, 14.21. HRMS (ESI, positive): Calc. for C<sub>13</sub>H<sub>29</sub>N [M+H]<sup>+</sup> 200.2373, found 200.2368.

### 2,9-di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone

(PDI-Symmetric-Greasy): Procedure adapted from Ref. <sup>200</sup>. In an oven dried 250 mL RBF with a stir bar is added perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) (1.12 g, 2.85 mmol), tridecan-7-amine (1.42 g, 7.13 mmol), and imidazole (4.86 g, 71.3 mmol). The solids reaction mixture was stirred and heated to 180°C for 4 hours. The reaction was then allowed to cool to room temperature. Then 30 mL of ethanol was added to the reaction mixture, which was then transferred to an Erlenmeyer flask, and the RBF was washed out with IPA (~10 mL) and H<sub>2</sub>O (~10 mL) to help remove all the product. To this flask was then added 125 mL 2M H<sub>2</sub>SO<sub>4</sub>. The reaction mixture was then stirred overnight at room temperature. The next day, the solid crude product was filtered and rinsed with H<sub>2</sub>O (~500 mL) and dried under vacuum. The crude material was then loaded onto silica using DCM, reduced, and dried under vacuum. The crude material adsorbed onto silica was then purified via column chromatography (2:1 (v/v) DCM:hexanes) and concentrated under vacuum to yield PDI-Symmetric-Greasy as a dark red oily solid (1.54 g, 2.04 mmol, 71.6% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.74 – 8.58 (m, 8H), 5.19 (tt, J = 9.2, 5.8 Hz, 2H), 2.25 (dtd, J = 14.1, 9.7, 4.8 Hz, 4H), 1.91 – 1.80 (m, 4H), 1.39 – 1.16 (m, 33H), 0.82 (t, J = 6.8 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  134.69, 132.06, 131.30, 129.77, 126.63, 123.19, 54.92, 32.53, 31.91, 29.37, 27.08, 22.73, 14.19. HRMS (CI, negative): Calc. for C<sub>50</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>-</sup> 754.4710, found 754.4733.

9-(tridecan-7-yl)-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)tetraone (MIMA, monoimide-monoanhydride): Adapted from Ref. <sup>202</sup>. To a 230 mL 3-neck RBF with a stir bar was added 2,9-di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (PDI-Symmetric-Greasy) (1.03 g, 1.37 mmol), freshly ground KOH (0.383 g, 6.83 mmol, 5 equiv.), and t-BuOH (35 mL). The mixture was stirred and heated to reflux, and monitored via TLC. Disappearance of the starting PDI material was observed after 1.75 hours, at which time the reaction mixture was cooled and poured into a stirring flask containing 35 mL AcOH and 15 mL 2M HCl, which continued to stir for 1 hour following the addition. The mixture was then filtered and the solid was washed with copious amounts of water until the filtrate was colorless and pH 7 then the crude solid was dried under vacuum. The crude material was loaded onto silica using 10:1 DCM:AcOH (v/v), concentrated, and dried under vacuum. The crude material adsorbed onto silica was then purified via column chromatography (10:1 (v/v) DCM:AcOH) and concentrated under vacuum to yield MIMA as a red solid (397 mg 0.692 mmol, 50.6% yield). To aid in future reactions, MIMA was freeze dried from benzene with 1% AcOH to yield MIMA as a fluffy dark red powder. <sup>1</sup>H NMR (400 MHz, cdcl<sub>3</sub>)  $\delta$  8.77 – 8.64 (m, 8H), 5.18 (tt, J = 9.4, 5.8 Hz, 1H), 2.24 (dtd, J = 14.0, 9.7, 4.8 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.34 - 1.20 (m, 16H), 0.82 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.15, 136.62, 133.75, 132.08, 129.69, 127.03, 126.76, 124.09, 123.33, 119.23, 55.08, 32.51, 31.90, 29.34, 27.07, 22.72, 14.18. (HRMS (CI, Negative) Calc. for C<sub>37</sub>H<sub>35</sub>N<sub>2</sub>O<sub>5</sub> 573.2515, found 573.2528.

### 3-(1,3,8,10-tetraoxo-9-(tridecan-7-yl)-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-

*d'e'f'*]diisoquinolin-2(1*H*)-yl)propanoic acid (PDI-Beta-Alanine): To a 10 mL microwave tube with a stir-bar is added MIMA (12.9 mg, 0.0224 mmol), beta-Alanine (8.01 mg, 0.0899 mmol, 4 equivalents), 1.5 mL DMF, and 25  $\mu$ L of triethylamine (TEA). The microwave tube is then sonicated briefly. The reaction is then heated in a microwave reactor (T<sub>Max</sub> = 165°C, Power

= 80 W, Duration = 60 min) until the protocol is finished and the microwave tube is then allowed to cool. The microwave tube is then emptied into an Erlenmeyer flask, and rinsed with DMF (2 x 0.5mL) and 10% aq. KOH (2 x 1 mL). An additional 30 mL of 10% aq. KOH is added to the reaction mixture and is stirred for 2 hours at room temperature. The mixture was then acidified using 1M HCl to pH 1. The solid product was then filtered and washed with water (100 mL) and dried under vacuum. The crude product was then extracted off the dried filter paper by shaking the paper in a vial of 5 mL of 95/5 (v/v) DCM/acetic acid for 5 minutes. The isolated crude product was then reduced and dried under vacuum. Purification of the crude product by column chromatography was achieved using gradients to remove unwanted products starting with 100% DCM. Mobile phase gradients were then run as follows: 100/0/0 to 80/20/0 (v/v) of DCM/acetone/acetic acid, a return to 100% DCM, then a slow increase from 100/0/0 to 95/0/5 DCM/acetone/acetic acid, and finally a slow increase in acetone from 95/0/5 to 90/5/5 DCM/acetone/acetic acid to elute the entire product band. Product fractions were combined, reduced, and dried under vacuum. The final product was then freeze-dried from benzene to yield the **PDI-Beta-Alanine** product as a dark-red fluffy solid (9.3 mg, 0.014 mmol, 64%). HRMS (ESI, negative): Calc. for  $C_{40}H_{40}N_2O_6$  [M]<sup>+</sup> 643.2814, found 643.2820.

### 6-(1,3,8,10-tetraoxo-9-(tridecan-7-yl)-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-

*d'e'f'*]diisoquinolin-2(1*H*)-yl)hexanoic acid (PDI-Hexanoic Acid): To a 10 mL microwave tube with a stir-bar is added MIMA (10.0 mg, 0.0174 mmol), 6-aminohexanoic acid (9.15 mg, 0.0697 mmol, 4 equivalents), 1.5 mL DMF, and 25  $\mu$ L of triethylamine (TEA). The microwave tube is then sonicated briefly. The reaction is then heated in a microwave reactor (T<sub>Max</sub> = 165°C, Power = 80 W, Duration = 60 min) until the protocol is finished and the microwave tube is then allowed to cool. The microwave tube is then emptied into an Erlenmeyer flask, and rinsed with DMF (2 x 0.5mL) and 10% aq. KOH (2 x 1 mL). An additional 30 mL of 10% aq. KOH is added to the reaction mixture, which is stirred for 2 hours at room temperature. The mixture was then

acidified using 1M HCl to pH 1. The solid product was then filtered and washed with water (100 mL) and dried under vacuum. The crude product was then extracted off the dried filter paper by shaking the paper in a vial of 5 mL of 95/5 (v/v) DCM/acetic acid for 5 minutes. The isolated crude product was then reduced and dried under vacuum. Purification of the crude product by column chromatography was achieved using gradients to remove unwanted products starting with 100% DCM. Mobile phase gradients were then run as follows: 100/0/0 to 80/20/0 (v/v) of DCM/acetone/acetic acid, a return to 100% DCM, then a slow increase from 100/0/0 to 95/0/5 DCM/acetone/acetic acid, and finally a slow increase in acetone from 95/0/5 to 90/5/5 DCM/acetone/acetic acid to elute the entire product band. Product fractions were combined, reduced, and dried under vacuum. The final product was then freeze-dried from benzene to yield the **PDI-Hexanoic Acid** product as a dark-red fluffy solid (7.5 mg, 0.0109 mmol, 62.8%). HRMS (ESI, negative): Calc. for  $C_{43}H_{46}N_2O_6$  [M]<sup>+</sup> 686.3361, found 686.3341.

# APPENDIX

# Single-Crystal X-ray Diffraction Data

Single-Crystal X-ray Diffraction information for Dyads 6y, 6y', 7y, 7y', 8y, 1bo, 6o, 7o, 8o, 9o, 10o, 12o, M6N8, M8N6, M10N8, and for PDI derivatives PDI-26F, PDI-34F, PDI-35F.

### **CRYSTALLOGRAPHIC INFORMATION FOR 6**Y

Crystallographic Material for **6**Y (**6**y).

X-ray Experimental.

Table 6Y.1. Crystallographic Data for 6Y.

Table **6Y.2**. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **6Y**.

Table 6Y.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 6Y.

Table 6Y.4. Anisotropic thermal parameters for the non-hydrogen atoms of 6Y.

Table **6Y.5**. Fractional coordinates and isotropic thermal parameters ( $Å^2$ ) for the hydrogen atoms of **6Y**.

Table **6Y.6**. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **6Y**.

X-ray Experimental for complex  $C_{36}H_{37}NO_3$  (**6Y**): Crystals grew as long, yellow needles by slow evaporation from 1:1:1 Toluene:MeOH:EtOAc in a vial with the cap resting on top. The data crystal was cut from a much longer crystal and had approximate dimensions; 0.26 x 0.06 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1032 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 15 seconds per frame with a detector offset of +/- 40.8° and 46 seconds per frame with a detector offset of +/- 108.3°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.' The structure was solved by direct methods using SuperFlip<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.' Structure analysis was

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aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

There are two molecules in the asymmetric unit. A portion of the n-hexyl side chain on one molecule was disordered about two primary conformations. The disorder was modeled by assigning the variable x to the site occupancy of one of the components and (1-x) to the alternate component of the disorder. A common isotropic displacement parameter was refined while refining x. The geometry of the two components was restrained to be equivalent throughout the refinement process.

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.0767*P)^2 + (0.4225*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.161, with R(F) equal to 0.0546 and a goodness of fit, S, = 0.991. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

# <u>References</u>

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  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
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Empirical formula	C36 H37 N O3	
Formula weight	531.66	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.7840(5)  Å	α= 88.389(4)°.
	b = 13.4586(7) Å	β= 87.333(4)°.
	c = 24.0283(12)  Å	$\gamma = 81.921(4)^{\circ}$ .
Volume	2808.7(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.257 Mg/m <sup>3</sup>	
Absorption coefficient	0.619 mm <sup>-1</sup>	
F(000)	1136	
Crystal size	$0.260 \text{ x} 0.060 \text{ x} 0.030 \text{ mm}^3$	
Theta range for data collection	3.317 to 74.321°.	
Index ranges	-10<=h<=10, -16<=k<=13, -20	)<=1<=29
Reflections collected	16816	
Independent reflections	10845 [R(int) = 0.0292]	
Completeness to theta = $67.684^{\circ}$	98.7 %	
Absorption correction	Semi-empirical from equivaler	nts
Max. and min. transmission	1.00 and 0.804	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	10845 / 3 / 755	
Goodness-of-fit on F <sup>2</sup>	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1381	
R indices (all data)	R1 = 0.0855, wR2 = 0.1611	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.372 and -0.238 e.Å <sup>-3</sup>	

Table 6Y.1 Crystal data and structure refinement for 6Y.

	X	у	Z	U(eq)
 N1	6021(2)	4759(1)	7638(1)	20(1)
01	3488(2)	4749(1)	7481(1)	29(1)
O2	8540(2)	4806(1)	7800(1)	27(1)
O3	10086(2)	7626(1)	2528(1)	21(1)
C1	4755(2)	4884(2)	7298(1)	20(1)
C2	5061(2)	5166(1)	6706(1)	18(1)
C3	6549(2)	5341(1)	6514(1)	16(1)
C4	7778(2)	5232(1)	6882(1)	17(1)
C5	7514(2)	4919(1)	7469(1)	20(1)
C6	3873(2)	5249(1)	6347(1)	19(1)
C7	4130(2)	5510(1)	5785(1)	20(1)
C8	5558(2)	5704(1)	5589(1)	18(1)
C9	6803(2)	5622(1)	5947(1)	17(1)
C10	8319(2)	5806(1)	5764(1)	18(1)
C11	9491(2)	5683(1)	6135(1)	18(1)
C12	9227(2)	5403(1)	6694(1)	20(1)
C13	8618(2)	6115(1)	5199(1)	19(1)
C14	8869(2)	6394(1)	4730(1)	18(1)
C15	9175(2)	6706(1)	4166(1)	18(1)
C16	8028(2)	6803(1)	3790(1)	18(1)
C17	8284(2)	7091(1)	3228(1)	19(1)
C18	9714(2)	7308(1)	3050(1)	17(1)
C19	10950(2)	7216(1)	3423(1)	16(1)
C20	12437(2)	7412(1)	3240(1)	19(1)
C21	13621(2)	7305(1)	3599(1)	20(1)
C22	13360(2)	7019(1)	4159(1)	20(1)
C23	11929(2)	6821(1)	4348(1)	19(1)
C24	10686(2)	6909(1)	3984(1)	16(1)
C25	5796(2)	4438(2)	8226(1)	24(1)
C26	6295(2)	3316(2)	8315(1)	22(1)
C27	5169(2)	2657(2)	8110(1)	24(1)

Table **6Y.2**. Atomic coordinates (  $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **6Y.** U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C28	5721(2)	1529(2)	8158(1)	25(1)
C29	5985(2)	1129(2)	8752(1)	25(1)
C30	6322(3)	-17(2)	8772(1)	30(1)
C31	8931(2)	7715(2)	2118(1)	21(1)
C32	9660(2)	8108(2)	1588(1)	23(1)
C33	8495(2)	8466(2)	1151(1)	24(1)
C34	9278(3)	8796(2)	610(1)	29(1)
C35	8151(3)	9275(2)	180(1)	31(1)
C36	7380(3)	10330(2)	324(1)	36(1)
N2	8951(2)	10554(1)	2300(1)	22(1)
O4	11444(2)	10628(1)	2481(1)	29(1)
O5	6455(2)	10464(1)	2115(1)	26(1)
O6	4989(2)	7448(1)	7356(1)	23(1)
C37	10196(2)	10402(2)	2643(1)	21(1)
C38	9921(2)	9984(1)	3213(1)	19(1)
C39	8438(2)	9768(1)	3385(1)	17(1)
C40	7224(2)	9916(1)	3016(1)	18(1)
C41	7473(2)	10325(2)	2444(1)	21(1)
C42	11109(2)	9856(1)	3572(1)	20(1)
C43	10852(2)	9521(2)	4124(1)	21(1)
C44	9422(2)	9310(1)	4303(1)	21(1)
C45	8182(2)	9424(1)	3941(1)	18(1)
C46	6665(2)	9228(1)	4111(1)	18(1)
C47	5504(2)	9374(1)	3736(1)	20(1)
C48	5776(2)	9713(1)	3187(1)	20(1)
C49	6353(2)	8890(1)	4667(1)	20(1)
C50	6099(2)	8618(1)	5137(1)	20(1)
C51	5813(2)	8313(1)	5702(1)	19(1)
C52	6983(2)	8225(1)	6070(1)	19(1)
C53	6757(2)	7952(1)	6634(1)	21(1)
C54	5332(2)	7734(1)	6822(1)	19(1)
C55	4076(2)	7806(1)	6459(1)	18(1)
C56	2604(2)	7600(1)	6652(1)	21(1)
C57	1403(2)	7696(2)	6301(1)	22(1)
C58	1634(2)	7987(2)	5739(1)	22(1)
C59	3056(2)	8191(1)	5541(1)	22(1)

C60	4309(2)	8107(1)	5895(1)	18(1)
C61	9167(2)	11061(2)	1754(1)	25(1)
C62	8973(2)	12199(2)	1813(1)	25(1)
C63	9076(2)	12759(2)	1255(1)	26(1)
C64	9010(3)	13891(2)	1333(1)	31(1)
C65	9178(4)	14481(2)	790(1)	51(1)
C66	9275(6)	15588(2)	900(1)	94(2)
C67	6116(2)	7500(2)	7763(1)	22(1)
C68	5385(2)	7272(2)	8325(1)	25(1)
C69	6551(3)	7148(2)	8777(1)	34(1)
C70	5592(8)	6876(6)	9329(2)	32(1)
C71	6638(6)	6557(4)	9803(2)	37(1)
C72	5702(8)	6469(5)	10352(2)	47(2)
C70A	6004(8)	7209(4)	9380(3)	33(1)
C71A	5269(6)	6280(4)	9545(2)	40(1)
C72A	4587(8)	6320(5)	10142(2)	55(2)

N1-C1	1.400(3)	C18-C19	1.429(3)
N1-C5	1.399(2)	C19-C20	1.416(3)
N1-C25	1.477(2)	C19-C24	1.418(3)
O1-C1	1.214(2)	C20-C21	1.371(3)
O2-C5	1.221(3)	C20-H20	0.95
O3-C18	1.356(2)	C21-C22	1.407(3)
O3-C31	1.438(2)	C21-H21	0.95
C1-C2	1.484(3)	C22-C23	1.375(3)
C2-C6	1.376(3)	C22-H22	0.95
C2-C3	1.414(3)	C23-C24	1.419(3)
C3-C4	1.416(3)	С23-Н23	0.95
C3-C9	1.421(3)	C25-C26	1.525(3)
C4-C12	1.379(3)	C25-H25A	0.99
C4-C5	1.477(3)	C25-H25B	0.99
C6-C7	1.401(3)	C26-C27	1.525(3)
С6-Н6	0.95	C26-H26A	0.99
C7-C8	1.376(3)	C26-H26B	0.99
С7-Н7	0.95	C27-C28	1.530(3)
C8-C9	1.412(3)	C27-H27A	0.99
С8-Н8	0.95	С27-Н27В	0.99
C9-C10	1.435(3)	C28-C29	1.526(3)
C10-C11	1.383(3)	C28-H28A	0.99
C10-C13	1.430(3)	C28-H28B	0.99
C11-C12	1.402(3)	C29-C30	1.530(3)
C11-H11	0.95	С29-Н29А	0.99
С12-Н12	0.95	C29-H29B	0.99
C13-C14	1.200(3)	C30-H30A	0.98
C14-C15	1.432(3)	C30-H30B	0.98
C15-C16	1.374(3)	C30-H30C	0.98
C15-C24	1.438(2)	C31-C32	1.514(3)
C16-C17	1.411(3)	C31-H31A	0.99
C16-H16	0.95	C31-H31B	0.99
C17-C18	1.376(3)	C32-C33	1.522(3)
C17-H17	0.95	C32-H32A	0.99

Table 6Y.3. Bond lengths [Å] and angles  $[\circ]$  for 6Y.

С32-Н32В	0.99	C47-C48	1.403(3)
C33-C34	1.527(3)	С47-Н47	0.95
С33-Н33А	0.99	C48-H48	0.95
С33-Н33В	0.99	C49-C50	1.197(3)
C34-C35	1.529(3)	C50-C51	1.429(3)
C34-H34A	0.99	C51-C52	1.378(3)
C34-H34B	0.99	C51-C60	1.441(3)
C35-C36	1.526(3)	C52-C53	1.406(3)
С35-Н35А	0.99	С52-Н52	0.95
С35-Н35В	0.99	C53-C54	1.378(3)
С36-Н36А	0.98	С53-Н53	0.95
С36-Н36В	0.98	C54-C55	1.429(3)
С36-Н36С	0.98	C55-C56	1.415(3)
N2-C37	1.389(3)	C55-C60	1.417(3)
N2-C41	1.401(2)	C56-C57	1.371(3)
N2-C61	1.479(2)	С56-Н56	0.95
O4-C37	1.222(2)	C57-C58	1.409(3)
O5-C41	1.213(3)	С57-Н57	0.95
O6-C54	1.361(2)	C58-C59	1.377(3)
O6-C67	1.434(2)	С58-Н58	0.95
C37-C38	1.487(3)	C59-C60	1.412(3)
C38-C42	1.373(3)	С59-Н59	0.95
C38-C39	1.415(3)	C61-C62	1.526(3)
C39-C40	1.407(3)	C61-H61A	0.99
C39-C45	1.421(3)	C61-H61B	0.99
C40-C48	1.380(3)	C62-C63	1.525(3)
C40-C41	1.484(3)	С62-Н62А	0.99
C42-C43	1.409(3)	С62-Н62В	0.99
С42-Н42	0.95	C63-C64	1.533(3)
C43-C44	1.373(3)	С63-Н63А	0.99
С43-Н43	0.95	С63-Н63В	0.99
C44-C45	1.414(3)	C64-C65	1.520(3)
C44-H44	0.95	C64-H64A	0.99
C45-C46	1.433(3)	C64-H64B	0.99
C46-C47	1.382(3)	C65-C66	1.536(4)
C46-C49	1.426(3)	C65-H65A	0.99

С65-Н65В	0.99	С70-Н70А	0.99
С66-Н66А	0.98	С70-Н70В	0.99
С66-Н66В	0.98	C71-C72	1.534(6)
С66-Н66С	0.98	C71-H71A	0.99
C67-C68	1.511(3)	C71-H71B	0.99
С67-Н67А	0.99	C72-H72A	0.98
С67-Н67В	0.99	C72-H72B	0.98
C68-C69	1.517(3)	C72-H72C	0.98
C68-H68A	0.99	C70A-C71A	1.520(6)
C68-H68B	0.99	C70A-H70C	0.99
C69-C70A	1.506(7)	C70A-H70D	0.99
C69-C70	1.598(7)	C71A-C72A	1.527(6)
С69-Н69С	0.96	C71A-H71C	0.99
C69-H69D	0.96	C71A-H71D	0.99
С69-Н69А	0.96	C72A-H72D	0.98
С69-Н69В	0.96	C72A-H72E	0.98
C70-C71	1.512(6)	C72A-H72F	0.98
C1-N1-C5	125 12(16)	N1-C5-C4	117 35(17)
C1-N1-C25	118 79(16)	C2-C6-C7	119.97(18)
C5-N1-C25	116.09(16)	С2-С6-Н6	120.0
C18-O3-C31	118 45(14)	С7-С6-Н6	120.0
01-C1-N1	120 93(18)	C8-C7-C6	120.63(18)
01-C1-C2	122.61(19)	С8-С7-Н7	119.7
N1-C1-C2	116.45(16)	С6-С7-Н7	119.7
C6-C2-C3	120.70(17)	C7-C8-C9	120.74(17)
C6-C2-C1	118.76(17)	С7-С8-Н8	119.6
C3-C2-C1	120.53(18)	С9-С8-Н8	119.6
C2-C3-C4	120.52(17)	C8-C9-C3	118.68(17)
C2-C3-C9	119.26(18)	C8-C9-C10	123.06(17)
C4-C3-C9	120.22(17)	C3-C9-C10	118.26(17)
C12-C4-C3	120.28(17)	C11-C10-C13	120.07(17)
C12-C4-C5	119.76(18)	C11-C10-C9	119.75(17)
C3-C4-C5	119.95(17)	C13-C10-C9	120.19(18)
O2-C5-N1	120.34(17)	C10-C11-C12	121.40(17)
O2-C5-C4	122.32(18)	C10-C11-H11	119.3

C12-C11-H11	119.3	119.3 N1-C25-C26	
C4-C12-C11	120.07(18)	120.07(18) N1-C25-H25A	
C4-C12-H12	120.0	C26-C25-H25A	109.2
С11-С12-Н12	120.0	N1-C25-H25B	109.2
C14-C13-C10	178.7(2)	С26-С25-Н25В	109.2
C13-C14-C15	178.9(2)	H25A-C25-H25B	107.9
C16-C15-C14	120.14(17)	C25-C26-C27	114.13(17)
C16-C15-C24	119.31(17)	С25-С26-Н26А	108.7
C14-C15-C24	120.54(17)	С27-С26-Н26А	108.7
C15-C16-C17	122.11(17)	С25-С26-Н26В	108.7
С15-С16-Н16	118.9	С27-С26-Н26В	108.7
С17-С16-Н16	118.9	H26A-C26-H26B	107.6
C18-C17-C16	119.35(18)	C26-C27-C28	114.32(17)
С18-С17-Н17	120.3	С26-С27-Н27А	108.7
С16-С17-Н17	120.3	С28-С27-Н27А	108.7
O3-C18-C17	124.87(17)	С26-С27-Н27В	108.7
O3-C18-C19	114.32(16)	С28-С27-Н27В	108.7
C17-C18-C19	120.80(17)	H27A-C27-H27B	107.6
C20-C19-C24	119.45(18)	C29-C28-C27	114.83(18)
C20-C19-C18	121.23(17)	C29-C28-H28A	108.6
C24-C19-C18	119.31(17)	C27-C28-H28A	108.6
C21-C20-C19	120.76(17)	C29-C28-H28B	108.6
С21-С20-Н20	119.6	C27-C28-H28B	108.6
С19-С20-Н20	119.6	H28A-C28-H28B	107.5
C20-C21-C22	120.09(17)	C28-C29-C30	111.45(18)
C20-C21-H21	120.0	С28-С29-Н29А	109.3
C22-C21-H21	120.0	С30-С29-Н29А	109.3
C23-C22-C21	120.39(18)	С28-С29-Н29В	109.3
С23-С22-Н22	119.8	С30-С29-Н29В	109.3
C21-C22-H22	119.8	H29A-C29-H29B	108.0
C22-C23-C24	120.88(17)	С29-С30-Н30А	109.5
С22-С23-Н23	119.6	С29-С30-Н30В	109.5
С24-С23-Н23	119.6	H30A-C30-H30B	109.5
C19-C24-C23	118.42(17)	С29-С30-Н30С	109.5
C19-C24-C15	119.09(17)	H30A-C30-H30C	109.5
C23-C24-C15	122.49(17)	H30B-C30-H30C	109.5

O3-C31-C32	106.37(15)	C37-N2-C41	125.22(16)
O3-C31-H31A	110.5	C37-N2-C61	117.55(16)
C32-C31-H31A	110.5	C41-N2-C61	117.10(17)
O3-C31-H31B	110.5	C54-O6-C67	117.76(15)
C32-C31-H31B	110.5	O4-C37-N2	120.55(18)
H31A-C31-H31B	108.6	O4-C37-C38	122.40(19)
C31-C32-C33	112.99(16)	N2-C37-C38	117.03(16)
C31-C32-H32A	109.0	C42-C38-C39	121.13(18)
C33-C32-H32A	109.0	C42-C38-C37	118.82(17)
С31-С32-Н32В	109.0	C39-C38-C37	119.98(18)
С33-С32-Н32В	109.0	C40-C39-C38	120.65(17)
H32A-C32-H32B	107.8	C40-C39-C45	120.37(17)
C32-C33-C34	111.61(17)	C38-C39-C45	118.95(18)
С32-С33-Н33А	109.3	C48-C40-C39	120.43(18)
С34-С33-Н33А	109.3	C48-C40-C41	119.19(18)
С32-С33-Н33В	109.3	C39-C40-C41	120.34(17)
С34-С33-Н33В	109.3	O5-C41-N2	120.99(18)
H33A-C33-H33B	108.0	O5-C41-C40	122.27(18)
C33-C34-C35	113.70(18)	N2-C41-C40	116.73(17)
C33-C34-H34A	108.8	C38-C42-C43	119.91(18)
C35-C34-H34A	108.8	С38-С42-Н42	120.0
C33-C34-H34B	108.8	С43-С42-Н42	120.0
C35-C34-H34B	108.8	C44-C43-C42	120.17(19)
H34A-C34-H34B	107.7	С44-С43-Н43	119.9
C36-C35-C34	114.1(2)	С42-С43-Н43	119.9
С36-С35-Н35А	108.7	C43-C44-C45	121.19(18)
C34-C35-H35A	108.7	C43-C44-H44	119.4
С36-С35-Н35В	108.7	C45-C44-H44	119.4
С34-С35-Н35В	108.7	C44-C45-C39	118.64(17)
H35A-C35-H35B	107.6	C44-C45-C46	123.18(18)
С35-С36-Н36А	109.5	C39-C45-C46	118.17(18)
С35-С36-Н36В	109.5	C47-C46-C49	120.15(18)
H36A-C36-H36B	109.5	C47-C46-C45	119.82(18)
С35-С36-Н36С	109.5	C49-C46-C45	120.03(18)
H36A-C36-H36C	109.5	C46-C47-C48	121.34(17)
H36B-C36-H36C	109.5	С46-С47-Н47	119.3

С48-С47-Н47	119.3	N2-C61-C62	111.00(17)
C40-C48-C47	119.86(18)	N2-C61-H61A	109.4
C40-C48-H48	120.1	C62-C61-H61A	109.4
C47-C48-H48	120.1	N2-C61-H61B	109.4
C50-C49-C46	179.1(2)	С62-С61-Н61В	109.4
C49-C50-C51	178.6(2)	H61A-C61-H61B	108.0
C52-C51-C50	119.74(17)	C63-C62-C61	112.94(17)
C52-C51-C60	119.34(17)	С63-С62-Н62А	109.0
C50-C51-C60	120.92(18)	C61-C62-H62A	109.0
C51-C52-C53	122.15(17)	С63-С62-Н62В	109.0
С51-С52-Н52	118.9	C61-C62-H62B	109.0
С53-С52-Н52	118.9	H62A-C62-H62B	107.8
C54-C53-C52	119.15(18)	C62-C63-C64	111.46(18)
С54-С53-Н53	120.4	С62-С63-Н63А	109.3
С52-С53-Н53	120.4	С64-С63-Н63А	109.3
O6-C54-C53	124.22(18)	С62-С63-Н63В	109.3
O6-C54-C55	114.56(16)	С64-С63-Н63В	109.3
C53-C54-C55	121.22(17)	H63A-C63-H63B	108.0
C56-C55-C60	119.44(18)	C65-C64-C63	113.6(2)
C56-C55-C54	121.49(18)	С65-С64-Н64А	108.8
C60-C55-C54	119.06(17)	С63-С64-Н64А	108.8
C57-C56-C55	120.73(19)	С65-С64-Н64В	108.8
С57-С56-Н56	119.6	С63-С64-Н64В	108.8
С55-С56-Н56	119.6	H64A-C64-H64B	107.7
C56-C57-C58	119.95(18)	C64-C65-C66	111.1(2)
С56-С57-Н57	120.0	С64-С65-Н65А	109.4
С58-С57-Н57	120.0	С66-С65-Н65А	109.4
C59-C58-C57	120.39(19)	С64-С65-Н65В	109.4
С59-С58-Н58	119.8	С66-С65-Н65В	109.4
С57-С58-Н58	119.8	H65A-C65-H65B	108.0
C58-C59-C60	120.81(19)	С65-С66-Н66А	109.5
С58-С59-Н59	119.6	С65-С66-Н66В	109.5
С60-С59-Н59	119.6	H66A-C66-H66B	109.5
C59-C60-C55	118.68(17)	С65-С66-Н66С	109.5
C59-C60-C51	122.28(18)	H66A-C66-H66C	109.5
C55-C60-C51	119.04(18)	H66B-C66-H66C	109.5

O6-C67-C68	107.28(16)	H70A-C70-H70B	108.0
O6-C67-H67A	110.3	C70-C71-C72	110.9(5)
С68-С67-Н67А	110.3	С70-С71-Н71А	109.5
О6-С67-Н67В	110.3	С72-С71-Н71А	109.5
С68-С67-Н67В	110.3	С70-С71-Н71В	109.5
H67A-C67-H67B	108.5	С72-С71-Н71В	109.5
C67-C68-C69	111.74(18)	H71A-C71-H71B	108.1
C67-C68-H68A	109.3	С71-С72-Н72А	109.5
C69-C68-H68A	109.3	С71-С72-Н72В	109.5
C67-C68-H68B	109.3	H72A-C72-H72B	109.5
C69-C68-H68B	109.3	С71-С72-Н72С	109.5
H68A-C68-H68B	107.9	H72A-C72-H72C	109.5
C70A-C69-C68	119.7(3)	H72B-C72-H72C	109.5
C68-C69-C70	104.5(3)	C69-C70A-C71A	109.3(4)
С70А-С69-Н69С	107.0	С69-С70А-Н70С	109.8
С68-С69-Н69С	107.3	С71А-С70А-Н70С	109.8
C70A-C69-H69D	107.5	C69-C70A-H70D	109.8
C68-C69-H69D	107.6	C71A-C70A-H70D	109.8
C70-C69-H69D	98.4	H70C-C70A-H70D	108.3
H69C-C69-H69D	107.1	C70A-C71A-C72A	112.4(5)
С68-С69-Н69А	110.7	C70A-C71A-H71C	109.1
С70-С69-Н69А	111.4	C72A-C71A-H71C	109.1
С70А-С69-Н69В	115.3	C70A-C71A-H71D	109.1
С68-С69-Н69В	110.8	C72A-C71A-H71D	109.1
С70-С69-Н69В	110.4	H71C-C71A-H71D	107.9
H69A-C69-H69B	109.0	C71A-C72A-H72D	109.5
C71-C70-C69	111.4(5)	С71А-С72А-Н72Е	109.5
С71-С70-Н70А	109.4	H72D-C72A-H72E	109.5
С69-С70-Н70А	109.4	C71A-C72A-H72F	109.5
С71-С70-Н70В	109.4	H72D-C72A-H72F	109.5
С69-С70-Н70В	109.4	H72E-C72A-H72F	109.5

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
 N1	20(1)	23(1)	16(1)	4(1)	2(1)	-4(1)
01	18(1)	39(1)	28(1)	10(1)	6(1)	-6(1)
O2	24(1)	37(1)	23(1)	8(1)	-5(1)	-12(1)
O3	18(1)	31(1)	15(1)	8(1)	-2(1)	-6(1)
C1	18(1)	21(1)	22(1)	3(1)	2(1)	-3(1)
C2	18(1)	16(1)	20(1)	2(1)	2(1)	-2(1)
C3	17(1)	13(1)	19(1)	2(1)	0(1)	-4(1)
C4	20(1)	15(1)	17(1)	3(1)	1(1)	-4(1)
C5	20(1)	19(1)	21(1)	2(1)	-1(1)	-6(1)
C6	15(1)	17(1)	25(1)	2(1)	2(1)	-3(1)
C7	18(1)	19(1)	24(1)	1(1)	-4(1)	-2(1)
C8	20(1)	17(1)	18(1)	2(1)	0(1)	-2(1)
C9	18(1)	12(1)	20(1)	2(1)	1(1)	-2(1)
C10	20(1)	15(1)	18(1)	3(1)	3(1)	-3(1)
C11	15(1)	18(1)	23(1)	4(1)	3(1)	-5(1)
C12	17(1)	19(1)	24(1)	3(1)	-3(1)	-4(1)
C13	16(1)	18(1)	23(1)	3(1)	1(1)	-3(1)
C14	15(1)	18(1)	21(1)	3(1)	2(1)	-4(1)
C15	19(1)	14(1)	19(1)	2(1)	3(1)	-4(1)
C16	16(1)	17(1)	22(1)	3(1)	3(1)	-4(1)
C17	17(1)	21(1)	20(1)	4(1)	-3(1)	-3(1)
C18	19(1)	17(1)	16(1)	3(1)	-1(1)	-3(1)
C19	17(1)	13(1)	18(1)	2(1)	0(1)	-3(1)
C20	19(1)	17(1)	21(1)	4(1)	2(1)	-3(1)
C21	14(1)	20(1)	25(1)	3(1)	1(1)	-5(1)
C22	18(1)	18(1)	24(1)	1(1)	-4(1)	-1(1)
C23	22(1)	17(1)	18(1)	2(1)	1(1)	-3(1)
C24	17(1)	13(1)	19(1)	2(1)	0(1)	-2(1)
C25	26(1)	30(1)	16(1)	6(1)	3(1)	-6(1)
C26	19(1)	28(1)	20(1)	7(1)	0(1)	-5(1)
C27	20(1)	29(1)	24(1)	8(1)	-1(1)	-6(1)

Table **6Y.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **6Y**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C28	23(1)	29(1)	22(1)	5(1)	-2(1)	-7(1)
C29	23(1)	29(1)	23(1)	7(1)	-2(1)	-6(1)
C30	29(1)	31(1)	29(1)	8(1)	-5(1)	-4(1)
C31	20(1)	26(1)	17(1)	4(1)	-4(1)	-4(1)
C32	18(1)	32(1)	20(1)	6(1)	-2(1)	-4(1)
C33	22(1)	31(1)	19(1)	7(1)	-1(1)	-5(1)
C34	25(1)	38(1)	22(1)	10(1)	0(1)	-5(1)
C35	34(1)	38(1)	20(1)	10(1)	-4(1)	-5(1)
C36	37(1)	40(1)	28(1)	11(1)	-3(1)	-1(1)
N2	21(1)	25(1)	21(1)	3(1)	1(1)	-7(1)
O4	20(1)	40(1)	28(1)	6(1)	4(1)	-12(1)
05	24(1)	31(1)	24(1)	8(1)	-6(1)	-8(1)
O6	21(1)	30(1)	18(1)	4(1)	-2(1)	-9(1)
C37	20(1)	22(1)	21(1)	1(1)	1(1)	-7(1)
C38	19(1)	17(1)	20(1)	1(1)	1(1)	-4(1)
C39	18(1)	14(1)	21(1)	1(1)	0(1)	-3(1)
C40	19(1)	14(1)	23(1)	2(1)	0(1)	-3(1)
C41	20(1)	20(1)	23(1)	2(1)	-1(1)	-4(1)
C42	15(1)	19(1)	27(1)	-1(1)	0(1)	-4(1)
C43	20(1)	21(1)	23(1)	2(1)	-4(1)	-2(1)
C44	22(1)	19(1)	23(1)	2(1)	-2(1)	-2(1)
C45	20(1)	13(1)	22(1)	1(1)	0(1)	-2(1)
C46	19(1)	14(1)	22(1)	2(1)	1(1)	-2(1)
C47	16(1)	17(1)	26(1)	3(1)	0(1)	-5(1)
C48	18(1)	17(1)	26(1)	1(1)	-5(1)	-4(1)
C49	16(1)	19(1)	26(1)	2(1)	0(1)	-4(1)
C50	18(1)	17(1)	24(1)	2(1)	0(1)	-4(1)
C51	20(1)	16(1)	21(1)	1(1)	2(1)	-3(1)
C52	15(1)	19(1)	24(1)	1(1)	3(1)	-4(1)
C53	18(1)	21(1)	23(1)	2(1)	-3(1)	-4(1)
C54	21(1)	17(1)	18(1)	0(1)	0(1)	-4(1)
C55	18(1)	15(1)	22(1)	-2(1)	2(1)	-2(1)
C56	21(1)	18(1)	24(1)	-1(1)	4(1)	-4(1)
C57	17(1)	20(1)	32(1)	-4(1)	2(1)	-5(1)
C58	17(1)	19(1)	30(1)	-2(1)	-5(1)	-2(1)
C59	22(1)	18(1)	24(1)	1(1)	-1(1)	-1(1)

C60	18(1)	13(1)	22(1)	0(1)	0(1)	-2(1)
C61	24(1)	30(1)	21(1)	6(1)	1(1)	-7(1)
C62	24(1)	28(1)	22(1)	4(1)	1(1)	-6(1)
C63	24(1)	29(1)	23(1)	6(1)	-1(1)	-5(1)
C64	34(1)	30(1)	29(1)	6(1)	1(1)	-6(1)
C65	90(2)	31(1)	32(1)	11(1)	-5(1)	-11(1)
C66	206(5)	30(2)	45(2)	15(1)	4(3)	-25(2)
C67	19(1)	26(1)	21(1)	3(1)	-1(1)	-4(1)
C68	25(1)	28(1)	21(1)	5(1)	1(1)	-4(1)
C69	35(1)	40(1)	23(1)	3(1)	-3(1)	7(1)
C70	31(4)	42(4)	20(3)	-1(3)	1(2)	1(3)
C71	40(3)	47(3)	24(2)	0(2)	-2(2)	-7(2)
C72	69(4)	50(3)	22(2)	1(2)	4(3)	-9(3)
C70A	40(4)	35(4)	23(3)	-1(2)	-11(2)	-3(2)
C71A	57(3)	44(3)	20(2)	4(2)	5(2)	-14(2)
C72A	67(4)	73(4)	28(3)	0(3)	7(3)	-25(3)

	x	У	Z	U(eq)
H6	2878	5129	6479	23
H7	3311	5553	5537	24
H8	5709	5896	5209	22
H11	10497	5792	6009	22
H12	10046	5330	6943	24
H16	7030	6672	3913	22
H17	7477	7134	2975	23
H20	12616	7619	2864	23
H21	14619	7425	3469	23
H22	14178	6962	4408	24
H23	11771	6622	4726	23
H25A	4695	4604	8342	29
H25B	6396	4815	8464	29
H26A	6429	3177	8718	26
H26B	7308	3129	8120	26
H27A	4973	2834	7714	29
H27B	4179	2808	8326	29
H28A	4950	1165	7995	30
H28B	6696	1376	7934	30
H29A	5059	1350	8992	30
H29B	6862	1412	8900	30
H30A	5455	-299	8627	45
H30B	6471	-251	9159	45
H30C	7258	-237	8545	45
H31A	8018	8186	2242	25
H31B	8605	7053	2056	25
H32A	10429	7569	1430	28
H32B	10210	8672	1680	28
H33A	7765	9036	1298	29
H33B	7900	7916	1073	29

Table **6Y.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **6Y.** 

H34A	9918	8205	444	35
H34B	9973	9284	698	35
H35A	8710	9305	-186	37
H35B	7344	8840	143	37
H36A	6804	10308	682	54
H36B	6674	10586	33	54
H36C	8167	10773	349	54
H42	12102	9993	3447	24
H43	11670	9440	4374	25
H44	9263	9083	4676	25
H47	4502	9241	3851	23
H48	4965	9804	2935	24
H52	7976	8352	5939	23
Н53	7575	7917	6881	25
H56	2447	7393	7029	25
H57	415	7566	6437	27
H58	804	8042	5495	26
Н59	3196	8391	5162	26
H61A	8407	10884	1496	30
H61B	10210	10824	1594	30
H62A	7961	12424	2000	30
H62B	9779	12373	2052	30
H63A	8214	12636	1026	31
H63B	10051	12499	1052	31
H64A	8015	14149	1524	38
H64B	9841	14005	1578	38
H65A	8284	14435	561	61
H65B	10119	14184	579	61
H66A	8375	15870	1130	140
H66B	9298	15962	545	140
H66C	10214	15638	1096	140
H67A	6431	8178	7757	26
H67B	7039	7004	7682	26
H68A	4915	6648	8305	30
H68B	4556	7824	8423	30
H69C	7209	7655	8711	41

H69D	7179	6510	8729	41
H69A	6982	7758	8818	41
H69B	7367	6615	8692	41
H70A	4851	7469	9439	38
H70B	4999	6326	9250	38
H71A	7354	7055	9840	44
H71B	7258	5901	9719	44
H72A	5076	7115	10432	71
H72B	6403	6282	10655	71
H72C	5028	5953	10321	71
H70C	5245	7818	9436	40
H70D	6885	7252	9617	40
H71C	6054	5679	9508	48
H71D	4446	6214	9287	48
H72D	5418	6284	10403	82
H72E	4015	5752	10214	82
H72F	3890	6950	10192	82

C5-N1-C1-O1	-178.46(19)	C8-C9-C10-C11	-178.23(18)
C25-N1-C1-O1	1.2(3)	C3-C9-C10-C11	1.5(3)
C5-N1-C1-C2	2.7(3)	C8-C9-C10-C13	1.8(3)
C25-N1-C1-C2	-177.56(17)	C3-C9-C10-C13	-178.42(17)
O1-C1-C2-C6	-2.0(3)	C13-C10-C11-C12	178.54(18)
N1-C1-C2-C6	176.76(18)	C9-C10-C11-C12	-1.4(3)
01-C1-C2-C3	178.36(19)	C3-C4-C12-C11	-0.1(3)
N1-C1-C2-C3	-2.9(3)	C5-C4-C12-C11	178.92(17)
C6-C2-C3-C4	-178.50(18)	C10-C11-C12-C4	0.7(3)
C1-C2-C3-C4	1.1(3)	C14-C15-C16-C17	-178.76(18)
C6-C2-C3-C9	1.2(3)	C24-C15-C16-C17	0.4(3)
C1-C2-C3-C9	-179.21(17)	C15-C16-C17-C18	-1.7(3)
C2-C3-C4-C12	179.99(18)	C31-O3-C18-C17	-2.3(3)
C9-C3-C4-C12	0.3(3)	C31-O3-C18-C19	178.24(16)
C2-C3-C4-C5	0.9(3)	C16-C17-C18-O3	-177.50(17)
C9-C3-C4-C5	-178.75(17)	C16-C17-C18-C19	2.0(3)
C1-N1-C5-O2	178.74(19)	O3-C18-C19-C20	-2.2(3)
C25-N1-C5-O2	-1.0(3)	C17-C18-C19-C20	178.30(18)
C1-N1-C5-C4	-0.8(3)	O3-C18-C19-C24	178.64(16)
C25-N1-C5-C4	179.49(16)	C17-C18-C19-C24	-0.9(3)
C12-C4-C5-O2	0.3(3)	C24-C19-C20-C21	0.2(3)
C3-C4-C5-O2	179.33(19)	C18-C19-C20-C21	-178.95(18)
C12-C4-C5-N1	179.79(18)	C19-C20-C21-C22	-1.4(3)
C3-C4-C5-N1	-1.1(3)	C20-C21-C22-C23	1.6(3)
C3-C2-C6-C7	-0.1(3)	C21-C22-C23-C24	-0.6(3)
C1-C2-C6-C7	-179.73(17)	C20-C19-C24-C23	0.7(3)
C2-C6-C7-C8	-1.2(3)	C18-C19-C24-C23	179.91(17)
C6-C7-C8-C9	1.5(3)	C20-C19-C24-C15	-179.67(17)
С7-С8-С9-С3	-0.4(3)	C18-C19-C24-C15	-0.5(3)
C7-C8-C9-C10	179.32(18)	C22-C23-C24-C19	-0.5(3)
C2-C3-C9-C8	-0.9(3)	C22-C23-C24-C15	179.87(18)
C4-C3-C9-C8	178.77(17)	C16-C15-C24-C19	0.7(3)
C2-C3-C9-C10	179.34(17)	C14-C15-C24-C19	179.86(17)
C4-C3-C9-C10	-1.0(3)	C16-C15-C24-C23	-179.69(18)

Table **6Y.6**. Torsion angles [°] for **6Y.** 

C14-C15-C24-C23	-0.5(3)	C39-C38-C42-C43	-1.1(3)
C1-N1-C25-C26	99.2(2)	C37-C38-C42-C43	176.04(17)
C5-N1-C25-C26	-81.1(2)	C38-C42-C43-C44	0.8(3)
N1-C25-C26-C27	-75.7(2)	C42-C43-C44-C45	-0.1(3)
C25-C26-C27-C28	175.67(17)	C43-C44-C45-C39	-0.3(3)
C26-C27-C28-C29	61.7(2)	C43-C44-C45-C46	-179.01(18)
C27-C28-C29-C30	172.33(17)	C40-C39-C45-C44	-178.37(17)
C18-O3-C31-C32	178.49(16)	C38-C39-C45-C44	0.0(3)
O3-C31-C32-C33	-167.10(17)	C40-C39-C45-C46	0.4(3)
C31-C32-C33-C34	-176.48(18)	C38-C39-C45-C46	178.78(17)
C32-C33-C34-C35	-173.4(2)	C44-C45-C46-C47	178.83(18)
C33-C34-C35-C36	73.1(3)	C39-C45-C46-C47	0.2(3)
C41-N2-C37-O4	-179.83(19)	C44-C45-C46-C49	-0.7(3)
C61-N2-C37-O4	-4.3(3)	C39-C45-C46-C49	-179.36(17)
C41-N2-C37-C38	-1.5(3)	C49-C46-C47-C48	179.44(18)
C61-N2-C37-C38	174.13(17)	C45-C46-C47-C48	-0.1(3)
O4-C37-C38-C42	0.6(3)	C39-C40-C48-C47	1.0(3)
N2-C37-C38-C42	-177.74(18)	C41-C40-C48-C47	-176.80(17)
O4-C37-C38-C39	177.82(19)	C46-C47-C48-C40	-0.5(3)
N2-C37-C38-C39	-0.5(3)	C50-C51-C52-C53	178.37(18)
C42-C38-C39-C40	179.12(18)	C60-C51-C52-C53	-0.9(3)
C37-C38-C39-C40	2.0(3)	C51-C52-C53-C54	2.1(3)
C42-C38-C39-C45	0.7(3)	C67-O6-C54-C53	8.4(3)
C37-C38-C39-C45	-176.45(17)	C67-O6-C54-C55	-171.08(16)
C38-C39-C40-C48	-179.36(18)	C52-C53-C54-O6	178.94(17)
C45-C39-C40-C48	-1.0(3)	C52-C53-C54-C55	-1.6(3)
C38-C39-C40-C41	-1.5(3)	O6-C54-C55-C56	0.6(3)
C45-C39-C40-C41	176.85(17)	C53-C54-C55-C56	-178.96(18)
C37-N2-C41-O5	-178.58(19)	O6-C54-C55-C60	179.53(16)
C61-N2-C41-O5	5.8(3)	C53-C54-C55-C60	0.0(3)
C37-N2-C41-C40	1.9(3)	C60-C55-C56-C57	-0.5(3)
C61-N2-C41-C40	-173.73(17)	C54-C55-C56-C57	178.45(18)
C48-C40-C41-O5	-2.0(3)	C55-C56-C57-C58	1.0(3)
C39-C40-C41-O5	-179.86(19)	C56-C57-C58-C59	-1.0(3)
C48-C40-C41-N2	177.53(18)	C57-C58-C59-C60	0.4(3)
C39-C40-C41-N2	-0.3(3)	C58-C59-C60-C55	0.1(3)

C58-C59-C60-C51	179.89(18)	C61-C62-C63-C64	-175.26(18)
C56-C55-C60-C59	0.0(3)	C62-C63-C64-C65	177.5(2)
C54-C55-C60-C59	-179.03(17)	C63-C64-C65-C66	-174.0(3)
C56-C55-C60-C51	-179.86(17)	C54-O6-C67-C68	172.96(16)
C54-C55-C60-C51	1.1(3)	O6-C67-C68-C69	171.21(17)
C52-C51-C60-C59	179.46(18)	C67-C68-C69-C70A	162.8(3)
C50-C51-C60-C59	0.2(3)	C67-C68-C69-C70	-178.0(3)
C52-C51-C60-C55	-0.7(3)	C68-C69-C70-C71	170.5(4)
C50-C51-C60-C55	-179.98(17)	C69-C70-C71-C72	170.5(5)
C37-N2-C61-C62	-82.0(2)	C68-C69-C70A-C71A	70.9(5)
C41-N2-C61-C62	93.9(2)	C69-C70A-C71A-C72A	-176.1(5)
N2-C61-C62-C63	-176.02(17)		

End of crystallographic info for 6Y.

### **CRYSTALLOGRAPHIC MATERIAL FOR 6Y'**

## Crystallographic Material for 6y'

X-ray Experimental.

Table **6y'.**1. Crystallographic Data for **6y'**.

Table **6y'.**2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **6y'.** 

Table 6y'.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 6y'.

Table **6y**'.4. Anisotropic thermal parameters for the non-hydrogen atoms of **6y**'.

Table **6y'.5**. Fractional coordinates and isotropic thermal parameters ( $Å^2$ ) for the hydrogen atoms of **6y'**.

Table **6y'.6**. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **6y'**.

Crystallographic Material for **6Y'**:

X-ray Experimental for complex  $C_{36}H_{37}NO_3$  (**6Y**'): Crystals grew as long, yellow needles by slow evaporation from EtOAc The data crystal was cut from a longer crystal and had approximate dimensions; 0.26 x 0.06 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1251 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 8 seconds per frame with a detector offset of +/- 40.8° and 28 seconds per frame with a detector offset of +/- 108.3°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>1</sup> The structure was solved by direct methods using SuperFlip<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.<sup>3</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1327*P)^2 + (1.4735*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.234, with R(F) equal to 0.0772 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

### **References**

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- 2) SuperFlip. Palatinus, L. Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.
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- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.
| 5  |   |                                |
|--|---|--------------------------------|
| Empirical formula                        | C36 H37 N O3                                |                                |
| Formula weight                           | 531.66                                      |                                |
| Temperature                              | 100(2) K                                    |                                |
| Wavelength                               | 1.54184 Å                                   |                                |
| Crystal system                           | triclinic                                   |                                |
| Space group                              | P -1  |                                |
| Unit cell dimensions                     | a = 10.7586(4) Å                            | α= 95.314(3)°.                 |
|  | b = 10.7921(4) Å                            | β= 98.742(3)°.                 |
|  | c = 24.7104(9) Å                            | $\gamma = 93.190(3)^{\circ}$ . |
| Volume                                   | 2816.46(18) Å <sup>3</sup>                  |                                |
| Z  | 4   |                                |
| Density (calculated)                     | 1.254 Mg/m <sup>3</sup>                     |                                |
| Absorption coefficient                   | 0.617 mm <sup>-1</sup>                      |                                |
| F(000)                                   | 1136  |                                |
| Crystal size                             | 0.260 x 0.063 x 0.025 mm <sup>3</sup>       |                                |
| Theta range for data collection          | 3.639 to 74.236°.                           |                                |
| Index ranges                             | -12<=h<=13, -9<=k<=13, -30<                 | =1<=23                         |
| Reflections collected                    | 20035                                       |                                |
| Independent reflections                  | 10747 [R(int) = 0.0267]                     |                                |
| Completeness to theta = $67.684^{\circ}$ | 97.7 %                                      |                                |
| Absorption correction                    | Semi-empirical from equivalen               | ts                             |
| Max. and min. transmission               | 1.00 and 0.777                              |                                |
| Refinement method                        | Full-matrix least-squares on F <sup>2</sup> |                                |
| Data / restraints / parameters           | 10747 / 0 / 725                             |                                |
| Goodness-of-fit on F <sup>2</sup>        | 1.029                                       |                                |
| Final R indices [I>2sigma(I)]            | R1 = 0.0772, wR2 = 0.2077                   |                                |
| R indices (all data)                     | R1 = 0.1010, wR2 = 0.2345                   |                                |
| Extinction coefficient                   | n/a   |                                |
| Largest diff. peak and hole              | 0.793 and -0.315 e.Å <sup>-3</sup>          |                                |

Table **6Y'.1**. Crystal data and structure refinement for **6Y'**.

	Х	у	Z	U(eq)
C1	5649(2)	5487(2)	2814(1)	20(1)
C2	5637(2)	6137(2)	3367(1)	16(1)
C3	4579(2)	6771(2)	3483(1)	15(1)
C4	3529(2)	6822(2)	3068(1)	16(1)
C5	3514(2)	6169(2)	2512(1)	20(1)
C6	6662(2)	6087(2)	3773(1)	17(1)
C7	6655(2)	6648(2)	4307(1)	18(1)
C8	5635(2)	7273(2)	4432(1)	16(1)
C9	4576(2)	7355(2)	4024(1)	15(1)
C10	3489(2)	7994(2)	4131(1)	15(1)
C11	2484(2)	8025(2)	3709(1)	16(1)
C12	2502(2)	7441(2)	3182(1)	17(1)
C13	3479(2)	8590(2)	4671(1)	16(1)
C14	3546(2)	9059(2)	5139(1)	15(1)
C15	3726(2)	9545(2)	5704(1)	16(1)
C16	4855(2)	9371(2)	6034(1)	17(1)
C17	5101(2)	9798(2)	6596(1)	16(1)
C18	4204(2)	10432(2)	6832(1)	15(1)
C19	3037(2)	10665(2)	6508(1)	15(1)
C20	2125(2)	11333(2)	6741(1)	16(1)
C21	1001(2)	11540(2)	6430(1)	17(1)
C22	746(2)	11079(2)	5867(1)	17(1)
C23	1615(2)	10422(2)	5629(1)	16(1)
C24	2791(2)	10204(2)	5942(1)	15(1)
C25	4496(2)	4797(2)	1884(1)	24(1)
C26	3701(2)	3560(2)	1842(1)	26(1)
C27	3518(3)	2883(3)	1264(1)	33(1)
C28	2550(3)	1755(3)	1186(1)	33(1)
C29	2355(3)	1066(3)	609(1)	41(1)
C30	1452(4)	-82(3)	547(2)	53(1)
C31	5351(2)	10454(3)	7746(1)	25(1)

Table **6Y'.2**. Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters  $(Å^2x \ 10^3)$  for **6Y'**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	5021(2)	10683(3)	8319(1)	29(1)
C33	4918(2)	12048(2)	8503(1)	27(1)
C34	4482(2)	12233(3)	9065(1)	29(1)
C35	4308(3)	13594(3)	9250(1)	32(1)
C36	3753(3)	13750(3)	9780(1)	36(1)
C37	-727(2)	9445(2)	7178(1)	18(1)
C38	-678(2)	8832(2)	6624(1)	16(1)
C39	396(2)	8220(2)	6513(1)	14(1)
C40	1436(2)	8175(2)	6932(1)	16(1)
C41	1422(2)	8799(2)	7491(1)	17(1)
C42	-1688(2)	8887(2)	6214(1)	17(1)
C43	-1662(2)	8340(2)	5678(1)	18(1)
C44	-632(2)	7725(2)	5561(1)	16(1)
C45	419(2)	7651(2)	5972(1)	15(1)
C46	1516(2)	7022(2)	5868(1)	15(1)
C47	2520(2)	7003(2)	6292(1)	17(1)
C48	2482(2)	7579(2)	6821(1)	17(1)
C49	1538(2)	6430(2)	5330(1)	17(1)
C50	1462(2)	5962(2)	4859(1)	16(1)
C51	1278(2)	5473(2)	4294(1)	16(1)
C52	157(2)	5653(2)	3962(1)	17(1)
C53	-92(2)	5204(2)	3402(1)	16(1)
C54	789(2)	4543(2)	3173(1)	15(1)
C55	1965(2)	4324(2)	3498(1)	15(1)
C56	2873(2)	3641(2)	3268(1)	16(1)
C57	3995(2)	3442(2)	3582(1)	17(1)
C58	4254(2)	3922(2)	4141(1)	17(1)
C59	3389(2)	4591(2)	4375(1)	16(1)
C60	2215(2)	4805(2)	4062(1)	15(1)
C61	355(2)	10109(2)	8118(1)	23(1)
C62	1022(2)	11408(2)	8147(1)	26(1)
C63	965(2)	12198(3)	8688(1)	29(1)
C64	-297(2)	12784(3)	8715(1)	30(1)
C65	-320(3)	13533(3)	9266(1)	34(1)
C66	-1542(3)	14166(3)	9292(1)	39(1)
C67	-465(2)	4304(2)	2276(1)	22(1)

C68	-386(2)	3632(3)	1718(1)	26(1)
C69	-1645(2)	3538(3)	1329(1)	31(1)
C70	-1565(3)	2868(3)	766(1)	35(1)
C71	-2856(3)	2469(3)	421(1)	40(1)
C72	-3492(3)	1313(3)	609(1)	45(1)
N1	4569(2)	5517(2)	2425(1)	19(1)
N2	340(2)	9407(2)	7577(1)	19(1)
O1	6547(2)	4932(2)	2698(1)	27(1)
O2	2628(2)	6177(2)	2141(1)	27(1)
O3	4331(1)	10865(2)	7372(1)	20(1)
O4	-1639(2)	9978(2)	7293(1)	27(1)
O5	2296(2)	8789(2)	7868(1)	24(1)
O6	648(1)	4052(2)	2639(1)	19(1)

C1-O1	1.220(3)	C19-C24	1.421(3)
C1-N1	1.395(3)	C20-C21	1.373(3)
C1-C2	1.479(3)	C20-H20	0.95
C2-C6	1.381(3)	C21-C22	1.413(3)
C2-C3	1.412(3)	C21-H21	0.95
C3-C4	1.413(3)	C22-C23	1.373(3)
C3-C9	1.425(3)	C22-H22	0.95
C4-C12	1.374(3)	C23-C24	1.422(3)
C4-C5	1.481(3)	C23-H23	0.95
C5-O2	1.218(3)	C25-N1	1.472(3)
C5-N1	1.402(3)	C25-C26	1.531(3)
C6-C7	1.402(3)	C25-H25A	0.99
С6-Н6	0.95	C25-H25B	0.99
C7-C8	1.378(3)	C26-C27	1.522(4)
С7-Н7	0.95	C26-H26A	0.99
C8-C9	1.414(3)	C26-H26B	0.99
С8-Н8	0.95	C27-C28	1.535(4)
C9-C10	1.436(3)	C27-H27A	0.99
C10-C11	1.387(3)	C27-H27B	0.99
C10-C13	1.430(3)	C28-C29	1.525(4)
C11-C12	1.398(3)	C28-H28A	0.99
C11-H11	0.95	C28-H28B	0.99
C12-H12	0.95	C29-C30	1.513(4)
C13-C14	1.208(3)	С29-Н29А	0.99
C14-C15	1.426(3)	C29-H29B	0.99
C15-C16	1.390(3)	C30-H30A	0.98
C15-C24	1.430(3)	C30-H30B	0.98
C16-C17	1.401(3)	C30-H30C	0.98
C16-H16	0.95	C31-O3	1.441(3)
C17-C18	1.382(3)	C31-C32	1.512(4)
C17-H17	0.95	C31-H31A	0.99
C18-O3	1.358(3)	C31-H31B	0.99
C18-C19	1.430(3)	C32-C33	1.516(4)
C19-C20	1.410(3)	C32-H32A	0.99

Table **6Y'.3**. Bond lengths [Å] and angles  $[\circ]$  for **6Y'**.

С32-Н32В	0.99	C49-C50	1.216(3)
C33-C34	1.532(4)	C50-C51	1.425(3)
С33-Н33А	0.99	C51-C52	1.385(3)
С33-Н33В	0.99	C51-C60	1.430(3)
C34-C35	1.527(4)	C52-C53	1.403(3)
C34-H34A	0.99	С52-Н52	0.95
C34-H34B	0.99	C53-C54	1.376(3)
C35-C36	1.519(4)	С53-Н53	0.95
С35-Н35А	0.99	C54-O6	1.358(3)
С35-Н35В	0.99	C54-C55	1.435(3)
С36-Н36А	0.98	C55-C56	1.411(3)
С36-Н36В	0.98	C55-C60	1.423(3)
С36-Н36С	0.98	C56-C57	1.373(3)
C37-O4	1.220(3)	С56-Н56	0.95
C37-N2	1.401(3)	C57-C58	1.409(3)
C37-C38	1.473(3)	С57-Н57	0.95
C38-C42	1.377(3)	C58-C59	1.373(3)
C38-C39	1.413(3)	С58-Н58	0.95
C39-C40	1.411(3)	C59-C60	1.419(3)
C39-C45	1.421(3)	С59-Н59	0.95
C40-C48	1.377(3)	C61-N2	1.471(3)
C40-C41	1.481(3)	C61-C62	1.529(3)
C41-O5	1.220(3)	C61-H61A	0.99
C41-N2	1.402(3)	С61-Н61В	0.99
C42-C43	1.405(3)	C62-C63	1.530(4)
C42-H42	0.95	С62-Н62А	0.99
C43-C44	1.376(3)	С62-Н62В	0.99
С43-Н43	0.95	C63-C64	1.537(4)
C44-C45	1.413(3)	С63-Н63А	0.99
C44-H44	0.95	С63-Н63В	0.99
C45-C46	1.439(3)	C64-C65	1.523(4)
C46-C47	1.388(3)	C64-H64A	0.99
C46-C49	1.424(3)	C64-H64B	0.99
C47-C48	1.402(3)	C65-C66	1.523(4)
C47-H47	0.95	C65-H65A	0.99
C48-H48	0.95	С65-Н65В	0.99

С66-Н66А	0.98	0.98 C69-H69A	
С66-Н66В	0.98	С69-Н69В	0.99
C66-H66C	0.98	C70-C71	1.531(4)
C67-O6	1.438(2)	С70-Н70А	0.99
C67-C68	1.513(4)	С70-Н70В	0.99
С67-Н67А	0.99	C71-C72	1.532(4)
С67-Н67В	0.99	C71-H71A	0.99
C68-C69	1.530(3)	C71-H71B	0.99
C68-H68A	0.99	C72-H72A	0.98
C68-H68B	0.99	С72-Н72В	0.98
C69-C70	1.525(4)	С72-Н72С	0.98
01-C1-N1	120.7(2)	C8-C9-C3	118.8(2)
O1-C1-C2	122.4(2)	C8-C9-C10	123.0(2)
N1-C1-C2	116.9(2)	C3-C9-C10	118.3(2)
C6-C2-C3	120.4(2)	C11-C10-C13	121.7(2)
C6-C2-C1	119.0(2)	C11-C10-C9	119.5(2)
C3-C2-C1	120.6(2)	C13-C10-C9	118.79(19)
C2-C3-C4	120.5(2)	C10-C11-C12	121.4(2)
C2-C3-C9	119.4(2)	C10-C11-H11	119.3
C4-C3-C9	120.2(2)	C12-C11-H11	119.3
C12-C4-C3	120.3(2)	C4-C12-C11	120.4(2)
C12-C4-C5	119.7(2)	C4-C12-H12	119.8
C3-C4-C5	119.9(2)	С11-С12-Н12	119.8
O2-C5-N1	120.2(2)	C14-C13-C10	175.5(2)
O2-C5-C4	122.5(2)	C13-C14-C15	174.6(2)
N1-C5-C4	117.2(2)	C16-C15-C14	118.5(2)
C2-C6-C7	120.3(2)	C16-C15-C24	118.9(2)
С2-С6-Н6	119.8	C14-C15-C24	122.56(19)
С7-С6-Н6	119.8	C15-C16-C17	122.3(2)
C8-C7-C6	120.5(2)	С15-С16-Н16	118.9
С8-С7-Н7	119.8	C17-C16-H16	118.9
С6-С7-Н7	119.8	C18-C17-C16	119.42(19)
C7-C8-C9	120.7(2)	C18-C17-H17	120.3
С7-С8-Н8	119.7	C16-C17-H17	120.3
С9-С8-Н8	119.7	O3-C18-C17	124.40(19)

O3-C18-C19	114.88(19)	114.88(19) C28-C27-H27B	
C17-C18-C19	120.7(2)	H27A-C27-H27B	107.8
C20-C19-C24	119.5(2)	C29-C28-C27	113.6(2)
C20-C19-C18	121.3(2)	C29-C28-H28A	108.8
C24-C19-C18	119.2(2)	C27-C28-H28A	108.8
C21-C20-C19	121.0(2)	C29-C28-H28B	108.8
С21-С20-Н20	119.5	C27-C28-H28B	108.8
С19-С20-Н20	119.5	H28A-C28-H28B	107.7
C20-C21-C22	119.8(2)	C30-C29-C28	112.9(3)
C20-C21-H21	120.1	С30-С29-Н29А	109.0
С22-С21-Н21	120.1	С28-С29-Н29А	109.0
C23-C22-C21	120.47(19)	С30-С29-Н29В	109.0
С23-С22-Н22	119.8	С28-С29-Н29В	109.0
С21-С22-Н22	119.8	H29A-C29-H29B	107.8
C22-C23-C24	120.8(2)	С29-С30-Н30А	109.5
С22-С23-Н23	119.6	С29-С30-Н30В	109.5
С24-С23-Н23	119.6	H30A-C30-H30B	109.5
C19-C24-C23	118.4(2)	С29-С30-Н30С	109.5
C19-C24-C15	119.45(19)	H30A-C30-H30C	109.5
C23-C24-C15	122.2(2)	H30B-C30-H30C	109.5
N1-C25-C26	112.2(2)	O3-C31-C32	106.95(19)
N1-C25-H25A	109.2	O3-C31-H31A	110.3
С26-С25-Н25А	109.2	С32-С31-Н31А	110.3
N1-C25-H25B	109.2	O3-C31-H31B	110.3
С26-С25-Н25В	109.2	С32-С31-Н31В	110.3
H25A-C25-H25B	107.9	H31A-C31-H31B	108.6
C27-C26-C25	111.9(2)	C31-C32-C33	113.7(2)
С27-С26-Н26А	109.2	C31-C32-H32A	108.8
С25-С26-Н26А	109.2	C33-C32-H32A	108.8
С27-С26-Н26В	109.2	C31-C32-H32B	108.8
С25-С26-Н26В	109.2	С33-С32-Н32В	108.8
H26A-C26-H26B	107.9	H32A-C32-H32B	107.7
C26-C27-C28	112.9(2)	C32-C33-C34	112.2(2)
С26-С27-Н27А	109.0	С32-С33-Н33А	109.2
С28-С27-Н27А	109.0	С34-С33-Н33А	109.2
С26-С27-Н27В	109.0	С32-С33-Н33В	109.2

С34-С33-Н33В	109.2	109.2 C38-C42-H42	
H33A-C33-H33B	107.9	С43-С42-Н42	119.8
C35-C34-C33	113.4(2)	C44-C43-C42	120.1(2)
C35-C34-H34A	108.9	С44-С43-Н43	119.9
C33-C34-H34A	108.9	С42-С43-Н43	119.9
C35-C34-H34B	108.9	C43-C44-C45	120.8(2)
C33-C34-H34B	108.9	C43-C44-H44	119.6
H34A-C34-H34B	107.7	C45-C44-H44	119.6
C36-C35-C34	112.8(2)	C44-C45-C39	118.9(2)
C36-C35-H35A	109.0	C44-C45-C46	122.7(2)
C34-C35-H35A	109.0	C39-C45-C46	118.43(19)
С36-С35-Н35В	109.0	C47-C46-C49	121.8(2)
С34-С35-Н35В	109.0	C47-C46-C45	119.4(2)
H35A-C35-H35B	107.8	C49-C46-C45	118.83(19)
C35-C36-H36A	109.5	C46-C47-C48	121.3(2)
С35-С36-Н36В	109.5	С46-С47-Н47	119.4
H36A-C36-H36B	109.5	С48-С47-Н47	119.4
С35-С36-Н36С	109.5	C40-C48-C47	120.4(2)
H36A-C36-H36C	109.5	C40-C48-H48	119.8
H36B-C36-H36C	109.5	С47-С48-Н48	119.8
O4-C37-N2	120.4(2)	C50-C49-C46	174.7(2)
O4-C37-C38	122.8(2)	C49-C50-C51	175.0(2)
N2-C37-C38	116.86(19)	C52-C51-C50	118.8(2)
C42-C38-C39	120.4(2)	C52-C51-C60	119.3(2)
C42-C38-C37	118.9(2)	C50-C51-C60	121.89(19)
C39-C38-C37	120.7(2)	C51-C52-C53	122.2(2)
C40-C39-C38	120.4(2)	С51-С52-Н52	118.9
C40-C39-C45	120.3(2)	С53-С52-Н52	118.9
C38-C39-C45	119.3(2)	C54-C53-C52	119.49(19)
C48-C40-C39	120.2(2)	С54-С53-Н53	120.3
C48-C40-C41	119.7(2)	С52-С53-Н53	120.3
C39-C40-C41	120.1(2)	O6-C54-C53	124.80(19)
O5-C41-N2	120.2(2)	O6-C54-C55	114.48(19)
O5-C41-C40	122.7(2)	C53-C54-C55	120.7(2)
N2-C41-C40	117.10(19)	C56-C55-C60	119.6(2)
C38-C42-C43	120.5(2)	C56-C55-C54	121.2(2)

C60-C55-C54	119.2(2)	119.2(2) C63-C64-H64A	
C57-C56-C55	120.7(2)	C65-C64-H64B	109.1
С57-С56-Н56	119.7	C63-C64-H64B	109.1
С55-С56-Н56	119.7	H64A-C64-H64B	107.9
C56-C57-C58	120.1(2)	C64-C65-C66	113.2(2)
С56-С57-Н57	119.9	C64-C65-H65A	108.9
С58-С57-Н57	119.9	С66-С65-Н65А	108.9
C59-C58-C57	120.43(19)	С64-С65-Н65В	108.9
С59-С58-Н58	119.8	С66-С65-Н65В	108.9
С57-С58-Н58	119.8	H65A-C65-H65B	107.8
C58-C59-C60	120.8(2)	С65-С66-Н66А	109.5
С58-С59-Н59	119.6	С65-С66-Н66В	109.5
С60-С59-Н59	119.6	H66A-C66-H66B	109.5
C59-C60-C55	118.4(2)	С65-С66-Н66С	109.5
C59-C60-C51	122.5(2)	H66A-C66-H66C	109.5
C55-C60-C51	119.10(19)	H66B-C66-H66C	109.5
N2-C61-C62	111.2(2)	O6-C67-C68	106.61(19)
N2-C61-H61A	109.4	O6-C67-H67A	110.4
С62-С61-Н61А	109.4	С68-С67-Н67А	110.4
N2-C61-H61B	109.4	O6-C67-H67B	110.4
С62-С61-Н61В	109.4	С68-С67-Н67В	110.4
H61A-C61-H61B	108.0	H67A-C67-H67B	108.6
C61-C62-C63	112.5(2)	C67-C68-C69	112.3(2)
С61-С62-Н62А	109.1	C67-C68-H68A	109.1
С63-С62-Н62А	109.1	C69-C68-H68A	109.1
С61-С62-Н62В	109.1	C67-C68-H68B	109.1
С63-С62-Н62В	109.1	C69-C68-H68B	109.1
H62A-C62-H62B	107.8	H68A-C68-H68B	107.9
C62-C63-C64	114.4(2)	C70-C69-C68	112.4(2)
С62-С63-Н63А	108.7	С70-С69-Н69А	109.1
С64-С63-Н63А	108.7	С68-С69-Н69А	109.1
С62-С63-Н63В	108.7	С70-С69-Н69В	109.1
С64-С63-Н63В	108.7	С68-С69-Н69В	109.1
H63A-C63-H63B	107.6	H69A-C69-H69B	107.9
C65-C64-C63	112.4(2)	C69-C70-C71	113.4(2)
C65-C64-H64A	109.1	С69-С70-Н70А	108.9

С71-С70-Н70А	108.9	H72A-C72-H72B	109.5
С69-С70-Н70В	108.9	С71-С72-Н72С	109.5
С71-С70-Н70В	108.9	H72A-C72-H72C	109.5
H70A-C70-H70B	107.7	H72B-C72-H72C	109.5
C70-C71-C72	112.8(3)	C1-N1-C5	124.8(2)
С70-С71-Н71А	109.0	C1-N1-C25	118.76(19)
С72-С71-Н71А	109.0	C5-N1-C25	116.45(19)
С70-С71-Н71В	109.0	C37-N2-C41	124.8(2)
С72-С71-Н71В	109.0	C37-N2-C61	117.66(19)
H71A-C71-H71B	107.8	C41-N2-C61	117.48(19)
С71-С72-Н72А	109.5	C18-O3-C31	118.22(18)
С71-С72-Н72В	109.5	C54-O6-C67	117.96(17)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	17(1)	21(1)	22(1)	4(1)	6(1)	4(1)
C2	14(1)	16(1)	18(1)	3(1)	4(1)	2(1)
C3	12(1)	15(1)	19(1)	4(1)	3(1)	-1(1)
C4	15(1)	16(1)	18(1)	4(1)	2(1)	2(1)
C5	19(1)	21(1)	19(1)	2(1)	2(1)	3(1)
C6	11(1)	17(1)	26(1)	7(1)	4(1)	3(1)
C7	11(1)	20(1)	23(1)	4(1)	-2(1)	0(1)
C8	14(1)	17(1)	18(1)	2(1)	0(1)	0(1)
C9	11(1)	16(1)	19(1)	3(1)	4(1)	0(1)
C10	12(1)	15(1)	18(1)	2(1)	4(1)	1(1)
C11	10(1)	16(1)	23(1)	2(1)	4(1)	3(1)
C12	11(1)	20(1)	20(1)	4(1)	-2(1)	2(1)
C13	11(1)	18(1)	20(1)	2(1)	4(1)	3(1)
C14	12(1)	17(1)	18(1)	3(1)	3(1)	3(1)
C15	14(1)	15(1)	18(1)	4(1)	3(1)	0(1)
C16	13(1)	18(1)	20(1)	2(1)	4(1)	4(1)
C17	11(1)	18(1)	20(1)	3(1)	2(1)	3(1)
C18	14(1)	16(1)	15(1)	3(1)	3(1)	2(1)
C19	12(1)	16(1)	17(1)	4(1)	3(1)	1(1)
C20	14(1)	18(1)	18(1)	4(1)	3(1)	3(1)
C21	12(1)	18(1)	22(1)	4(1)	5(1)	4(1)
C22	11(1)	20(1)	21(1)	5(1)	1(1)	3(1)
C23	13(1)	18(1)	18(1)	3(1)	2(1)	1(1)
C24	12(1)	14(1)	19(1)	5(1)	3(1)	1(1)
C25	26(1)	29(1)	17(1)	0(1)	7(1)	5(1)
C26	31(1)	25(1)	21(1)	0(1)	6(1)	5(1)
C27	43(2)	30(1)	26(1)	-1(1)	11(1)	2(1)
C28	30(1)	33(1)	36(2)	2(1)	5(1)	7(1)
C29	44(2)	38(2)	40(2)	-1(1)	9(1)	-2(1)
C30	57(2)	50(2)	49(2)	-9(2)	12(2)	-11(2)
C31	19(1)	34(1)	22(1)	3(1)	-3(1)	11(1)

Table **6Y'.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **6Y'.** The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	28(1)	35(1)	24(1)	4(1)	-1(1)	8(1)
C33	22(1)	30(1)	30(1)	5(1)	1(1)	2(1)
C34	26(1)	32(1)	28(1)	3(1)	1(1)	4(1)
C35	30(1)	34(1)	32(2)	-1(1)	6(1)	1(1)
C36	30(1)	42(2)	37(2)	-2(1)	7(1)	3(1)
C37	16(1)	20(1)	20(1)	3(1)	5(1)	3(1)
C38	12(1)	16(1)	20(1)	3(1)	4(1)	1(1)
C39	11(1)	14(1)	17(1)	5(1)	3(1)	0(1)
C40	13(1)	16(1)	19(1)	3(1)	3(1)	1(1)
C41	16(1)	16(1)	19(1)	3(1)	1(1)	2(1)
C42	11(1)	16(1)	23(1)	4(1)	3(1)	3(1)
C43	11(1)	19(1)	22(1)	4(1)	-2(1)	0(1)
C44	13(1)	17(1)	17(1)	2(1)	0(1)	-1(1)
C45	11(1)	15(1)	18(1)	3(1)	3(1)	0(1)
C46	12(1)	14(1)	18(1)	4(1)	4(1)	0(1)
C47	10(1)	18(1)	24(1)	4(1)	4(1)	4(1)
C48	12(1)	18(1)	20(1)	5(1)	-2(1)	0(1)
C49	11(1)	19(1)	21(1)	3(1)	4(1)	2(1)
C50	12(1)	17(1)	19(1)	3(1)	4(1)	2(1)
C51	14(1)	15(1)	18(1)	4(1)	4(1)	1(1)
C52	12(1)	18(1)	22(1)	2(1)	7(1)	3(1)
C53	12(1)	17(1)	19(1)	4(1)	2(1)	2(1)
C54	14(1)	18(1)	14(1)	4(1)	3(1)	2(1)
C55	14(1)	15(1)	17(1)	4(1)	3(1)	1(1)
C56	14(1)	17(1)	20(1)	3(1)	5(1)	2(1)
C57	13(1)	18(1)	22(1)	2(1)	6(1)	4(1)
C58	11(1)	19(1)	22(1)	6(1)	1(1)	2(1)
C59	13(1)	19(1)	17(1)	3(1)	2(1)	1(1)
C60	11(1)	15(1)	19(1)	4(1)	2(1)	1(1)
C61	27(1)	26(1)	15(1)	-2(1)	5(1)	2(1)
C62	26(1)	26(1)	25(1)	-1(1)	5(1)	3(1)
C63	30(1)	30(1)	25(1)	-2(1)	3(1)	2(1)
C64	25(1)	32(1)	32(2)	2(1)	2(1)	5(1)
C65	34(1)	36(2)	32(2)	-2(1)	2(1)	8(1)
C66	36(2)	49(2)	33(2)	-3(1)	7(1)	11(1)
C67	15(1)	30(1)	21(1)	5(1)	-3(1)	7(1)

C68	21(1)	35(1)	24(1)	5(1)	3(1)	6(1)
C69	26(1)	36(1)	30(1)	7(1)	-2(1)	6(1)
C70	30(1)	44(2)	30(2)	7(1)	3(1)	1(1)
C71	40(2)	44(2)	32(2)	7(1)	-4(1)	1(1)
C72	40(2)	52(2)	39(2)	-2(2)	2(1)	-9(1)
N1	20(1)	22(1)	17(1)	2(1)	3(1)	4(1)
N2	18(1)	22(1)	17(1)	2(1)	3(1)	4(1)
01	25(1)	33(1)	26(1)	1(1)	9(1)	14(1)
02	27(1)	34(1)	20(1)	-1(1)	-4(1)	9(1)
O3	16(1)	28(1)	14(1)	2(1)	-2(1)	9(1)
O4	22(1)	33(1)	28(1)	0(1)	6(1)	13(1)
O5	23(1)	29(1)	17(1)	1(1)	-4(1)	5(1)
06	13(1)	28(1)	16(1)	1(1)	0(1)	7(1)

	х	У	Z	U(eq)
H6	7375	5669	3690	21
H7	7358	6598	4586	22
H8	5642	7651	4795	20
H11	1768	8452	3781	20
H12	1800	7473	2900	21
H16	5483	8948	5874	20
H17	5877	9653	6812	20
H20	2292	11645	7119	20
H21	395	11993	6592	20
H22	-32	11224	5652	21
H23	1429	10110	5252	19
H25A	5359	4625	1819	28
H25B	4126	5301	1593	28
H26A	4120	3018	2106	31
H26B	2867	3724	1945	31
H27A	4337	2597	1186	39
H27B	3237	3475	995	39
H28A	2832	1166	1455	39
H28B	1732	2043	1265	39
H29A	2025	1641	340	49
H29B	3179	816	521	49
H30A	1793	-675	798	80
H30B	1341	-473	167	80
H30C	635	157	636	80
H31A	6151	10929	7722	30
H31B	5450	9556	7655	30
H32A	5673	10348	8582	35
H32B	4207	10217	8330	35
H33A	4313	12404	8227	33
H33B	5750	12506	8523	33

Table **6Y'.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **6Y'.** 

H34A	3673	11736	9049	35
H34B	5110	11910	9344	35
H35A	5136	14075	9304	39
H35B	3746	13943	8955	39
H36A	2925	13290	9727	54
H36B	3661	14637	9879	54
H36C	4315	13423	10076	54
H42	-2406	9299	6293	20
H43	-2357	8393	5395	21
H44	-628	7346	5198	19
H47	3246	6593	6222	20
H48	3182	7558	7105	20
Н52	-463	6095	4118	20
Н53	-863	5355	3184	19
Н56	2706	3317	2891	20
H57	4599	2979	3423	21
H58	5032	3781	4357	20
Н59	3578	4915	4752	19
H61A	792	9645	8409	27
H61B	-522	10191	8185	27
H62A	627	11842	7836	31
H62B	1916	11321	8107	31
H63A	1647	12874	8746	35
H63B	1128	11668	8994	35
H64A	-453	13339	8418	36
H64B	-986	12115	8651	36
H65A	394	14177	9337	41
H65B	-197	12970	9561	41
H66A	-1725	14645	8975	59
H66B	-1455	14729	9632	59
H66C	-2234	13532	9286	59
H67A	-499	5212	2252	27
H67B	-1231	3993	2413	27
H68A	-117	2782	1767	32
H68B	261	4082	1550	32
H69A	-2291	3085	1496	37

H69B	-1917	4389	1283	37
H70A	-1087	2119	817	42
H70B	-1092	3427	561	42
H71A	-2752	2291	31	48
H71B	-3410	3167	445	48
H72A	-2952	615	583	67
H72B	-4307	1093	373	67
H72C	-3623	1492	992	67

01-C1-C2-C6 -1.9(4)C10-C11-C12-C4 -0.2(3)N1-C1-C2-C6 177.1(2) C14-C15-C16-C17 -178.8(2)01-C1-C2-C3 C24-C15-C16-C17 179.9(2) 1.2(3)N1-C1-C2-C3 -1.2(3)C15-C16-C17-C18 -1.0(3)C6-C2-C3-C4 -179.9(2) C16-C17-C18-O3 178.7(2) C1-C2-C3-C4 C16-C17-C18-C19 -1.6(3)-0.6(3)C6-C2-C3-C9 -0.2(3)O3-C18-C19-C20 2.0(3)C1-C2-C3-C9 177.99(19) C17-C18-C19-C20 -178.6(2)C2-C3-C4-C12 -179.9(2) O3-C18-C19-C24 -177.46(18)C9-C3-C4-C12 C17-C18-C19-C24 0.5(3) 1.9(3) C2-C3-C4-C5 2.2(3)C24-C19-C20-C21 0.3(3)C9-C3-C4-C5 -177.47(19) C18-C19-C20-C21 -179.2(2)C12-C4-C5-O2 C19-C20-C21-C22 0.0(3) 1.5(4)C3-C4-C5-O2 179.5(2) C20-C21-C22-C23 0.1(3) C12-C4-C5-N1 -177.8(2)C21-C22-C23-C24 -0.6(3)C3-C4-C5-N1 0.1(3) C20-C19-C24-C23 -0.8(3)C3-C2-C6-C7 1.0(3) C18-C19-C24-C23 178.71(19) C1-C2-C6-C7 C20-C19-C24-C15 -177.3(2)178.89(19) C2-C6-C7-C8 -1.0(3)C18-C19-C24-C15 -1.6(3)C6-C7-C8-C9 0.2(3) C22-C23-C24-C19 1.0(3) C7-C8-C9-C3 0.5(3)C22-C23-C24-C15 -178.7(2)C7-C8-C9-C10 180.0(2) C16-C15-C24-C19 0.1(3)C2-C3-C9-C8 -0.5(3)C14-C15-C24-C19 -179.88(19)179.8(2) C4-C3-C9-C8 179.12(19) C16-C15-C24-C23 C2-C3-C9-C10 -179.99(19)C14-C15-C24-C23 -0.2(3)C4-C3-C9-C10 -0.4(3)N1-C25-C26-C27 174.1(2) C8-C9-C10-C11 -179.5(2)C25-C26-C27-C28 -170.5(2)C3-C9-C10-C11 0.0(3) C26-C27-C28-C29 180.0(2) C8-C9-C10-C13 C27-C28-C29-C30 1.0(3)176.9(3) C3-C9-C10-C13 -179.58(19)O3-C31-C32-C33 -63.0(3)C13-C10-C11-C12 179.9(2) C31-C32-C33-C34 175.5(2) C9-C10-C11-C12 0.3(3) C32-C33-C34-C35 -177.2(2)C3-C4-C12-C11 -0.2(3)C33-C34-C35-C36 174.3(2) C5-C4-C12-C11 177.8(2) O4-C37-C38-C42 1.8(3)

Table **6Y'.**6. Torsion angles [°] for **6Y'.** 

N2-C37-C38-C42	-177.5(2)	C51-C52-C53-C54	1.1(3)
O4-C37-C38-C39	-179.6(2)	C52-C53-C54-O6	179.3(2)
N2-C37-C38-C39	1.1(3)	C52-C53-C54-C55	-0.9(3)
C42-C38-C39-C40	179.3(2)	06-C54-C55-C56	-0.5(3)
C37-C38-C39-C40	0.7(3)	C53-C54-C55-C56	179.7(2)
C42-C38-C39-C45	-0.6(3)	O6-C54-C55-C60	179.52(18)
C37-C38-C39-C45	-179.21(19)	C53-C54-C55-C60	-0.4(3)
C38-C39-C40-C48	-179.9(2)	C60-C55-C56-C57	-0.2(3)
C45-C39-C40-C48	0.1(3)	C54-C55-C56-C57	179.8(2)
C38-C39-C40-C41	-1.7(3)	C55-C56-C57-C58	-0.2(3)
C45-C39-C40-C41	178.29(19)	C56-C57-C58-C59	0.0(3)
C48-C40-C41-O5	-1.6(3)	C57-C58-C59-C60	0.5(3)
C39-C40-C41-O5	-179.9(2)	C58-C59-C60-C55	-0.8(3)
C48-C40-C41-N2	179.0(2)	C58-C59-C60-C51	178.5(2)
C39-C40-C41-N2	0.7(3)	C56-C55-C60-C59	0.7(3)
C39-C38-C42-C43	-0.2(3)	C54-C55-C60-C59	-179.29(19)
C37-C38-C42-C43	178.4(2)	C56-C55-C60-C51	-178.69(19)
C38-C42-C43-C44	1.0(3)	C54-C55-C60-C51	1.3(3)
C42-C43-C44-C45	-1.0(3)	C52-C51-C60-C59	179.6(2)
C43-C44-C45-C39	0.2(3)	C50-C51-C60-C59	-0.4(3)
C43-C44-C45-C46	-179.8(2)	C52-C51-C60-C55	-1.1(3)
C40-C39-C45-C44	-179.36(19)	C50-C51-C60-C55	178.98(19)
C38-C39-C45-C44	0.6(3)	N2-C61-C62-C63	175.6(2)
C40-C39-C45-C46	0.7(3)	C61-C62-C63-C64	-79.0(3)
C38-C39-C45-C46	-179.38(19)	C62-C63-C64-C65	178.5(2)
C44-C45-C46-C47	179.1(2)	C63-C64-C65-C66	177.6(3)
C39-C45-C46-C47	-0.9(3)	O6-C67-C68-C69	165.6(2)
C44-C45-C46-C49	-1.1(3)	C67-C68-C69-C70	179.7(2)
C39-C45-C46-C49	178.86(19)	C68-C69-C70-C71	165.4(2)
C49-C46-C47-C48	-179.3(2)	C69-C70-C71-C72	-76.4(3)
C45-C46-C47-C48	0.4(3)	O1-C1-N1-C5	-177.4(2)
C39-C40-C48-C47	-0.6(3)	C2-C1-N1-C5	3.6(3)
C41-C40-C48-C47	-178.80(19)	O1-C1-N1-C25	4.0(3)
C46-C47-C48-C40	0.3(3)	C2-C1-N1-C25	-174.99(19)
C50-C51-C52-C53	179.8(2)	O2-C5-N1-C1	177.5(2)
C60-C51-C52-C53	-0.2(3)	C4-C5-N1-C1	-3.1(3)

O2-C5-N1-C25	-3.8(3)	O5-C41-N2-C61	5.1(3)
C4-C5-N1-C25	175.52(19)	C40-C41-N2-C61	-175.52(19)
C26-C25-N1-C1	100.5(2)	C62-C61-N2-C37	-94.7(2)
C26-C25-N1-C5	-78.2(3)	C62-C61-N2-C41	82.3(3)
O4-C37-N2-C41	178.5(2)	C17-C18-O3-C31	-11.7(3)
C38-C37-N2-C41	-2.1(3)	C19-C18-O3-C31	167.6(2)
O4-C37-N2-C61	-4.7(3)	C32-C31-O3-C18	-160.6(2)
C38-C37-N2-C61	174.64(19)	C53-C54-O6-C67	4.1(3)
O5-C41-N2-C37	-178.2(2)	C55-C54-O6-C67	-175.79(19)
C40-C41-N2-C37	1.2(3)	C68-C67-O6-C54	-178.99(19)

End of Crystallographic info for 6Y'

## **CRYSTALLOGRAPHIC MATERIAL FOR 7Y**

Crystallographic Material for 7y (7Y).

X-ray Experimental.

Table 7y.1. Crystallographic Data for 7y.

Table 7y.2. Fractional coordinates and equivalent isotropic thermal parameters  $(Å^2)$  for the non-hydrogen atoms of 7y.

Table 7y.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 7y.

Table 7y.4. Anisotropic thermal parameters for the non-hydrogen atoms of 7y.

Table 7y.5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of 7y.

Table 7y.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of 7y.

Crystallographic Material for 7y:

X-ray Experimental for  $C_{38}H_{41}NO_3$ : (**7y**) Crystals grew as long, yellow laths by vapor-vapor diffusion of Toluene and MeCN. The data crystal was cut from a larger crystal and had an approximate maximum dimensions of 0.15 x 0.10 x 0.04 mm. The data were collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength = 0.97741Å. A total of 190 frames of data were collected using  $\phi$ -scans with a scan range of 1° and a counting time of 4 seconds per frame for frames collected with a detector offset of 0.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection was performed using the Beamline Operating Software, BOS/B3. The unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.40.53.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup>, OLEX2<sup>5</sup> and WinGX.<sup>6</sup> The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). There are two molecules in the asymmetric unit. In one molecule, one of the heptyl side chains was disordered. The disorder affected the last six carbon atoms of the n-heptyl group.

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1262*P)^2 + (4.9486*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.175, with R(F) equal to 0.0573 and a goodness of fit, S, = 0.948. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>7</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>8</sup> All figures were generated using SHELXTL/PC.<sup>9</sup>

## **References**

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- 7) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 8) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 9) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table / 1.1. Crystal data and subclute term		
Empirical formula	C38 H41 N O3	
Formula weight	559.72	
Temperature	100.15 K	
Wavelength	0.97741 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 53.0277(7) Å	$\alpha = 90^{\circ}$ .
	b = 7.43870(10) Å	β= 94.613(2)°.
	c = 15.4897(3)  Å	$\gamma = 90^{\circ}$ .
Volume	6090.23(17) Å <sup>3</sup>	
Ζ	8	
Density (calculated)	1.221 Mg/m <sup>3</sup>	
Absorption coefficient	0.174 mm <sup>-1</sup>	
F(000)	2400	
Crystal size	$0.15 \ge 0.1 \ge 0.04 \text{ mm}^3$	
Theta range for data collection	2.120 to 26.304°.	
Index ranges	-43<=h<=47, -6<=k<=6,	-13<=1<=13
Reflections collected	7445	
Independent reflections	3474 [R(int) = 0.0175]	
Completeness to theta = $26.304^{\circ}$	73.0 %	
Absorption correction	Semi-empirical from equ	ivalents
Max. and min. transmission	1.00 and 0.210	
Refinement method	Full-matrix least-squares	on F <sup>2</sup>
Data / restraints / parameters	3474 / 1246 / 822	
Goodness-of-fit on F <sup>2</sup>	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0573, $wR2 = 0.15$	593
R indices (all data)	R1 = 0.0637, wR2 = 0.17	754
Extinction coefficient	n/a	
Largest diff. peak and hole	0.282 and -0.193 e.Å <sup>-3</sup>	

	Х	у	Z	U(eq)
01	3614(1)	3397(4)	10047(2)	50(1)
02	3795(1)	5776(4)	7472(2)	51(1)
O3	1373(1)	2849(4)	5337(2)	38(1)
N1	3705(1)	4638(5)	8767(3)	40(1)
C1	3540(1)	3790(6)	9308(4)	40(1)
C2	3278(1)	3434(6)	8937(3)	30(1)
C3	3110(1)	2655(5)	9449(3)	32(1)
C4	2861(1)	2355(5)	9124(3)	33(1)
C5	2783(1)	2784(5)	8292(3)	32(1)
C6	2950(1)	3597(6)	7740(3)	29(1)
C7	2877(1)	4113(6)	6878(3)	32(1)
C8	3052(1)	4906(5)	6385(3)	32(1)
C9	3301(1)	5178(5)	6720(3)	32(1)
C10	3379(1)	4721(6)	7550(3)	28(1)
C11	3635(1)	5077(6)	7911(4)	37(1)
C12	3204(1)	3908(5)	8081(3)	30(1)
C13	2620(1)	3855(6)	6524(3)	37(1)
C14	2405(1)	3649(5)	6258(3)	36(1)
C15	2142(1)	3419(6)	5995(3)	29(1)
C16	1990(1)	2649(5)	6572(3)	32(1)
C17	1730(1)	2449(5)	6372(3)	30(1)
C18	1621(1)	2962(5)	5587(3)	29(1)
C19	1774(1)	3681(5)	4945(3)	27(1)
C20	1670(1)	4169(6)	4116(3)	34(1)
C21	1816(1)	4896(5)	3526(3)	34(1)
C22	2074(1)	5166(5)	3739(3)	33(1)
C23	2182(1)	4711(5)	4540(3)	31(1)
C24	2035(1)	3934(5)	5161(3)	28(1)
C25	3957(1)	5028(7)	9151(3)	51(1)
C26	3973(1)	6685(7)	9712(3)	55(1)
C27	4232(1)	6891(8)	10170(3)	70(2)

Table 7Y.2. Atomic coordinates (  $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for 7Y. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C28	4257(1)	8318(8)	10853(3)	74(2)
C29	4511(1)	8341(9)	11375(4)	86(2)
C30	4536(1)	9612(9)	12116(4)	91(2)
C31	4789(1)	9563(11)	12631(4)	122(3)
C32	1203(1)	2463(6)	6004(3)	39(1)
C33	942(1)	2914(6)	5620(3)	39(1)
C34	854(1)	1852(6)	4828(3)	41(1)
C35	599(1)	2410(6)	4405(3)	45(1)
C36	521(1)	1503(6)	3553(3)	46(1)
C37	272(1)	2147(7)	3128(3)	60(2)
C38	203(1)	1350(8)	2250(3)	72(2)
O4	1400(1)	9576(4)	2838(2)	54(1)
O5	1166(1)	7153(4)	5329(2)	53(1)
O6	3589(1)	9873(4)	7771(2)	47(1)
N2	1286(1)	8302(5)	4075(3)	35(1)
C39	1462(1)	9106(6)	3580(4)	37(1)
C48	1593(1)	8024(6)	5337(3)	28(1)
C57	3187(1)	8884(6)	8066(3)	32(1)
C50	1780(1)	8774(5)	4843(3)	30(1)
C56	3344(1)	9658(6)	7461(3)	34(1)
C44	2035(1)	8968(6)	5214(3)	35(1)
C55	3248(1)	10113(5)	6654(3)	34(1)
C62	2929(1)	8591(6)	7806(3)	34(1)
C40	1719(1)	9322(6)	3992(3)	32(1)
C49	1337(1)	7775(6)	4931(3)	38(1)
C46	1912(1)	7650(5)	6529(3)	34(1)
C53	2831(1)	9075(6)	6968(3)	35(1)
C45	2092(1)	8394(6)	6061(3)	40(1)
C58	3281(1)	8406(6)	8902(3)	38(1)
C43	2216(1)	9722(5)	4675(3)	35(1)
C61	2775(1)	7806(6)	8422(3)	40(1)
C52	2572(1)	8817(6)	6691(3)	44(1)
C60	2876(1)	7375(6)	9229(3)	45(1)
C54	2991(1)	9849(5)	6413(3)	38(1)
C42	2144(1)	10219(6)	3857(3)	44(1)
C51	2354(1)	8596(6)	6440(3)	45(1)

C68	456(1)	7918(7)	501(3)	51(1)
C67	491(1)	6714(6)	1273(3)	48(1)
C59	3132(1)	7645(6)	9473(3)	45(1)
C41	1900(1)	10042(6)	3506(3)	40(1)
C47	1660(1)	7472(5)	6175(3)	37(1)
C63	1035(1)	7956(6)	3645(3)	49(1)
C66	731(1)	7107(7)	1873(3)	48(1)
C64	1024(1)	6174(6)	3172(3)	47(1)
C70	3768(1)	10319(9)	7154(4)	57(2)
C65	770(1)	5913(6)	2641(3)	52(1)
C69	222(1)	7573(7)	-91(3)	67(2)
C71	4037(2)	9966(19)	7459(8)	57(4)
C72	4116(2)	11156(12)	8208(6)	54(3)
C73	4386(2)	10806(14)	8557(7)	63(3)
C74	4478(2)	12040(15)	9296(7)	55(3)
C75	4741(2)	11690(20)	9681(9)	67(4)
C76	4823(4)	12910(30)	10437(11)	91(6)
C71A	4010(2)	10310(30)	7808(10)	61(5)
C72A	4234(2)	11008(16)	7412(7)	58(3)
C73A	4483(2)	10756(18)	7944(8)	64(4)
C74A	4509(3)	11750(20)	8790(9)	61(5)
C75A	4767(3)	11580(30)	9272(10)	62(5)
C76A	4799(5)	12690(40)	10080(12)	64(6)

O1-C1	1.216(5)	C18-C19	1.435(6)
O2-C11	1.240(5)	C19-C20	1.404(6)
O3-C18	1.341(5)	C19-C24	1.411(6)
O3-C32	1.455(5)	C20-H20	0.95
N1-C1	1.406(6)	C20-C21	1.358(6)
N1-C11	1.386(6)	C21-H21	0.95
N1-C25	1.451(5)	C21-C22	1.395(5)
C1-C2	1.482(6)	C22-H22	0.95
C2-C3	1.370(6)	C22-C23	1.368(5)
C2-C12	1.399(6)	C23-H23	0.95
С3-Н3	0.95	C23-C24	1.409(6)
C3-C4	1.391(5)	C25-H25A	0.99
C4-H4	0.95	C25-H25B	0.99
C4-C5	1.360(5)	C25-C26	1.506(6)
С5-Н5	0.95	C26-H26A	0.99
C5-C6	1.415(6)	C26-H26B	0.99
C6-C7	1.413(6)	C26-C27	1.503(6)
C6-C12	1.426(6)	C27-H27A	0.99
C7-C8	1.379(6)	С27-Н27В	0.99
C7-C13	1.441(6)	C27-C28	1.497(7)
С8-Н8	0.95	C28-H28A	0.99
C8-C9	1.393(5)	C28-H28B	0.99
С9-Н9	0.95	C28-C29	1.513(7)
C9-C10	1.361(6)	С29-Н29А	0.99
C10-C11	1.454(6)	C29-H29B	0.99
C10-C12	1.424(6)	C29-C30	1.485(7)
C13-C14	1.193(6)	C30-H30A	0.99
C14-C15	1.428(6)	C30-H30B	0.99
C15-C16	1.377(6)	C30-C31	1.505(7)
C15-C24	1.422(6)	C31-H31A	0.98
С16-Н16	0.95	C31-H31B	0.98
C16-C17	1.395(5)	C31-H31C	0.98
C17-H17	0.95	C32-H32A	0.99
C17-C18	1.359(6)	C32-H32B	0.99

Table 7Y.3. Bond lengths [Å] and angles  $[\circ]$  for 7Y.

C32-C33	1.499(5)	C44-C45	1.390(6)
С33-Н33А	0.99	C44-C43	1.436(6)
С33-Н33В	0.99	С55-Н55	0.95
C33-C34	1.502(6)	C55-C54	1.398(6)
C34-H34A	0.99	C62-C53	1.406(6)
C34-H34B	0.99	C62-C61	1.429(6)
C34-C35	1.510(6)	C40-C41	1.377(6)
С35-Н35А	0.99	C46-H46	0.95
С35-Н35В	0.99	C46-C45	1.360(6)
C35-C36	1.511(6)	C46-C47	1.412(6)
С36-Н36А	0.99	C53-C52	1.421(6)
С36-Н36В	0.99	C53-C54	1.380(6)
C36-C37	1.503(6)	C45-C51	1.470(7)
С37-Н37А	0.99	С58-Н58	0.95
С37-Н37В	0.99	C58-C59	1.356(6)
C37-C38	1.502(6)	С43-Н43	0.95
C38-H38A	0.98	C43-C42	1.343(6)
C38-H38B	0.98	С61-Н61	0.95
C38-H38C	0.98	C61-C60	1.358(6)
O4-C39	1.222(5)	C52-C51	1.203(6)
O5-C49	1.229(5)	С60-Н60	0.95
O6-C56	1.354(5)	C60-C59	1.393(6)
O6-C70	1.438(6)	С54-Н54	0.95
N2-C39	1.393(6)	C42-H42	0.95
N2-C49	1.389(6)	C42-C41	1.370(6)
N2-C63	1.460(5)	C68-H68A	0.99
C39-C40	1.465(6)	C68-H68B	0.99
C48-C50	1.417(6)	C68-C67	1.493(6)
C48-C49	1.459(6)	C68-C69	1.505(6)
C48-C47	1.380(6)	С67-Н67А	0.99
C57-C56	1.425(6)	С67-Н67В	0.99
C57-C62	1.415(6)	C67-C66	1.542(6)
C57-C58	1.396(6)	С59-Н59	0.95
C50-C44	1.430(6)	C41-H41	0.95
C50-C40	1.393(6)	C47-H47	0.95
C56-C55	1.354(6)	С63-Н63А	0.99

С63-Н63В	0.99	C74-H74B	0.99
C63-C64	1.513(6)	C74-C75	1.496(12)
С66-Н66А	0.99	С75-Н75А	0.99
С66-Н66В	0.99	С75-Н75В	0.99
C66-C65	1.486(6)	C75-C76	1.520(14)
C64-H64A	0.99	С76-Н76А	0.98
C64-H64B	0.99	С76-Н76В	0.98
C64-C65	1.530(6)	С76-Н76С	0.98
C70-C71	1.493(11)	C71A-H71C	0.99
C70-C71A	1.570(14)	C71A-H71D	0.99
С70-Н70А	1.03(4)	C71A-C72A	1.478(15)
С70-Н70В	1.09(5)	С72А-Н72С	0.99
С65-Н65А	0.99	C72A-H72D	0.99
С65-Н65В	0.99	C72A-C73A	1.509(11)
С69-Н69А	0.98	С73А-Н73С	0.99
С69-Н69В	0.98	C73A-H73D	0.99
С69-Н69С	0.98	C73A-C74A	1.500(14)
C71-H71A	0.99	C74A-H74C	0.99
С71-Н71В	0.99	C74A-H74D	0.99
C71-C72	1.491(12)	C74A-C75A	1.509(15)
С72-Н72А	0.99	С75А-Н75С	0.99
С72-Н72В	0.99	C75A-H75D	0.99
C72-C73	1.516(10)	C75A-C76A	1.501(16)
С73-Н73А	0.99	C76A-H76D	0.98
С73-Н73В	0.99	С76А-Н76Е	0.98
C73-C74	1.516(12)	C76A-H76F	0.98
C74-H74A	0.99		
C18-O3-C32	117.2(3)	C3-C2-C12	120.5(4)
C1-N1-C25	116.3(4)	C12-C2-C1	120.4(5)
C11-N1-C1	123.1(4)	С2-С3-Н3	119.9
C11-N1-C25	120.6(4)	C2-C3-C4	120.2(4)
01-C1-N1	120.1(4)	С4-С3-Н3	119.9
O1-C1-C2	122.7(5)	С3-С4-Н4	119.6
N1-C1-C2	117.1(5)	C5-C4-C3	120.8(4)
C3-C2-C1	119.1(4)	С5-С4-Н4	119.6

С4-С5-Н5	119.5	O3-C18-C19	114.6(4)
C4-C5-C6	121.0(4)	C17-C18-C19	120.0(4)
С6-С5-Н5	119.5	C20-C19-C18	121.9(4)
C5-C6-C12	117.6(4)	C20-C19-C24	119.2(4)
C7-C6-C5	123.5(4)	C24-C19-C18	118.9(4)
C7-C6-C12	118.9(4)	С19-С20-Н20	119.5
C6-C7-C13	120.0(4)	C21-C20-C19	121.0(4)
C8-C7-C6	119.8(4)	С21-С20-Н20	119.5
C8-C7-C13	120.2(4)	С20-С21-Н21	120.0
С7-С8-Н8	119.5	C20-C21-C22	120.0(4)
C7-C8-C9	120.9(4)	С22-С21-Н21	120.0
С9-С8-Н8	119.5	С21-С22-Н22	119.7
С8-С9-Н9	119.3	C23-C22-C21	120.6(4)
C10-C9-C8	121.5(4)	С23-С22-Н22	119.7
С10-С9-Н9	119.3	С22-С23-Н23	119.8
C9-C10-C11	121.5(5)	C22-C23-C24	120.5(4)
C9-C10-C12	119.3(4)	С24-С23-Н23	119.8
C12-C10-C11	119.2(4)	C19-C24-C15	119.6(4)
O2-C11-N1	118.9(4)	C23-C24-C15	121.8(4)
O2-C11-C10	121.5(5)	C23-C24-C19	118.6(4)
N1-C11-C10	119.5(5)	N1-C25-H25A	108.8
C2-C12-C6	119.8(5)	N1-C25-H25B	108.8
C2-C12-C10	120.5(4)	N1-C25-C26	113.9(4)
C10-C12-C6	119.7(4)	H25A-C25-H25B	107.7
C14-C13-C7	177.8(5)	С26-С25-Н25А	108.8
C13-C14-C15	176.4(5)	С26-С25-Н25В	108.8
C16-C15-C14	118.2(4)	С25-С26-Н26А	109.4
C16-C15-C24	119.2(4)	С25-С26-Н26В	109.4
C24-C15-C14	122.6(4)	H26A-C26-H26B	108.0
С15-С16-Н16	119.3	C27-C26-C25	111.1(4)
C15-C16-C17	121.4(4)	С27-С26-Н26А	109.4
С17-С16-Н16	119.3	С27-С26-Н26В	109.4
С16-С17-Н17	119.6	С26-С27-Н27А	108.4
C18-C17-C16	120.8(4)	С26-С27-Н27В	108.4
С18-С17-Н17	119.6	H27A-C27-H27B	107.4
O3-C18-C17	125.3(4)	C28-C27-C26	115.6(4)

С28-С27-Н27А	108.4	C34-C33-H33A	108.5
С28-С27-Н27В	108.4	С34-С33-Н33В	108.5
C27-C28-H28A	108.7	С33-С34-Н34А	108.6
C27-C28-H28B	108.7	C33-C34-H34B	108.6
C27-C28-C29	114.3(5)	C33-C34-C35	114.8(4)
H28A-C28-H28B	107.6	H34A-C34-H34B	107.5
C29-C28-H28A	108.7	C35-C34-H34A	108.6
C29-C28-H28B	108.7	C35-C34-H34B	108.6
C28-C29-H29A	108.3	C34-C35-H35A	108.4
С28-С29-Н29В	108.3	С34-С35-Н35В	108.4
H29A-C29-H29B	107.4	C34-C35-C36	115.5(4)
C30-C29-C28	116.1(5)	H35A-C35-H35B	107.5
С30-С29-Н29А	108.3	С36-С35-Н35А	108.4
С30-С29-Н29В	108.3	С36-С35-Н35В	108.4
С29-С30-Н30А	108.6	С35-С36-Н36А	108.7
С29-С30-Н30В	108.6	С35-С36-Н36В	108.7
C29-C30-C31	114.5(5)	H36A-C36-H36B	107.6
H30A-C30-H30B	107.6	C37-C36-C35	114.3(4)
С31-С30-Н30А	108.6	С37-С36-Н36А	108.7
С31-С30-Н30В	108.6	С37-С36-Н36В	108.7
C30-C31-H31A	109.5	С36-С37-Н37А	108.7
С30-С31-Н31В	109.5	С36-С37-Н37В	108.7
С30-С31-Н31С	109.5	H37A-C37-H37B	107.6
H31A-C31-H31B	109.5	C38-C37-C36	114.4(4)
H31A-C31-H31C	109.5	С38-С37-Н37А	108.7
H31B-C31-H31C	109.5	С38-С37-Н37В	108.7
O3-C32-H32A	110.5	С37-С38-Н38А	109.5
ОЗ-С32-Н32В	110.5	С37-С38-Н38В	109.5
O3-C32-C33	106.2(4)	С37-С38-Н38С	109.5
H32A-C32-H32B	108.7	H38A-C38-H38B	109.5
С33-С32-Н32А	110.5	H38A-C38-H38C	109.5
С33-С32-Н32В	110.5	H38B-C38-H38C	109.5
С32-С33-Н33А	108.5	C56-O6-C70	117.0(4)
С32-С33-Н33В	108.5	C39-N2-C63	116.9(4)
C32-C33-C34	115.1(4)	C49-N2-C39	123.8(4)
H33A-C33-H33B	107.5	C49-N2-C63	119.2(4)

O4-C39-N2	119.8(4)	C44-C45-C51	118.2(5)
O4-C39-C40	123.5(5)	C46-C45-C44	121.3(4)
N2-C39-C40	116.7(5)	C46-C45-C51	120.5(5)
C50-C48-C49	119.0(4)	С57-С58-Н58	119.1
C47-C48-C50	119.1(4)	C59-C58-C57	121.8(4)
C47-C48-C49	121.8(5)	С59-С58-Н58	119.1
C62-C57-C56	118.6(4)	C44-C43-H43	119.8
C58-C57-C56	122.0(4)	C42-C43-C44	120.4(4)
C58-C57-C62	119.4(5)	С42-С43-Н43	119.8
C48-C50-C44	120.2(4)	С62-С61-Н61	119.8
C40-C50-C48	120.4(4)	C60-C61-C62	120.3(4)
C40-C50-C44	119.4(5)	C60-C61-H61	119.8
O6-C56-C57	114.0(4)	C51-C52-C53	178.7(5)
C55-C56-O6	125.2(5)	С61-С60-Н60	119.3
C55-C56-C57	120.8(4)	C61-C60-C59	121.4(5)
C50-C44-C43	117.3(4)	С59-С60-Н60	119.3
C45-C44-C50	118.4(5)	С55-С54-Н54	119.1
C45-C44-C43	124.4(4)	C53-C54-C55	121.8(4)
С56-С55-Н55	120.1	С53-С54-Н54	119.1
C56-C55-C54	119.8(4)	С43-С42-Н42	118.9
С54-С55-Н55	120.1	C43-C42-C41	122.1(5)
C57-C62-C61	117.7(4)	C41-C42-H42	118.9
C53-C62-C57	119.9(5)	C52-C51-C45	175.0(5)
C53-C62-C61	122.3(4)	H68A-C68-H68B	107.5
C50-C40-C39	121.2(5)	C67-C68-H68A	108.4
C41-C40-C39	118.0(5)	C67-C68-H68B	108.4
C41-C40-C50	120.8(4)	C67-C68-C69	115.4(4)
O5-C49-N2	119.2(5)	C69-C68-H68A	108.4
O5-C49-C48	122.0(5)	C69-C68-H68B	108.4
N2-C49-C48	118.7(5)	С68-С67-Н67А	108.7
С45-С46-Н46	119.6	С68-С67-Н67В	108.7
C45-C46-C47	120.9(4)	C68-C67-C66	114.3(4)
С47-С46-Н46	119.6	H67A-C67-H67B	107.6
C62-C53-C52	121.2(5)	С66-С67-Н67А	108.7
C54-C53-C62	118.9(4)	С66-С67-Н67В	108.7
C54-C53-C52	119.8(5)	C58-C59-C60	119.3(5)

С58-С59-Н59	120.3	C66-C65-H65A	108.6
С60-С59-Н59	120.3	С66-С65-Н65В	108.6
C40-C41-H41	120.0	С64-С65-Н65А	108.6
C42-C41-C40	120.0(5)	С64-С65-Н65В	108.6
C42-C41-H41	120.0	H65A-C65-H65B	107.6
C48-C47-C46	120.1(4)	С68-С69-Н69А	109.5
С48-С47-Н47	119.9	С68-С69-Н69В	109.5
С46-С47-Н47	119.9	С68-С69-Н69С	109.5
N2-C63-H63A	109.2	H69A-C69-H69B	109.5
N2-C63-H63B	109.2	Н69А-С69-Н69С	109.5
N2-C63-C64	112.0(3)	H69B-C69-H69C	109.5
H63A-C63-H63B	107.9	C70-C71-H71A	109.7
С64-С63-Н63А	109.2	C70-C71-H71B	109.7
С64-С63-Н63В	109.2	H71A-C71-H71B	108.2
С67-С66-Н66А	108.5	C72-C71-C70	110.0(9)
С67-С66-Н66В	108.5	C72-C71-H71A	109.7
H66A-C66-H66B	107.5	C72-C71-H71B	109.7
C65-C66-C67	115.2(4)	С71-С72-Н72А	109.2
С65-С66-Н66А	108.5	С71-С72-Н72В	109.3
С65-С66-Н66В	108.5	C71-C72-C73	111.8(8)
C63-C64-H64A	109.2	H72A-C72-H72B	107.9
C63-C64-H64B	109.2	С73-С72-Н72А	109.2
C63-C64-C65	111.8(4)	С73-С72-Н72В	109.2
H64A-C64-H64B	107.9	С72-С73-Н73А	108.8
C65-C64-H64A	109.2	С72-С73-Н73В	108.8
C65-C64-H64B	109.2	H73A-C73-H73B	107.7
O6-C70-C71	114.5(7)	C74-C73-C72	113.7(8)
O6-C70-C71A	96.8(6)	С74-С73-Н73А	108.8
О6-С70-Н70А	113(2)	С74-С73-Н73В	108.8
O6-C70-H70B	108(2)	С73-С74-Н74А	108.4
С71-С70-Н70А	112(2)	С73-С74-Н74В	108.4
С71-С70-Н70В	104(2)	H74A-C74-H74B	107.5
C71A-C70-H70A	109(2)	C75-C74-C73	115.3(9)
С71А-С70-Н70В	126(3)	С75-С74-Н74А	108.4
H70A-C70-H70B	104(3)	С75-С74-Н74В	108.4
C66-C65-C64	114.6(4)	С74-С75-Н75А	108.8

С74-С75-Н75В	108.8	C72A-C73A-H73D	108.4
C74-C75-C76	113.7(12)	H73C-C73A-H73D	107.4
Н75А-С75-Н75В	107.7	C74A-C73A-C72A	115.7(10)
С76-С75-Н75А	108.8	С74А-С73А-Н73С	108.4
С76-С75-Н75В	108.8	C74A-C73A-H73D	108.4
С75-С76-Н76А	109.5	С73А-С74А-Н74С	108.7
С75-С76-Н76В	109.5	C73A-C74A-H74D	108.7
С75-С76-Н76С	109.5	C73A-C74A-C75A	114.1(11)
Н76А-С76-Н76В	109.5	H74C-C74A-H74D	107.6
H76A-C76-H76C	109.5	С75А-С74А-Н74С	108.7
Н76В-С76-Н76С	109.5	C75A-C74A-H74D	108.7
С70-С71А-Н71С	109.2	С74А-С75А-Н75С	108.8
C70-C71A-H71D	109.2	C74A-C75A-H75D	108.8
H71C-C71A-H71D	107.9	H75C-C75A-H75D	107.7
C72A-C71A-C70	112.0(11)	C76A-C75A-C74A	113.8(14)
C72A-C71A-H71C	109.2	С76А-С75А-Н75С	108.8
C72A-C71A-H71D	109.2	C76A-C75A-H75D	108.8
C71A-C72A-H72C	108.5	C75A-C76A-H76D	109.5
C71A-C72A-H72D	108.5	С75А-С76А-Н76Е	109.5
C71A-C72A-C73A	115.2(10)	C75A-C76A-H76F	109.5
H72C-C72A-H72D	107.5	H76D-C76A-H76E	109.5
С73А-С72А-Н72С	108.5	H76D-C76A-H76F	109.5
C73A-C72A-H72D	108.5	H76E-C76A-H76F	109.5
С72А-С73А-Н73С	108.4		

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
01	44(2)	64(2)	41(2)	9(2)	-7(2)	1(2)
O2	36(2)	64(2)	52(2)	1(2)	1(2)	-11(2)
O3	24(2)	48(2)	40(2)	2(2)	-5(2)	-2(2)
N1	26(2)	56(3)	36(3)	5(2)	-11(2)	-1(2)
C1	37(3)	40(3)	44(3)	0(3)	3(3)	6(2)
C2	33(3)	28(3)	30(3)	1(2)	2(3)	3(2)
C3	40(3)	29(3)	25(3)	-1(2)	-1(3)	3(2)
C4	32(3)	30(3)	37(3)	-2(2)	-1(3)	4(2)
C5	23(3)	35(3)	36(3)	-4(2)	-3(3)	1(2)
C6	30(3)	27(3)	30(3)	-3(2)	2(3)	3(2)
C7	40(3)	28(3)	29(3)	-3(2)	2(3)	5(2)
C8	41(3)	31(3)	21(3)	2(2)	-6(3)	7(2)
С9	35(3)	30(3)	31(3)	-1(2)	-3(3)	5(2)
C10	27(3)	32(3)	24(3)	-2(2)	-11(2)	3(2)
C11	33(3)	40(3)	37(3)	-4(3)	-6(3)	5(2)
C12	38(3)	20(3)	33(3)	-1(2)	6(3)	4(2)
C13	42(3)	32(3)	36(3)	0(2)	-2(3)	6(3)
C14	41(3)	28(3)	36(3)	1(2)	-4(3)	7(2)
C15	28(3)	27(3)	28(3)	-5(2)	-8(3)	4(2)
C16	37(3)	28(3)	29(3)	-1(2)	-6(3)	8(2)
C17	30(3)	24(3)	37(3)	-1(2)	1(3)	3(2)
C18	27(3)	22(3)	37(3)	-1(2)	-6(3)	2(2)
C19	21(3)	25(3)	34(3)	-3(2)	-6(3)	1(2)
C20	33(3)	30(3)	37(3)	0(2)	-9(3)	2(2)
C21	38(3)	31(3)	32(3)	-3(2)	-8(3)	0(2)
C22	41(3)	28(3)	29(3)	-2(2)	3(3)	-1(2)
C23	25(3)	27(3)	39(3)	-6(2)	-2(3)	2(2)
C24	33(3)	24(3)	25(3)	-5(2)	-1(3)	4(2)
C25	23(3)	76(4)	52(3)	3(3)	-12(3)	-5(2)
C26	44(3)	66(4)	52(3)	10(3)	-17(3)	-18(3)
C27	50(3)	107(4)	53(3)	-4(3)	-6(3)	-32(3)

Table 7Y.4. Anisotropic displacement parameters  $(Å^2 x \ 10^3)$  for 7Y. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [  $h^2 \ a^{*2}U^{11} + ... + 2 \ h \ k \ a^* \ b^* \ U^{12}$ ]
C28	52(3)	101(4)	66(4)	-4(3)	-7(3)	-41(3)
C29	56(3)	135(5)	67(4)	-25(4)	6(3)	-39(3)
C30	70(4)	130(5)	71(4)	-22(4)	-6(3)	-25(4)
C31	78(4)	197(7)	89(5)	-64(5)	-17(4)	-21(4)
C32	28(3)	47(3)	42(3)	-3(2)	-5(3)	0(2)
C33	37(3)	44(3)	37(3)	-4(2)	2(2)	-4(2)
C34	28(3)	49(3)	44(3)	2(3)	-5(2)	-1(2)
C35	36(3)	51(3)	48(3)	-6(3)	-2(3)	0(2)
C36	30(3)	56(3)	50(3)	-5(3)	-10(3)	-4(2)
C37	40(3)	80(4)	56(4)	-7(3)	-7(3)	0(3)
C38	50(3)	92(4)	69(4)	-12(3)	-26(3)	4(3)
O4	64(2)	60(2)	38(2)	6(2)	-7(2)	7(2)
O5	41(2)	58(2)	61(2)	-7(2)	14(2)	-7(2)
O6	36(2)	49(2)	54(2)	2(2)	-7(2)	-2(2)
N2	24(2)	46(2)	33(3)	-4(2)	-11(2)	2(2)
C39	45(3)	33(3)	33(3)	-2(3)	-6(3)	8(2)
C48	32(3)	29(3)	22(3)	-4(2)	-8(3)	5(2)
C57	36(3)	30(3)	29(3)	-2(2)	-6(3)	5(2)
C50	35(3)	23(3)	33(3)	-4(2)	2(3)	7(2)
C56	38(3)	34(3)	27(3)	-3(2)	-12(3)	5(2)
C44	43(3)	29(3)	33(3)	-6(2)	-2(3)	7(2)
C55	36(3)	32(3)	35(3)	-2(2)	3(3)	-1(2)
C62	39(3)	27(3)	34(3)	-6(2)	-1(3)	7(2)
C40	40(3)	29(3)	26(3)	-2(2)	4(3)	3(2)
C49	47(3)	35(3)	32(3)	-7(3)	4(3)	5(3)
C46	53(3)	28(3)	18(3)	-1(2)	-14(3)	5(2)
C53	31(3)	28(3)	45(3)	-7(3)	-11(3)	-1(2)
C45	52(3)	30(3)	38(3)	-5(3)	1(3)	2(2)
C58	45(3)	34(3)	34(3)	-4(3)	-3(3)	6(2)
C43	24(3)	29(3)	51(3)	-4(3)	-5(3)	2(2)
C61	34(3)	31(3)	53(3)	-6(3)	-1(3)	3(2)
C52	48(3)	30(3)	54(4)	-5(3)	-5(3)	-2(3)
C60	56(3)	30(3)	51(3)	-1(3)	7(3)	9(2)
C54	52(3)	25(3)	34(3)	-4(2)	-7(3)	3(2)
C42	49(3)	39(3)	44(3)	-2(3)	0(3)	5(2)
C51	56(3)	29(3)	50(4)	-2(3)	-2(3)	1(3)

C68	45(3)	65(3)	44(3)	2(3)	-4(3)	3(3)
C67	38(3)	57(3)	51(3)	4(3)	2(3)	4(2)
C59	62(3)	38(3)	33(3)	-4(3)	-2(3)	12(3)
C41	46(3)	35(3)	38(3)	-7(2)	1(3)	5(2)
C47	51(3)	26(3)	34(3)	-4(2)	4(3)	2(2)
C63	34(3)	57(3)	53(3)	-13(3)	-11(3)	7(2)
C66	30(3)	66(3)	46(3)	12(3)	-1(3)	1(2)
C64	36(3)	55(3)	49(3)	-7(3)	-12(3)	1(2)
C70	39(3)	58(4)	74(4)	5(4)	0(3)	-9(3)
C65	51(3)	50(3)	54(3)	-3(3)	-3(3)	-1(2)
C69	57(3)	91(4)	51(4)	5(3)	-13(3)	4(3)
C71	48(5)	56(7)	70(7)	-6(6)	13(5)	-11(5)
C72	44(5)	59(6)	60(6)	-5(5)	2(5)	1(5)
C73	54(6)	66(6)	69(6)	8(5)	-3(5)	-2(5)
C74	42(5)	62(6)	60(6)	8(5)	0(5)	1(5)
C75	54(6)	76(8)	69(9)	3(7)	-9(6)	7(6)
C76	76(9)	98(10)	95(13)	-17(10)	-15(9)	-11(8)
C71A	57(6)	70(10)	57(9)	-17(8)	10(6)	-14(7)
C72A	52(5)	59(7)	61(7)	1(6)	-2(5)	-8(6)
C73A	51(6)	72(8)	67(7)	2(6)	-7(6)	3(6)
C74A	49(7)	63(8)	68(8)	4(7)	-7(7)	14(7)
C75A	53(7)	71(8)	60(9)	-2(8)	-5(6)	18(6)
C76A	74(13)	63(13)	53(12)	8(9)	-6(9)	16(10)

	х	у	Z	U(eq)
H3	3163	2319	10027	38
H4	2744	1844	9488	40
H5	2613	2534	8078	38
H8	3002	5272	5809	38
H9	3419	5693	6361	39
H16	2063	2245	7117	38
H17	1629	1948	6789	36
H20	1494	3988	3966	40
H21	1743	5221	2968	41
H22	2175	5671	3322	39
H23	2357	4920	4680	37
H25A	4072	5181	8681	61
H25B	4019	3985	9504	61
H26A	3933	7758	9348	66
H26B	3846	6602	10145	66
H27A	4282	5726	10441	85
H27B	4353	7158	9732	85
H28A	4123	8143	11253	88
H28B	4229	9505	10572	88
H29A	4546	7113	11600	103
H29B	4643	8636	10980	103
H30A	4403	9338	12508	109
H30B	4506	10847	11893	109
H31A	4923	9763	12244	184
H31B	4813	8386	12911	184
H31C	4795	10506	13074	184
H32A	1247	3203	6525	47
H32B	1214	1179	6170	47
H33A	937	4208	5469	47
H33B	822	2720	6067	47

Table 7Y.5. Hydrogen coordinates (  $x\;10^4$  ) and isotropic displacement parameters (Å  $^2x\;10\;^3$  ) for 7Y.

H34A	845	567	4990	49
H34B	981	1968	4398	49
H35A	602	3726	4309	54
H35B	469	2160	4813	54
H36A	654	1706	3151	55
H36B	510	192	3652	55
H37A	137	1857	3510	71
H37B	279	3471	3071	71
H38A	327	1727	1849	108
H38B	34	1768	2034	108
H38C	203	36	2293	108
H55	3355	10612	6253	41
H46	1957	7244	7102	41
H58	3455	8620	9077	46
H43	2386	9871	4897	42
H61	2601	7585	8267	48
H60	2771	6878	9635	54
H54	2925	10211	5853	45
H42	2268	10710	3512	53
H68A	605	7793	162	62
H68B	451	9178	706	62
H67A	498	5454	1071	58
Н67В	341	6831	1613	58
Н59	3201	7300	10033	54
H41	1856	10416	2927	48
H47	1536	6971	6513	44
H63A	991	8935	3227	58
H63B	909	7958	4082	58
H66A	880	7006	1529	57
H66B	723	8366	2077	57
H64A	1049	5186	3598	57
H64B	1162	6117	2782	57
H65A	758	4648	2443	62
Н65В	632	6122	3022	62
H69A	220	8377	-593	101
H69B	71	7794	222	101

H69C	221	6321	-289	101
H71A	4058	8692	7635	69
H71B	4146	10194	6982	69
H72A	4002	10954	8675	65
H72B	4098	12428	8024	65
H73A	4401	9545	8760	76
H73B	4498	10951	8080	76
H74A	4469	13296	9084	66
H74B	4361	11933	9759	66
H75A	4860	11838	9226	81
H75B	4753	10424	9881	81
H76A	4996	12614	10658	136
H76B	4817	14169	10242	136
H76C	4709	12753	10899	136
H71C	3978	11048	8319	73
H71D	4044	9061	8010	73
H72C	4209	12309	7299	69
H72D	4245	10410	6845	69
H73C	4506	9457	8064	76
H73D	4621	11143	7593	76
H74C	4381	11294	9163	73
H74D	4474	13038	8678	73
H75C	4796	10298	9429	75
H75D	4897	11932	8882	75
H76D	4970	12519	10359	96
H76E	4775	13966	9930	96
H76F	4674	12330	10478	96
H70A	3744(	7) 11600(	6900(2	20) 47(14)
H70B	3732(	8) 9450(	70) 6590(	30) 81(17)

Table **7Y.6**. Torsion angles [°] for **7Y.** 

01-C1-C2-C3	1.1(6)	C11-N1-C1-O1	178.1(4)
01-C1-C2-C12	-179.7(4)	C11-N1-C1-C2	-2.6(6)
O3-C18-C19-C20	-1.8(5)	C11-N1-C25-C26	101.1(5)
O3-C18-C19-C24	177.0(3)	C11-C10-C12-C2	-0.8(6)
O3-C32-C33-C34	60.8(5)	C11-C10-C12-C6	178.3(3)
N1-C1-C2-C3	-178.2(4)	C12-C2-C3-C4	-1.1(6)
N1-C1-C2-C12	1.0(6)	C12-C6-C7-C8	-0.2(6)
N1-C25-C26-C27	173.4(4)	C12-C6-C7-C13	-178.5(3)
C1-N1-C11-O2	-177.9(4)	C12-C10-C11-O2	179.7(4)
C1-N1-C11-C10	2.5(6)	C12-C10-C11-N1	-0.7(6)
C1-N1-C25-C26	-79.6(5)	C13-C7-C8-C9	179.5(4)
C1-C2-C3-C4	178.1(4)	C14-C15-C16-C17	177.4(4)
C1-C2-C12-C6	-178.5(3)	C14-C15-C24-C19	-179.5(4)
C1-C2-C12-C10	0.7(6)	C14-C15-C24-C23	-0.1(6)
C2-C3-C4-C5	1.7(6)	C15-C16-C17-C18	2.0(6)
C3-C2-C12-C6	0.7(6)	C16-C15-C24-C19	1.3(6)
C3-C2-C12-C10	179.8(3)	C16-C15-C24-C23	-179.3(4)
C3-C4-C5-C6	-1.9(6)	C16-C17-C18-O3	-179.0(3)
C4-C5-C6-C7	-178.4(4)	C16-C17-C18-C19	1.4(6)
C4-C5-C6-C12	1.5(6)	C17-C18-C19-C20	177.7(4)
C5-C6-C7-C8	179.7(4)	C17-C18-C19-C24	-3.4(6)
C5-C6-C7-C13	1.4(6)	C18-O3-C32-C33	164.5(3)
C5-C6-C12-C2	-0.9(6)	C18-C19-C20-C21	178.1(4)
C5-C6-C12-C10	179.9(3)	C18-C19-C24-C15	2.0(6)
C6-C7-C8-C9	1.2(6)	C18-C19-C24-C23	-177.4(3)
C7-C6-C12-C2	179.0(3)	C19-C20-C21-C22	0.1(6)
C7-C6-C12-C10	-0.2(6)	C20-C19-C24-C15	-179.1(3)
C7-C8-C9-C10	-1.9(6)	C20-C19-C24-C23	1.5(6)
C8-C9-C10-C11	-177.2(4)	C20-C21-C22-C23	-0.2(6)
C8-C9-C10-C12	1.6(6)	C21-C22-C23-C24	1.0(6)
C9-C10-C11-O2	-1.5(6)	C22-C23-C24-C15	178.9(4)
C9-C10-C11-N1	178.1(4)	C22-C23-C24-C19	-1.7(6)
C9-C10-C12-C2	-179.7(4)	C24-C15-C16-C17	-3.4(6)
C9-C10-C12-C6	-0.5(6)	C24-C19-C20-C21	-0.8(6)

C25-N1-C1-O1	-1.2(6)	C50-C48-C49-N2	-0.7(6)
C25-N1-C1-C2	178.1(4)	C50-C48-C47-C46	-0.3(6)
C25-N1-C11-O2	1.4(6)	C50-C44-C45-C46	0.6(6)
C25-N1-C11-C10	-178.2(3)	C50-C44-C45-C51	180.0(3)
C25-C26-C27-C28	-170.5(4)	C50-C44-C43-C42	0.1(6)
C26-C27-C28-C29	172.9(4)	C50-C40-C41-C42	0.3(6)
C27-C28-C29-C30	-174.1(5)	C56-O6-C70-C71	-161.3(6)
C28-C29-C30-C31	178.7(5)	C56-O6-C70-C71A	-177.1(9)
C32-O3-C18-C17	12.0(5)	C56-C57-C62-C53	-0.5(6)
C32-O3-C18-C19	-168.5(3)	C56-C57-C62-C61	179.7(4)
C32-C33-C34-C35	-175.5(4)	C56-C57-C58-C59	-179.0(4)
C33-C34-C35-C36	173.4(4)	C56-C55-C54-C53	-2.2(6)
C34-C35-C36-C37	-177.3(4)	C44-C50-C40-C39	178.5(3)
C35-C36-C37-C38	175.6(4)	C44-C50-C40-C41	0.1(6)
O4-C39-C40-C50	179.6(4)	C44-C43-C42-C41	0.3(6)
O4-C39-C40-C41	-2.1(6)	C62-C57-C56-O6	-179.6(3)
O6-C56-C55-C54	-179.1(3)	C62-C57-C56-C55	0.4(6)
O6-C70-C71-C72	-64.8(11)	C62-C57-C58-C59	0.8(6)
O6-C70-C71A-C72A	-170.9(13)	C62-C53-C54-C55	2.0(6)
N2-C39-C40-C50	-1.1(6)	C62-C61-C60-C59	-1.3(6)
N2-C39-C40-C41	177.3(4)	C40-C50-C44-C45	-179.3(4)
N2-C63-C64-C65	-173.6(4)	C40-C50-C44-C43	-0.3(6)
C39-N2-C49-O5	176.5(4)	C49-N2-C39-O4	-178.0(4)
C39-N2-C49-C48	-1.8(6)	C49-N2-C39-C40	2.7(6)
C39-N2-C63-C64	86.1(5)	C49-N2-C63-C64	-92.1(5)
C39-C40-C41-C42	-178.1(4)	C49-C48-C50-C44	-177.5(3)
C48-C50-C44-C45	0.4(6)	C49-C48-C50-C40	2.2(6)
C48-C50-C44-C43	179.4(4)	C49-C48-C47-C46	176.6(4)
C48-C50-C40-C39	-1.3(6)	C53-C62-C61-C60	-179.4(4)
C48-C50-C40-C41	-179.6(4)	C45-C44-C43-C42	179.1(4)
C57-C56-C55-C54	0.9(6)	C45-C46-C47-C48	1.3(6)
C57-C62-C53-C52	-179.2(4)	C58-C57-C56-O6	0.2(6)
C57-C62-C53-C54	-0.6(6)	C58-C57-C56-C55	-179.9(4)
C57-C62-C61-C60	0.3(6)	C58-C57-C62-C53	179.7(4)
C57-C58-C59-C60	-1.8(6)	C58-C57-C62-C61	-0.1(6)
C50-C48-C49-O5	-179.0(4)	C43-C44-C45-C46	-178.3(4)

C43-C44-C45-C51	1.0(6)	C63-N2-C39-C40	-175.3(3)
C43-C42-C41-C40	-0.5(6)	C63-N2-C49-O5	-5.5(6)
C61-C62-C53-C52	0.5(6)	C63-N2-C49-C48	176.2(3)
C61-C62-C53-C54	179.1(4)	C63-C64-C65-C66	69.6(5)
C61-C60-C59-C58	2.1(6)	C70-O6-C56-C57	168.5(4)
C52-C53-C54-C55	-179.4(4)	C70-O6-C56-C55	-11.5(6)
C68-C67-C66-C65	-179.4(4)	C70-C71-C72-C73	178.4(9)
C67-C66-C65-C64	173.3(4)	C70-C71A-C72A-C73A	-170.2(11)
C47-C48-C50-C44	-0.6(6)	C69-C68-C67-C66	-179.5(4)
C47-C48-C50-C40	179.2(4)	C71-C72-C73-C74	177.6(9)
C47-C48-C49-O5	4.1(6)	C72-C73-C74-C75	177.7(11)
C47-C48-C49-N2	-177.6(4)	C73-C74-C75-C76	-178.2(13)
C47-C46-C45-C44	-1.4(6)	C71A-C72A-C73A-C74A	-64.6(18)
C47-C46-C45-C51	179.2(4)	C72A-C73A-C74A-C75A	-175.6(14)
C63-N2-C39-O4	4.0(6)	C73A-C74A-C75A-C76A	175.2(17)

End of crystallographic info for 7y.

#### **CRYSTALLOGRAPHIC MATERIAL FOR 7Y'**

### Crystallographic Material for 7Y':

X-ray Experimental for complex C<sub>38</sub>H<sub>41</sub>NO<sub>3</sub> (7Y'): Crystals grew as very long, very thin, yellow laths by slow evaporation from vapor:vapor diffusion Benzene:Dioxane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.83 x 0.07 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µfocus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1088 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 30 seconds per frame with a detector offset of +/- 39.8° and 90 seconds per frame with a detector offset of +/- 110.7°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

There are two molecules in the asymmetric unit. For each molecule, one of the heptyl side chains was disordered. The molecules stack in a head to tail manner with the lactam component of one molecule oriented on top of the ether end of an adjacent molecule. This stacking occurs in the b-axis direction. The disordered n-heptyl groups are intermingled with the disordered n-heptyl groups of adjacent molecules near inversion centers at  $c = \frac{1}{2}$ .

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.2*P)^2]$  and P =  $(|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.576, with R(F) equal to 0.222 and a goodness of fit, S, = 1.87. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

# **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
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- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 7Y'.1. Crystal data and structure refinement	t for <b>7Y'.</b>	
Empirical formula	C38 H41 N O3	
Formula weight	559.72	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 15.5987(11) Å	α= 90°.
	b = 7.4380(5) Å	β= 90.956(6)°.
	c = 105.361(8) Å	$\gamma = 90^{\circ}$ .
Volume	12222.6(15) Å <sup>3</sup>	
Z	16	
Density (calculated)	1.217 Mg/m <sup>3</sup>	
Absorption coefficient	0.593 mm <sup>-1</sup>	
F(000)	4800	
Crystal size	$0.83 \ x \ 0.074 \ x \ 0.027 \ mm^3$	
Theta range for data collection	2.517 to 76.550°.	
Index ranges	-18<=h<=19, -9<=k<=7, -131<	<=l<=124
Reflections collected	36582	
Independent reflections	12317 [R(int) = 0.1155]	
Completeness to theta = $67.684^{\circ}$	100.0 %	
Absorption correction	Semi-empirical from equivalent	its
Max. and min. transmission	1.00 and 0.438	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	12317 / 1654 / 859	
Goodness-of-fit on F <sup>2</sup>	1.870	
Final R indices [I>2sigma(I)]	R1 = 0.2225, wR2 = 0.5382	
R indices (all data)	R1 = 0.2532, wR2 = 0.5759	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.644 and -0.608 e.Å <sup>-3</sup>	

	Х	у	Z	U(eq)
01	9142(5)	-3270(10)	4412(1)	55(2)
02	11759(5)	-951(10)	4317(1)	54(2)
03	7548(4)	-369(8)	3192(1)	36(1)
N1	10449(6)	-2117(12)	4364(1)	51(2)
C1	9579(6)	-2593(12)	4333(1)	42(2)
C2	9308(6)	-2222(10)	4201(1)	36(2)
C3	8469(6)	-2672(11)	4163(1)	37(2)
C4	8217(5)	-2404(10)	4039(1)	32(2)
C5	8747(6)	-1603(10)	3949(1)	34(2)
C6	9608(5)	-1113(10)	3987(1)	33(1)
C7	10175(6)	-307(10)	3902(1)	34(2)
C8	11006(6)	144(10)	3940(1)	37(2)
С9	11263(6)	-163(10)	4067(1)	36(2)
C10	10712(5)	-956(10)	4150(1)	35(2)
C11	11028(7)	-1316(13)	4282(1)	47(2)
C12	9855(5)	-1418(10)	4113(1)	33(2)
C13	8458(5)	-1367(10)	3821(1)	32(2)
C14	8229(5)	-1165(10)	3711(1)	33(2)
C15	8040(6)	-920(10)	3580(1)	34(2)
C16	8644(6)	-166(11)	3502(1)	35(2)
C17	8514(5)	28(10)	3372(1)	33(2)
C18	7736(5)	-481(10)	3317(1)	31(1)
C19	7066(5)	-1195(10)	3394(1)	33(2)
C20	6262(5)	-1681(11)	3342(1)	35(2)
C21	5653(6)	-2372(11)	3415(1)	36(2)
C22	5786(6)	-2667(10)	3546(1)	37(2)
C23	6572(6)	-2207(10)	3600(1)	36(2)
C24	7235(6)	-1448(10)	3526(1)	34(2)
C25	10791(9)	-2660(17)	4490(1)	75(3)
C26	11230(30)	-4510(30)	4472(2)	85(3)
C27	11580(20)	-5360(30)	4595(2)	91(3)

Table **7Y'.2**. Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters  $(Å^2x \ 10^3)$  for **7Y'.** U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C28	12060(20)	-7160(30)	4575(2)	101(4)
C29	12571(15)	-7800(30)	4693(2)	110(4)
C30	12010(20)	-8640(50)	4797(2)	118(5)
C31	11350(30)	-10010(60)	4746(4)	141(9)
C26A	11330(30)	-4390(40)	4501(2)	86(3)
C27A	11710(20)	-4680(30)	4636(2)	93(4)
C28A	12170(20)	-6510(30)	4651(2)	103(4)
C29A	12410(15)	-6950(30)	4791(2)	112(4)
C30A	13186(18)	-5850(50)	4841(3)	116(6)
C31A	14018(18)	-6220(60)	4768(4)	122(8)
C32	8251(6)	51(12)	3105(1)	37(2)
C33	7925(6)	-430(11)	2973(1)	38(2)
C34	7137(6)	648(12)	2930(1)	44(2)
C35	6772(6)	79(13)	2802(1)	44(2)
C36	5940(6)	1014(13)	2763(1)	43(2)
C37	5587(8)	340(17)	2636(1)	61(3)
C38	4682(9)	1110(20)	2603(1)	74(3)
O4	7551(5)	5320(9)	3082(1)	53(2)
O5	5027(5)	2940(10)	3203(1)	55(2)
O6	9465(5)	2588(9)	4301(1)	51(2)
N2	6262(5)	4193(9)	3144(1)	42(2)
C39	7124(6)	4660(11)	3167(1)	41(2)
C40	7473(6)	4476(10)	3297(1)	36(2)
C41	8308(6)	5022(11)	3329(1)	44(2)
C42	8597(6)	4851(11)	3456(1)	44(2)
C43	8115(6)	4110(10)	3550(1)	40(2)
C44	7260(6)	3554(11)	3521(1)	41(2)
C45	6693(6)	2801(10)	3613(1)	40(2)
C46	5887(7)	2274(11)	3580(1)	45(2)
C47	5595(7)	2458(12)	3455(1)	44(2)
C48	6107(6)	3152(9)	3365(1)	35(2)
C49	5752(7)	3385(11)	3233(1)	44(2)
C50	6961(6)	3725(10)	3393(1)	35(2)
C51	8423(6)	3942(11)	3679(1)	42(2)
C52	8630(6)	3702(12)	3787(1)	43(2)
C53	8838(6)	3424(12)	3919(1)	44(2)

C54	8251(6)	2659(12)	4002(1)	43(2)
C55	8407(6)	2394(12)	4130(1)	45(2)
C56	9218(6)	2802(11)	4180(1)	42(2)
C57	9847(6)	3600(11)	4101(1)	41(2)
C58	10686(6)	4058(12)	4148(1)	48(2)
C59	11274(7)	4835(12)	4073(1)	50(2)
C60	11099(7)	5151(12)	3946(1)	49(2)
C61	10309(7)	4696(12)	3895(1)	46(2)
C62	9668(6)	3890(11)	3973(1)	40(2)
C63	5906(6)	4558(12)	3017(1)	44(2)
C64	5432(7)	6385(12)	3014(1)	49(2)
C65	4952(7)	6624(14)	2887(1)	53(2)
C66	4191(7)	5391(14)	2866(1)	52(2)
C67	3669(7)	5804(15)	2745(1)	51(2)
C68	2877(7)	4561(15)	2729(1)	54(2)
C69	2365(8)	4893(18)	2611(1)	64(3)
C70	8803(9)	2143(15)	4391(1)	61(2)
C71	9166(11)	2340(20)	4522(1)	83(3)
C72	9803(18)	1060(40)	4577(2)	91(4)
C73	9960(20)	1260(30)	4716(2)	98(4)
C74	10392(19)	-350(30)	4775(2)	108(5)
C75	10920(20)	30(40)	4891(2)	115(6)
C76	11590(20)	-1350(50)	4919(3)	128(9)
C72A	8678(19)	1270(30)	4615(2)	94(4)
C73A	9010(20)	1460(30)	4749(1)	100(4)
C74A	9050(30)	3360(30)	4793(2)	110(5)
C75A	9370(30)	3580(30)	4926(2)	115(6)
C76A	9360(30)	5480(40)	4973(3)	128(9)

O1-C1	1.195(11)	C18-C19	1.438(11)
O2-C11	1.223(13)	C19-C20	1.408(12)
O3-C18	1.348(9)	C19-C24	1.421(10)
O3-C32	1.472(9)	C20-C21	1.332(12)
N1-C11	1.395(13)	C20-H20	0.95
N1-C1	1.434(13)	C21-C22	1.407(11)
N1-C25	1.479(12)	C21-H21	0.95
C1-C2	1.471(11)	C22-C23	1.387(13)
C2-C12	1.403(11)	C22-H22	0.95
C2-C3	1.404(13)	C23-C24	1.422(12)
C3-C4	1.374(11)	С23-Н23	0.95
С3-Н3	0.95	C25-C26A	1.542(11)
C4-C5	1.398(11)	C25-C26	1.552(11)
С4-Н4	0.95	C25-H25A	0.99
C5-C13	1.424(11)	C25-H25B	0.99
C5-C6	1.440(12)	C26-C27	1.538(12)
C6-C7	1.401(11)	C26-H26A	0.99
C6-C12	1.402(11)	C26-H26B	0.99
C7-C8	1.392(12)	C27-C28	1.546(12)
С7-Н7	0.95	С27-Н27А	0.99
C8-C9	1.407(12)	C27-H27B	0.99
С8-Н8	0.95	C28-C29	1.544(11)
C9-C10	1.369(11)	C28-H28A	0.99
С9-Н9	0.95	C28-H28B	0.99
C10-C12	1.428(12)	C29-C30	1.543(11)
C10-C11	1.492(12)	С29-Н29А	0.99
C13-C14	1.214(11)	C29-H29B	0.99
C14-C15	1.419(11)	C30-C31	1.544(12)
C15-C16	1.382(12)	C30-H30A	0.99
C15-C24	1.426(12)	C30-H30B	0.99
C16-C17	1.391(10)	C31-H31A	0.98
C16-H16	0.95	C31-H31B	0.98
C17-C18	1.388(11)	C31-H31C	0.98
С17-Н17	0.95	C26A-C27A	1.550(11)

Table 7Y'.3. Bond lengths [Å] and angles  $[\circ]$  for 7Y'.

C26A-H26C	0.99	C38-H38B	0.98
C26A-H26D	0.99	C38-H38C	0.98
C27A-C28A	1.547(12)	O4-C39	1.232(10)
C27A-H27C	0.99	O5-C49	1.217(12)
C27A-H27D	0.99	O6-C56	1.333(11)
C28A-C29A	1.552(11)	O6-C70	1.455(13)
C28A-H28C	0.99	N2-C49	1.379(12)
C28A-H28D	0.99	N2-C39	1.407(13)
C29A-C30A	1.546(12)	N2-C63	1.466(12)
С29А-Н29С	0.99	C39-C40	1.472(12)
C29A-H29D	0.99	C40-C41	1.400(13)
C30A-C31A	1.544(12)	C40-C50	1.413(11)
C30A-H30C	0.99	C41-C42	1.407(13)
C30A-H30D	0.99	C41-H41	0.95
C31A-H31D	0.98	C42-C43	1.367(12)
C31A-H31E	0.98	C42-H42	0.95
C31A-H31F	0.98	C43-C44	1.425(14)
C32-C33	1.514(10)	C43-C51	1.440(13)
C32-H32A	0.99	C44-C50	1.424(12)
С32-Н32В	0.99	C44-C45	1.439(12)
C33-C34	1.530(13)	C45-C46	1.357(14)
С33-Н33А	0.99	C45-H45	0.95
С33-Н33В	0.99	C46-C47	1.393(13)
C34-C35	1.521(12)	C46-H46	0.95
C34-H34A	0.99	C47-C48	1.350(12)
C34-H34B	0.99	C47-H47	0.95
C35-C36	1.520(13)	C48-C50	1.424(13)
С35-Н35А	0.99	C48-C49	1.494(13)
С35-Н35В	0.99	C51-C52	1.193(13)
C36-C37	1.527(13)	C52-C53	1.436(13)
С36-Н36А	0.99	C53-C54	1.401(14)
C36-H36B	0.99	C53-C62	1.447(13)
C37-C38	1.558(17)	C54-C55	1.374(13)
С37-Н37А	0.99	C54-H54	0.95
С37-Н37В	0.99	C55-C56	1.398(13)
C38-H38A	0.98	С55-Н55	0.95

C56-C57	1.429(13)	C71-C72	1.484(13)
C57-C62	1.390(13)	C71-C72A	1.488(13)
C57-C58	1.433(13)	С71-Н71А	0.99
C58-C59	1.350(14)	С71-Н71В	0.99
С58-Н58	0.95	C72-C73	1.495(13)
C59-C60	1.388(14)	С72-Н72А	0.99
С59-Н59	0.95	С72-Н72В	0.99
C60-C61	1.378(15)	C73-C74	1.496(14)
С60-Н60	0.95	С73-Н73А	0.99
C61-C62	1.438(13)	С73-Н73В	0.99
С61-Н61	0.95	C74-C75	1.488(14)
C63-C64	1.546(12)	С74-Н74А	0.99
С63-Н63А	0.99	С74-Н74В	0.99
С63-Н63В	0.99	C75-C76	1.497(13)
C64-C65	1.528(14)	С75-Н75А	0.99
C64-H64A	0.99	С75-Н75В	0.99
C64-H64B	0.99	С76-Н76А	0.98
C65-C66	1.515(15)	С76-Н76В	0.98
С65-Н65А	0.99	С76-Н76С	0.98
С65-Н65В	0.99	C72A-C73A	1.498(13)
C66-C67	1.532(14)	С72А-Н72С	0.99
С66-Н66А	0.99	C72A-H72D	0.99
С66-Н66В	0.99	C73A-C74A	1.494(13)
C67-C68	1.550(15)	С73А-Н73С	0.99
С67-Н67А	0.99	C73A-H73D	0.99
С67-Н67В	0.99	C74A-C75A	1.490(14)
C68-C69	1.483(15)	С74А-Н74С	0.99
C68-H68A	0.99	C74A-H74D	0.99
C68-H68B	0.99	C75A-C76A	1.493(13)
С69-Н69А	0.98	С75А-Н75С	0.99
С69-Н69В	0.98	C75A-H75D	0.99
С69-Н69С	0.98	C76A-H76D	0.98
C70-C71	1.483(17)	С76А-Н76Е	0.98
С70-Н70А	0.99	C76A-H76F	0.98
С70-Н70В	0.99		

C18-O3-C32	117.9(7)	N1-C11-C10	116.6(9)
C11-N1-C1	125.7(8)	C6-C12-C2	122.5(8)
C11-N1-C25	116.5(10)	C6-C12-C10	117.3(7)
C1-N1-C25	117.6(9)	C2-C12-C10	120.1(7)
01-C1-N1	119.6(8)	C14-C13-C5	178.6(9)
O1-C1-C2	125.2(10)	C13-C14-C15	174.9(9)
N1-C1-C2	115.2(8)	C16-C15-C14	120.0(8)
C12-C2-C3	119.0(7)	C16-C15-C24	118.5(7)
C12-C2-C1	122.3(9)	C14-C15-C24	121.5(7)
C3-C2-C1	118.7(8)	C15-C16-C17	122.8(8)
C4-C3-C2	119.4(8)	С15-С16-Н16	118.6
С4-С3-Н3	120.3	C17-C16-H16	118.6
С2-С3-Н3	120.3	C18-C17-C16	119.7(7)
C3-C4-C5	122.7(8)	C18-C17-H17	120.2
С3-С4-Н4	118.6	С16-С17-Н17	120.2
С5-С4-Н4	118.6	O3-C18-C17	124.4(7)
C4-C5-C13	120.6(8)	O3-C18-C19	115.4(7)
C4-C5-C6	118.8(7)	C17-C18-C19	120.2(7)
C13-C5-C6	120.5(7)	C20-C19-C24	119.8(8)
C7-C6-C12	120.6(8)	C20-C19-C18	121.6(7)
C7-C6-C5	122.0(7)	C24-C19-C18	118.6(8)
C12-C6-C5	117.4(7)	C21-C20-C19	120.9(8)
C8-C7-C6	120.9(7)	С21-С20-Н20	119.6
С8-С7-Н7	119.5	С19-С20-Н20	119.6
С6-С7-Н7	119.5	C20-C21-C22	121.8(9)
C7-C8-C9	119.0(8)	C20-C21-H21	119.1
С7-С8-Н8	120.5	C22-C21-H21	119.1
С9-С8-Н8	120.5	C23-C22-C21	118.8(8)
C10-C9-C8	120.3(8)	С23-С22-Н22	120.6
С10-С9-Н9	119.9	C21-C22-H22	120.6
С8-С9-Н9	119.9	C22-C23-C24	121.1(7)
C9-C10-C12	121.8(7)	С22-С23-Н23	119.4
C9-C10-C11	118.1(8)	С24-С23-Н23	119.4
C12-C10-C11	120.1(8)	C19-C24-C23	117.5(8)
O2-C11-N1	121.2(8)	C19-C24-C15	120.2(8)
O2-C11-C10	122.1(9)	C23-C24-C15	122.3(7)

N1-C25-C26A	118.7(11)	H30A-C30-H30B	107.7
N1-C25-C26	106.4(10)	С30-С31-Н31А	109.5
N1-C25-H25A	110.4	C30-C31-H31B	109.5
С26-С25-Н25А	110.4	H31A-C31-H31B	109.5
N1-C25-H25B	110.4	С30-С31-Н31С	109.5
С26-С25-Н25В	110.4	H31A-C31-H31C	109.5
H25A-C25-H25B	108.6	H31B-C31-H31C	109.5
C27-C26-C25	114.3(10)	C25-C26A-C27A	112.4(10)
С27-С26-Н26А	108.7	С25-С26А-Н26С	109.1
С25-С26-Н26А	108.7	C27A-C26A-H26C	109.1
С27-С26-Н26В	108.7	C25-C26A-H26D	109.1
С25-С26-Н26В	108.7	C27A-C26A-H26D	109.1
H26A-C26-H26B	107.6	H26C-C26A-H26D	107.8
C26-C27-C28	114.0(11)	C28A-C27A-C26A	112.6(11)
С26-С27-Н27А	108.7	C28A-C27A-H27C	109.1
С28-С27-Н27А	108.7	C26A-C27A-H27C	109.1
С26-С27-Н27В	108.7	C28A-C27A-H27D	109.1
С28-С27-Н27В	108.7	C26A-C27A-H27D	109.1
H27A-C27-H27B	107.6	H27C-C27A-H27D	107.8
C29-C28-C27	113.7(11)	C27A-C28A-C29A	112.6(10)
С29-С28-Н28А	108.8	C27A-C28A-H28C	109.1
C27-C28-H28A	108.8	C29A-C28A-H28C	109.1
С29-С28-Н28В	108.8	C27A-C28A-H28D	109.1
С27-С28-Н28В	108.8	C29A-C28A-H28D	109.1
H28A-C28-H28B	107.7	H28C-C28A-H28D	107.8
C30-C29-C28	114.0(10)	C30A-C29A-C28A	112.7(10)
С30-С29-Н29А	108.8	C30A-C29A-H29C	109.0
С28-С29-Н29А	108.8	С28А-С29А-Н29С	109.0
С30-С29-Н29В	108.8	C30A-C29A-H29D	109.0
С28-С29-Н29В	108.8	C28A-C29A-H29D	109.0
H29A-C29-H29B	107.6	H29C-C29A-H29D	107.8
C29-C30-C31	113.8(10)	C31A-C30A-C29A	113.2(11)
С29-С30-Н30А	108.8	C31A-C30A-H30C	108.9
С31-С30-Н30А	108.8	С29А-С30А-Н30С	108.9
С29-С30-Н30В	108.8	C31A-C30A-H30D	108.9
С31-С30-Н30В	108.8	C29A-C30A-H30D	108.9

H30C-C30A-H30D	107.7	H36A-C36-H36B	107.9
C30A-C31A-H31D	109.5	C36-C37-C38	112.7(9)
C30A-C31A-H31E	109.5	С36-С37-Н37А	109.0
H31D-C31A-H31E	109.5	С38-С37-Н37А	109.0
C30A-C31A-H31F	109.5	С36-С37-Н37В	109.0
H31D-C31A-H31F	109.5	С38-С37-Н37В	109.0
H31E-C31A-H31F	109.5	H37A-C37-H37B	107.8
O3-C32-C33	106.1(7)	С37-С38-Н38А	109.5
O3-C32-H32A	110.5	C37-C38-H38B	109.5
С33-С32-Н32А	110.5	H38A-C38-H38B	109.5
O3-C32-H32B	110.5	С37-С38-Н38С	109.5
С33-С32-Н32В	110.5	H38A-C38-H38C	109.5
H32A-C32-H32B	108.7	H38B-C38-H38C	109.5
C32-C33-C34	113.9(7)	C56-O6-C70	117.1(9)
С32-С33-Н33А	108.8	C49-N2-C39	123.4(8)
С34-С33-Н33А	108.8	C49-N2-C63	119.3(8)
С32-С33-Н33В	108.8	C39-N2-C63	117.3(7)
С34-С33-Н33В	108.8	O4-C39-N2	119.9(9)
H33A-C33-H33B	107.7	O4-C39-C40	121.5(9)
C35-C34-C33	114.0(7)	N2-C39-C40	118.4(7)
С35-С34-Н34А	108.8	C41-C40-C50	118.4(8)
С33-С34-Н34А	108.8	C41-C40-C39	121.8(8)
С35-С34-Н34В	108.8	C50-C40-C39	119.7(8)
С33-С34-Н34В	108.8	C40-C41-C42	119.1(8)
H34A-C34-H34B	107.7	C40-C41-H41	120.4
C36-C35-C34	114.4(7)	C42-C41-H41	120.4
С36-С35-Н35А	108.6	C43-C42-C41	123.4(9)
С34-С35-Н35А	108.6	C43-C42-H42	118.3
С36-С35-Н35В	108.6	C41-C42-H42	118.3
С34-С35-Н35В	108.6	C42-C43-C44	119.1(8)
H35A-C35-H35B	107.6	C42-C43-C51	122.6(9)
C35-C36-C37	112.1(8)	C44-C43-C51	118.3(8)
С35-С36-Н36А	109.2	C50-C44-C43	117.9(8)
С37-С36-Н36А	109.2	C50-C44-C45	118.6(9)
С35-С36-Н36В	109.2	C43-C44-C45	123.5(8)
С37-С36-Н36В	109.2	C46-C45-C44	120.9(8)

С46-С45-Н45	119.5	С57-С58-Н58	119.2
С44-С45-Н45	119.5	C58-C59-C60	120.9(10)
C45-C46-C47	120.2(9)	С58-С59-Н59	119.6
С45-С46-Н46	119.9	С60-С59-Н59	119.6
С47-С46-Н46	119.9	C61-C60-C59	119.9(10)
C48-C47-C46	120.8(10)	С61-С60-Н60	120.1
С48-С47-Н47	119.6	С59-С60-Н60	120.1
С46-С47-Н47	119.6	C60-C61-C62	120.2(9)
C47-C48-C50	122.0(8)	С60-С61-Н61	119.9
C47-C48-C49	118.7(9)	С62-С61-Н61	119.9
C50-C48-C49	119.2(7)	C57-C62-C61	119.4(9)
O5-C49-N2	119.1(9)	C57-C62-C53	120.5(9)
O5-C49-C48	122.6(8)	C61-C62-C53	120.1(9)
N2-C49-C48	118.4(8)	N2-C63-C64	110.9(7)
C40-C50-C48	120.6(8)	N2-C63-H63A	109.5
C40-C50-C44	122.0(9)	С64-С63-Н63А	109.5
C48-C50-C44	117.4(7)	N2-C63-H63B	109.5
C52-C51-C43	174.9(10)	С64-С63-Н63В	109.5
C51-C52-C53	177.3(10)	H63A-C63-H63B	108.0
C54-C53-C52	121.7(9)	C65-C64-C63	110.5(8)
C54-C53-C62	116.2(8)	С65-С64-Н64А	109.6
C52-C53-C62	122.1(9)	С63-С64-Н64А	109.6
C55-C54-C53	124.3(9)	C65-C64-H64B	109.6
С55-С54-Н54	117.9	С63-С64-Н64В	109.6
С53-С54-Н54	117.9	H64A-C64-H64B	108.1
C54-C55-C56	119.1(9)	C66-C65-C64	115.5(8)
С54-С55-Н55	120.4	С66-С65-Н65А	108.4
С56-С55-Н55	120.4	С64-С65-Н65А	108.4
O6-C56-C55	125.7(9)	С66-С65-Н65В	108.4
O6-C56-C57	114.7(9)	С64-С65-Н65В	108.4
C55-C56-C57	119.5(9)	H65A-C65-H65B	107.5
C62-C57-C56	120.3(9)	C65-C66-C67	113.9(8)
C62-C57-C58	117.8(9)	С65-С66-Н66А	108.8
C56-C57-C58	121.8(9)	С67-С66-Н66А	108.8
C59-C58-C57	121.7(10)	С65-С66-Н66В	108.8
С59-С58-Н58	119.2	С67-С66-Н66В	108.8

H66A-C66-H66B	107.7	С73-С72-Н72В	108.5
C66-C67-C68	112.6(8)	Н72А-С72-Н72В	107.5
С66-С67-Н67А	109.1	C72-C73-C74	113.3(14)
С68-С67-Н67А	109.1	С72-С73-Н73А	108.9
С66-С67-Н67В	109.1	С74-С73-Н73А	108.9
С68-С67-Н67В	109.1	С72-С73-Н73В	108.9
H67A-C67-H67B	107.8	С74-С73-Н73В	108.9
C69-C68-C67	114.2(9)	Н73А-С73-Н73В	107.7
С69-С68-Н68А	108.7	C75-C74-C73	114.8(15)
С67-С68-Н68А	108.7	С75-С74-Н74А	108.6
С69-С68-Н68В	108.7	С73-С74-Н74А	108.6
С67-С68-Н68В	108.7	С75-С74-Н74В	108.6
H68A-C68-H68B	107.6	С73-С74-Н74В	108.6
С68-С69-Н69А	109.5	H74A-C74-H74B	107.5
С68-С69-Н69В	109.5	C74-C75-C76	113.9(14)
H69A-C69-H69B	109.5	С74-С75-Н75А	108.8
С68-С69-Н69С	109.5	С76-С75-Н75А	108.8
Н69А-С69-Н69С	109.5	С74-С75-Н75В	108.8
H69B-C69-H69C	109.5	С76-С75-Н75В	108.8
O6-C70-C71	108.6(11)	Н75А-С75-Н75В	107.7
О6-С70-Н70А	110.0	С75-С76-Н76А	109.5
С71-С70-Н70А	110.0	С75-С76-Н76В	109.5
О6-С70-Н70В	110.0	Н76А-С76-Н76В	109.5
С71-С70-Н70В	110.0	С75-С76-Н76С	109.5
H70A-C70-H70B	108.4	Н76А-С76-Н76С	109.5
C70-C71-C72	122.9(13)	Н76В-С76-Н76С	109.5
C70-C71-C72A	111.6(13)	C71-C72A-C73A	113.7(13)
С70-С71-Н71А	109.3	С71-С72А-Н72С	108.8
C72A-C71-H71A	109.3	С73А-С72А-Н72С	108.8
С70-С71-Н71В	109.3	C71-C72A-H72D	108.8
C72A-C71-H71B	109.3	C73A-C72A-H72D	108.8
H71A-C71-H71B	108.0	H72C-C72A-H72D	107.7
C71-C72-C73	115.2(14)	C74A-C73A-C72A	113.4(13)
С71-С72-Н72А	108.5	С74А-С73А-Н73С	108.9
С73-С72-Н72А	108.5	С72А-С73А-Н73С	108.9
С71-С72-Н72В	108.5	C74A-C73A-H73D	108.9

C72A-C73A-H73D	108.9	С76А-С75А-Н75С	108.8
H73C-C73A-H73D	107.7	C74A-C75A-H75D	108.8
C75A-C74A-C73A	114.2(15)	C76A-C75A-H75D	108.8
С75А-С74А-Н74С	108.7	H75C-C75A-H75D	107.6
С73А-С74А-Н74С	108.7	C75A-C76A-H76D	109.5
C75A-C74A-H74D	108.7	С75А-С76А-Н76Е	109.5
C73A-C74A-H74D	108.7	H76D-C76A-H76E	109.5
H74C-C74A-H74D	107.6	C75A-C76A-H76F	109.5
C74A-C75A-C76A	114.0(14)	H76D-C76A-H76F	109.5
С74А-С75А-Н75С	108.8	H76E-C76A-H76F	109.5

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
01	56(4)	80(5)	28(3)	8(3)	3(3)	-12(3)
O2	49(4)	71(4)	41(3)	8(3)	-10(3)	-11(3)
O3	34(3)	50(3)	24(2)	0(2)	7(2)	2(2)
N1	56(4)	65(4)	33(3)	3(3)	-5(3)	-12(3)
C1	42(4)	52(4)	33(3)	3(3)	5(3)	6(3)
C2	40(4)	36(4)	33(3)	2(3)	3(3)	5(3)
C3	38(4)	41(4)	32(3)	-1(3)	9(3)	5(3)
C4	33(4)	29(3)	35(3)	-2(2)	3(3)	-2(3)
C5	41(4)	32(3)	30(3)	-6(2)	1(3)	-6(3)
C6	34(3)	33(3)	32(3)	-6(2)	3(2)	2(3)
C7	43(4)	36(3)	25(3)	-3(2)	3(3)	-2(3)
C8	36(4)	33(3)	42(3)	-2(3)	7(3)	2(3)
C9	35(4)	31(3)	42(3)	-2(3)	3(3)	-4(3)
C10	33(3)	35(3)	36(3)	1(3)	1(3)	2(3)
C11	50(4)	55(4)	37(3)	0(3)	-4(3)	-1(3)
C12	33(3)	36(3)	31(3)	-6(2)	3(2)	0(3)
C13	35(4)	32(3)	29(3)	-2(2)	2(2)	0(3)
C14	31(4)	38(3)	29(3)	-2(3)	4(2)	-5(3)
C15	40(4)	31(3)	30(3)	-3(2)	-1(2)	7(3)
C16	35(4)	38(4)	32(3)	1(3)	-6(3)	5(3)
C17	32(3)	35(3)	31(3)	-3(3)	5(3)	0(3)
C18	33(3)	33(3)	28(3)	-7(2)	3(2)	2(3)
C19	30(3)	39(3)	30(3)	-2(3)	3(2)	3(3)
C20	31(3)	42(4)	33(3)	-2(3)	-2(3)	7(3)
C21	30(4)	39(4)	38(3)	-4(3)	3(3)	8(3)
C22	41(4)	29(3)	40(3)	-3(3)	6(3)	2(3)
C23	43(4)	31(3)	33(3)	-3(3)	0(3)	5(3)
C24	41(4)	36(3)	26(3)	-7(2)	0(2)	4(3)
C25	75(5)	95(5)	56(4)	20(4)	-15(4)	-18(4)
C26	85(6)	95(5)	75(5)	19(5)	-10(5)	-10(5)
C27	92(5)	97(5)	84(5)	14(4)	-9(5)	-6(4)

Table 7Y'.4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for 7Y'. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C28	101(6)	104(6)	98(6)	8(5)	-5(5)	0(5)
C29	110(6)	113(6)	107(6)	10(5)	-5(5)	5(5)
C30	120(7)	120(7)	114(7)	8(6)	-1(6)	2(6)
C31	138(14)	139(14)	147(15)	5(12)	1(12)	-15(11)
C26A	86(6)	96(5)	77(5)	21(5)	-10(5)	-10(5)
C27A	92(6)	101(6)	85(5)	16(5)	-7(5)	-6(5)
C28A	103(6)	107(5)	100(5)	12(5)	-3(5)	1(5)
C29A	113(6)	116(6)	107(6)	8(5)	-3(5)	3(5)
C30A	116(8)	123(8)	110(8)	0(7)	0(6)	-1(7)
C31A	119(11)	136(15)	112(14)	-2(12)	-1(11)	4(12)
C32	39(4)	47(4)	26(3)	5(3)	4(3)	0(3)
C33	40(4)	49(4)	27(3)	-1(3)	4(3)	0(3)
C34	47(4)	52(4)	33(3)	1(3)	-2(3)	6(4)
C35	45(4)	59(4)	30(3)	-5(3)	5(3)	11(4)
C36	42(4)	58(4)	30(3)	3(3)	5(3)	3(3)
C37	61(5)	83(6)	37(4)	-9(4)	-3(4)	12(5)
C38	70(7)	108(9)	44(5)	-3(5)	-13(5)	19(7)
O4	62(4)	57(4)	42(3)	4(3)	23(3)	2(3)
O5	45(4)	65(4)	55(4)	-5(3)	-1(3)	-8(3)
06	54(4)	51(3)	48(3)	-1(3)	0(3)	2(3)
N2	45(3)	41(3)	40(3)	-2(3)	5(3)	3(3)
C39	47(4)	35(3)	39(3)	0(3)	9(3)	-1(3)
C40	38(4)	29(3)	42(3)	4(3)	7(3)	0(3)
C41	40(4)	37(4)	54(4)	-1(3)	14(3)	2(3)
C42	35(4)	39(4)	58(4)	-1(3)	1(3)	-1(3)
C43	45(4)	29(3)	47(3)	-4(3)	4(3)	3(3)
C44	41(4)	40(4)	42(3)	-2(3)	1(3)	8(3)
C45	54(4)	29(3)	35(3)	1(3)	1(3)	7(3)
C46	49(4)	39(4)	47(4)	-1(3)	11(3)	5(3)
C47	42(4)	42(4)	47(4)	2(3)	11(3)	4(3)
C48	41(4)	23(3)	42(3)	2(3)	9(3)	2(3)
C49	46(4)	39(4)	47(4)	-2(3)	0(3)	-7(3)
C50	39(4)	30(3)	36(3)	-1(3)	6(3)	5(3)
C51	38(4)	36(4)	51(3)	-7(3)	2(3)	-2(3)
C52	32(4)	45(4)	52(3)	0(3)	2(3)	0(3)
C53	42(4)	42(4)	49(4)	-7(3)	-2(3)	1(3)

C54	37(4)	41(4)	51(4)	-8(3)	-7(3)	0(3)
C55	33(4)	48(4)	54(4)	-4(3)	6(3)	0(3)
C56	38(4)	40(4)	48(3)	-6(3)	0(3)	1(3)
C57	36(4)	36(4)	52(4)	-10(3)	-1(3)	-1(3)
C58	42(4)	37(4)	64(5)	-9(3)	-4(3)	-2(3)
C59	40(4)	36(4)	74(4)	-12(3)	-1(3)	-9(3)
C60	40(4)	33(4)	75(4)	-8(3)	10(4)	3(3)
C61	42(4)	41(4)	54(4)	-3(3)	6(3)	3(3)
C62	36(4)	32(3)	53(4)	-12(3)	5(3)	6(3)
C63	45(5)	47(4)	41(4)	-7(3)	5(3)	1(3)
C64	57(5)	47(4)	44(4)	-3(3)	5(3)	6(4)
C65	50(5)	62(5)	46(4)	1(4)	3(3)	-2(4)
C66	54(5)	60(5)	41(4)	0(3)	7(3)	-9(4)
C67	49(5)	70(5)	35(4)	0(4)	8(3)	-7(4)
C68	53(5)	64(5)	45(4)	1(4)	6(4)	-2(4)
C69	51(6)	89(7)	52(5)	5(5)	6(4)	-7(5)
C70	69(6)	56(5)	59(4)	-1(4)	11(4)	3(5)
C71	95(7)	85(7)	69(5)	3(5)	-4(5)	-7(6)
C72	93(7)	94(7)	84(6)	4(6)	1(6)	0(6)
C73	101(7)	105(6)	89(6)	4(5)	2(5)	2(5)
C74	108(8)	115(7)	99(7)	6(6)	1(6)	6(6)
C75	116(9)	122(9)	106(8)	3(7)	-3(7)	5(7)
C76	125(14)	136(14)	121(14)	6(12)	-9(11)	12(11)
C72A	97(7)	101(7)	85(6)	10(5)	6(6)	-2(6)
C73A	102(7)	107(6)	91(6)	7(5)	4(5)	0(6)
C74A	111(8)	113(7)	105(7)	1(6)	1(6)	1(6)
C75A	115(9)	119(8)	112(8)	-3(7)	0(7)	0(7)
C76A	129(16)	127(12)	126(14)	-14(11)	-2(13)	2(13)

	Х	У	Z	U(eq)
H3	8080	-3158	4222	44
H4	7659	-2777	4012	39
H7	9990	-64	3817	41
H8	11394	650	3882	44
Н9	11820	182	4095	43
H16	9170	238	3539	42
H17	8955	507	3321	39
H20	6153	-1514	3254	42
H21	5115	-2674	3377	43
H22	5346	-3171	3595	44
H23	6668	-2404	3688	43
H25A	10321	-2765	4552	90
H25B	11209	-1762	4522	90
H26A	10816	-5346	4432	102
H26B	11713	-4355	4412	102
H27A	11099	-5575	4653	109
H27B	11978	-4499	4637	109
H28A	11642	-8092	4550	121
H28B	12465	-7010	4504	121
H29A	12998	-8706	4667	132
H29B	12888	-6770	4730	132
H30A	11699	-7662	4841	142
H30B	12384	-9241	4860	142
H31A	11013	-10487	4816	212
H31B	10961	-9421	4684	212
H31C	11647	-11002	4704	212
H26C	11804	-4332	4439	104
H26D	10966	-5437	4478	104
H27C	12123	-3703	4656	111
H27D	11244	-4612	4698	111

Table **7Y'.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **7Y'**.

H28C	12703	-6496	4600	124
H28D	11797	-7473	4616	124
H29C	11909	-6697	4845	135
H29D	12543	-8247	4798	135
H30C	13049	-4555	4835	140
H30D	13286	-6139	4932	140
H31D	14485	-5494	4804	183
H31E	14166	-7501	4775	183
H31F	13929	-5916	4678	183
H32A	8767	-662	3127	45
H32B	8399	1344	3110	45
H33A	7780	-1725	2972	46
H33B	8390	-229	2912	46
H34A	6686	517	2994	53
H34B	7294	1937	2926	53
H35A	7204	325	2736	53
H35B	6671	-1235	2803	53
H36A	6042	2326	2758	52
H36B	5509	805	2830	52
H37A	5555	-989	2638	73
H37B	5988	682	2568	73
H38A	4282	785	2670	111
H38B	4478	610	2522	111
H38C	4715	2424	2597	111
H41	8674	5502	3267	52
H42	9155	5272	3478	53
H45	6885	2672	3699	47
H46	5521	1778	3642	54
H47	5030	2090	3432	52
H54	7709	2299	3968	52
H55	7970	1940	4182	54
H58	10831	3808	4234	58
Н59	11816	5170	4108	60
H60	11522	5680	3894	59
H61	10188	4917	3807	55
H63A	5502	3587	2992	53

H63B	6375	4572	2955	53
H64A	5021	6441	3084	59
H64B	5852	7372	3025	59
H65A	4750	7884	2881	63
H65B	5361	6430	2818	63
H66A	3809	5485	2940	62
H66B	4398	4135	2862	62
H67A	4042	5663	2671	61
H67B	3475	7070	2747	61
H68A	3074	3295	2729	65
H68B	2502	4722	2803	65
H69A	2217	6171	2606	96
H69B	1838	4175	2613	96
H69C	2701	4551	2537	96
H70A	8604	893	4378	73
H70B	8306	2959	4380	73
H71A	9155	3622	4546	100
H71B	9772	1938	4523	100
H72A	10353	1228	4533	109
H72B	9603	-177	4560	109
H73A	9410	1460	4759	118
H73B	10327	2327	4732	118
H74A	9946	-1240	4797	129
H74B	10765	-909	4711	129
H75A	10534	127	4964	138
H75B	11202	1215	4880	138
H76A	11909	-1016	4996	191
H76B	11313	-2524	4932	191
H76C	11983	-1434	4848	191
H72C	8702	-17	4591	113
H72D	8070	1645	4612	113
H73C	8626	776	4806	120
H73D	9585	917	4756	120
H74C	9436	4039	4736	132
H74D	8475	3905	4786	132
H75C	9968	3127	4932	138

H75D	9017	2831	4983	138
H76D	9573	5515	5061	192
H76E	9719	6225	4920	192
H76F	8766	5929	4970	192

Table **7Y'.6**. Torsion angles [°] for **7Y'.** 

C11-N1-C1-O1	-179.7(10)	C5-C6-C12-C10	179.1(7)
C25-N1-C1-O1	6.0(15)	C3-C2-C12-C6	-2.8(12)
C11-N1-C1-C2	1.6(14)	C1-C2-C12-C6	178.0(7)
C25-N1-C1-C2	-172.7(9)	C3-C2-C12-C10	-179.7(7)
O1-C1-C2-C12	179.8(9)	C1-C2-C12-C10	1.1(12)
N1-C1-C2-C12	-1.6(12)	C9-C10-C12-C6	3.2(11)
O1-C1-C2-C3	0.6(14)	C11-C10-C12-C6	-177.5(7)
N1-C1-C2-C3	179.2(8)	C9-C10-C12-C2	-179.7(7)
C12-C2-C3-C4	3.4(12)	C11-C10-C12-C2	-0.4(12)
C1-C2-C3-C4	-177.3(7)	C14-C15-C16-C17	176.8(7)
C2-C3-C4-C5	-3.6(12)	C24-C15-C16-C17	-2.9(12)
C3-C4-C5-C13	179.5(7)	C15-C16-C17-C18	2.7(12)
C3-C4-C5-C6	2.9(11)	C32-O3-C18-C17	10.0(11)
C4-C5-C6-C7	180.0(7)	C32-O3-C18-C19	-169.7(7)
C13-C5-C6-C7	3.4(11)	C16-C17-C18-O3	-179.2(7)
C4-C5-C6-C12	-2.1(11)	C16-C17-C18-C19	0.4(11)
C13-C5-C6-C12	-178.7(7)	O3-C18-C19-C20	-2.0(11)
C12-C6-C7-C8	2.6(12)	C17-C18-C19-C20	178.4(7)
C5-C6-C7-C8	-179.5(7)	O3-C18-C19-C24	176.5(7)
C6-C7-C8-C9	-2.3(12)	C17-C18-C19-C24	-3.1(11)
C7-C8-C9-C10	2.5(12)	C24-C19-C20-C21	0.2(12)
C8-C9-C10-C12	-3.1(12)	C18-C19-C20-C21	178.7(7)
C8-C9-C10-C11	177.6(7)	C19-C20-C21-C22	-0.8(12)
C1-N1-C11-O2	179.8(9)	C20-C21-C22-C23	0.6(12)
C25-N1-C11-O2	-5.9(15)	C21-C22-C23-C24	0.2(11)
C1-N1-C11-C10	-1.0(14)	C20-C19-C24-C23	0.5(11)
C25-N1-C11-C10	173.3(9)	C18-C19-C24-C23	-178.1(7)
C9-C10-C11-O2	-1.2(14)	C20-C19-C24-C15	-178.5(7)
C12-C10-C11-O2	179.5(9)	C18-C19-C24-C15	2.9(11)
C9-C10-C11-N1	179.7(8)	C22-C23-C24-C19	-0.7(11)
C12-C10-C11-N1	0.4(12)	C22-C23-C24-C15	178.3(7)
C7-C6-C12-C2	-179.9(7)	C16-C15-C24-C19	0.0(11)
C5-C6-C12-C2	2.1(11)	C14-C15-C24-C19	-179.6(7)
C7-C6-C12-C10	-2.9(11)	C16-C15-C24-C23	-179.0(7)

C14-C15-C24-C23	1.4(11)	C42-C43-C44-C45	-178.4(8)
C11-N1-C25-C26A	-77(2)	C51-C43-C44-C45	-1.2(12)
C1-N1-C25-C26A	97(2)	C50-C44-C45-C46	-0.4(12)
C11-N1-C25-C26	-82(2)	C43-C44-C45-C46	-179.2(8)
C1-N1-C25-C26	93(2)	C44-C45-C46-C47	-0.1(12)
N1-C25-C26-C27	-176(3)	C45-C46-C47-C48	0.3(13)
C25-C26-C27-C28	-177(3)	C46-C47-C48-C50	0.0(12)
C26-C27-C28-C29	168(3)	C46-C47-C48-C49	-177.7(8)
C27-C28-C29-C30	76(3)	C39-N2-C49-O5	-176.1(8)
C28-C29-C30-C31	47(4)	C63-N2-C49-O5	2.4(13)
N1-C25-C26A-C27A	175(2)	C39-N2-C49-C48	6.0(12)
C25-C26A-C27A-C28A	174(3)	C63-N2-C49-C48	-175.5(7)
C26A-C27A-C28A-C29A	-170(3)	C47-C48-C49-O5	-1.5(13)
C27A-C28A-C29A-C30A	-75(3)	C50-C48-C49-O5	-179.4(8)
C28A-C29A-C30A-C31A	-62(3)	C47-C48-C49-N2	176.2(8)
C18-O3-C32-C33	164.1(6)	C50-C48-C49-N2	-1.6(11)
O3-C32-C33-C34	61.5(9)	C41-C40-C50-C48	179.8(7)
C32-C33-C34-C35	-176.0(8)	C39-C40-C50-C48	-0.4(11)
C33-C34-C35-C36	174.4(8)	C41-C40-C50-C44	1.7(11)
C34-C35-C36-C37	-177.9(9)	C39-C40-C50-C44	-178.5(7)
C35-C36-C37-C38	173.1(10)	C47-C48-C50-C40	-178.8(7)
C49-N2-C39-O4	177.4(8)	C49-C48-C50-C40	-1.1(11)
C63-N2-C39-O4	-1.2(11)	C47-C48-C50-C44	-0.6(11)
C49-N2-C39-C40	-7.4(12)	C49-C48-C50-C44	177.2(7)
C63-N2-C39-C40	174.0(7)	C43-C44-C50-C40	-2.2(11)
O4-C39-C40-C41	-0.7(13)	C45-C44-C50-C40	179.0(7)
N2-C39-C40-C41	-175.8(7)	C43-C44-C50-C48	179.6(7)
O4-C39-C40-C50	179.5(8)	C45-C44-C50-C48	0.7(11)
N2-C39-C40-C50	4.4(11)	C52-C53-C54-C55	-178.6(8)
C50-C40-C41-C42	-1.7(12)	C62-C53-C54-C55	2.3(13)
C39-C40-C41-C42	178.5(8)	C53-C54-C55-C56	-4.1(14)
C40-C41-C42-C43	2.6(13)	C70-O6-C56-C55	-9.5(13)
C41-C42-C43-C44	-3.1(13)	C70-O6-C56-C57	167.3(8)
C41-C42-C43-C51	179.8(8)	C54-C55-C56-O6	-178.9(8)
C42-C43-C44-C50	2.8(12)	C54-C55-C56-C57	4.4(13)
C51-C43-C44-C50	-180.0(7)	O6-C56-C57-C62	179.8(7)

C55-C56-C57-C62	-3.1(13)	C49-N2-C63-C64	86.0(10)
O6-C56-C57-C58	2.5(12)	C39-N2-C63-C64	-95.4(9)
C55-C56-C57-C58	179.5(8)	N2-C63-C64-C65	-171.6(8)
C62-C57-C58-C59	3.5(13)	C63-C64-C65-C66	68.8(12)
C56-C57-C58-C59	-179.1(8)	C64-C65-C66-C67	173.8(8)
C57-C58-C59-C60	-2.8(14)	C65-C66-C67-C68	-178.0(9)
C58-C59-C60-C61	1.1(14)	C66-C67-C68-C69	-178.8(9)
C59-C60-C61-C62	-0.2(13)	C56-O6-C70-C71	-168.3(9)
C56-C57-C62-C61	180.0(8)	O6-C70-C71-C72	-72(2)
C58-C57-C62-C61	-2.6(12)	O6-C70-C71-C72A	-157.7(16)
C56-C57-C62-C53	1.4(12)	C70-C71-C72-C73	-168(2)
C58-C57-C62-C53	178.9(7)	C71-C72-C73-C74	163(2)
C60-C61-C62-C57	1.1(12)	C72-C73-C74-C75	153(3)
C60-C61-C62-C53	179.6(8)	C73-C74-C75-C76	-158(4)
C54-C53-C62-C57	-0.9(12)	C70-C71-C72A-C73A	-178.5(19)
C52-C53-C62-C57	180.0(8)	C71-C72A-C73A-C74A	55(4)
C54-C53-C62-C61	-179.5(8)	C72A-C73A-C74A-C75A	180(3)
C52-C53-C62-C61	1.5(12)	C73A-C74A-C75A-C76A	-176(4)

End of crystallographic info for **7Y**'

#### **CRYSTALLOGRAPHIC MATERIAL FOR 8Y**

Crystallographic Material for 8Y.

X-ray Experimental.

Table **8Y.**1. Crystallographic Data for **8Y**.

Table **8Y.**2. Fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for the non-hydrogen atoms of **8Y**.

Table 8Y.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 8Y.

Table **8Y.**4. Anisotropic thermal parameters for the non-hydrogen atoms of **8Y**.

Table **8Y.**5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **8Y**.

X-ray Experimental for complex C<sub>40</sub>H<sub>45</sub>NO<sub>2</sub> (**8Y**): Crystals grew as long yellow needles by vapor diffusion of Toluene in a jar of MeCN. The data crystal had approximate dimensions; 0.28 x 0.033 x 0.024 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 670 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 20 seconds per frame with a detector offset of +/- 38.1° and 60 seconds per frame with a detector offset of +/- 107.8°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.<sup>3</sup> atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.077*P)^2]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.290, with R(F) equal to 0.0989 and a goodness of fit, S, = 1.12. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

# **References**

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- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Empirical formula	C40 H45 N O3		
Formula weight	587.77		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	C c		
Unit cell dimensions	a = 56.522(6) Å	α= 90°.	
	b = 7.4288(11) Å	β= 95.814(10)°.	
	c = 15.489(2) Å	$\gamma = 90^{\circ}$ .	
Volume	6470.4(16) Å <sup>3</sup>		
Ζ	8		
Density (calculated)	1.207 Mg/m <sup>3</sup>		
Absorption coefficient	0.582 mm <sup>-1</sup>		
F(000)	2528		
Crystal size	0.280 x 0.033 x 0.024 mm <sup>3</sup>		
Theta range for data collection	5.742 to 58.927°.		
Index ranges	-62<=h<=62, -8<=k<=8, -12<=l<=17		
Reflections collected	8294		
Independent reflections	5494 [R(int) = 0.0796]		
Completeness to theta = $58.927^{\circ}$ 99.6 %			
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.00 and 0.136		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	5494 / 530 / 797		
Goodness-of-fit on F <sup>2</sup>	1.123		
Final R indices [I>2sigma(I)]	R1 = 0.0989, wR2 = 0.2201		
R indices (all data)	R1 = 0.1765, $wR2 = 0.2905$		
Absolute structure parameter	-0.6(10)		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.379 and -0.460 e.Å <sup>-3</sup>		

Table 8Y.1. Crystal data and structure refinement for 8Y.
	Х	У	Ζ	U(eq)
C1	6100(3)	4680(20)	4644(10)	44(4)
C2	5856(2)	4470(20)	4872(9)	38(4)
C3	5793(3)	5000(20)	5683(11)	51(4)
C4	5556(2)	4860(20)	5867(9)	42(4)
C5	5383(3)	4060(20)	5299(10)	45(4)
C6	5441(2)	3480(20)	4456(10)	40(4)
C7	5273(3)	2750(20)	3833(10)	44(4)
C8	5339(3)	2280(20)	3040(11)	49(4)
C9	5572(3)	2450(20)	2845(11)	47(4)
C10	5735(2)	3140(20)	3450(9)	38(4)
C11	5985(3)	3400(20)	3198(9)	42(4)
C12	5680(2)	3690(20)	4258(9)	37(4)
C13	5142(3)	3910(20)	5492(11)	52(4)
C14	4935(3)	3680(20)	5615(10)	43(4)
C15	4691(3)	3430(20)	5734(10)	40(4)
C16	4539(3)	2670(20)	5101(10)	41(4)
C17	4300(2)	2410(20)	5174(9)	37(4)
C18	4209(2)	2800(20)	5955(10)	38(4)
C19	4361(2)	3590(20)	6635(9)	40(4)
C20	4270(2)	4100(20)	7464(9)	40(4)
C21	4413(3)	4870(20)	8098(10)	45(4)
C22	4655(3)	5110(20)	7994(10)	47(4)
C23	4749(3)	4750(20)	7243(10)	40(4)
C24	4601(2)	3910(20)	6554(9)	36(4)
C25	6382(2)	4560(20)	3512(11)	52(4)
C26	6378(3)	6450(20)	3042(11)	51(4)
C27	6620(2)	6800(20)	2683(10)	52(4)
C28	6665(3)	5660(30)	1922(11)	59(5)
C29	6898(2)	6150(20)	1560(10)	50(4)
C30	6954(3)	5000(20)	770(10)	54(4)
C31	7187(3)	5500(30)	410(11)	60(5)

Table **8Y.2**. Atomic coordinates (  $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **8Y.** U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	7249(3)	4340(30)	-349(11)	71(6)
C33	3811(3)	2060(20)	5391(10)	48(4)
C34	3568(3)	2000(20)	5764(11)	52(4)
C35	3375(2)	1230(20)	5139(10)	53(4)
C36	3133(3)	1230(20)	5465(11)	60(5)
C37	3113(3)	-70(20)	6236(12)	58(5)
C38	2872(3)	30(30)	6627(11)	64(5)
C39	2863(3)	-1260(30)	7373(12)	66(5)
C40	2641(3)	-1120(30)	7835(13)	77(6)
C41	3929(3)	7380(20)	6179(10)	42(4)
C42	4177(3)	7770(20)	5995(9)	40(4)
C43	4251(2)	7320(20)	5215(10)	38(4)
C44	4487(3)	7620(20)	5029(11)	50(4)
C45	4647(2)	8390(20)	5651(9)	35(4)
C46	4574(2)	8910(20)	6483(9)	35(4)
C47	4734(3)	9700(20)	7132(9)	40(4)
C48	4654(3)	10150(20)	7938(10)	42(4)
C49	4417(3)	9870(20)	8082(10)	46(4)
C50	4265(2)	9070(20)	7460(9)	36(4)
C51	4016(3)	8690(20)	7651(10)	47(4)
C52	4336(2)	8590(20)	6638(10)	39(4)
C53	4887(2)	8670(20)	5461(9)	37(4)
C54	5092(3)	8880(20)	5330(10)	43(4)
C55	5338(2)	9090(20)	5230(9)	35(4)
C56	5485(2)	9850(20)	5881(9)	40(4)
C57	5730(3)	10040(20)	5842(9)	43(4)
C58	5831(2)	9540(20)	5104(9)	36(4)
C59	5685(2)	8820(20)	4379(9)	36(4)
C60	5782(2)	8330(20)	3597(9)	42(4)
C61	5638(3)	7580(20)	2915(10)	41(4)
C62	5396(3)	7370(20)	2981(10)	48(4)
C63	5297(3)	7770(20)	3739(11)	48(4)
C64	5436(2)	8560(20)	4441(10)	40(4)
C65	3625(2)	7310(20)	7230(10)	49(4)
C66	3624(3)	5520(20)	7712(10)	50(4)
C67	3378(3)	5050(30)	7919(11)	58(5)

C68	3378(3)	3340(20)	8445(12)	60(5)
C69	3121(3)	2830(30)	8641(12)	63(5)
C70	3030(3)	4060(30)	9345(11)	64(5)
C71	2785(3)	3430(30)	9584(12)	66(5)
C72	2691(3)	4630(30)	10298(13)	78(6)
C73	6234(3)	9980(20)	5767(10)	50(4)
C74	6479(2)	9550(20)	5549(10)	53(4)
C75	6557(3)	10640(30)	4808(11)	56(4)
C76	6800(3)	10100(30)	4528(10)	54(4)
C77	6869(3)	11130(20)	3734(10)	52(4)
C78	7098(3)	10480(30)	3380(11)	59(5)
C79	7145(3)	11480(30)	2585(11)	65(5)
C80	7363(3)	10830(30)	2168(12)	76(6)
N1	6148(2)	4216(19)	3803(8)	45(3)
N2	3868(2)	7838(19)	7018(8)	44(3)
O1	6261(2)	5320(18)	5148(7)	58(3)
O2	6040(2)	2893(18)	2483(7)	61(3)
O3	3980(2)	2586(16)	6121(6)	46(3)
O4	3785(2)	6684(17)	5642(6)	52(3)
O5	3944(2)	9033(18)	8364(7)	60(3)
O6	6066(2)	9610(15)	4994(6)	43(3)

C1-O1	1.234(18)	C19-C20	1.481(19)
C1-N1	1.40(2)	C20-C21	1.33(2)
C1-C2	1.46(2)	С20-Н20	0.95
C2-C3	1.40(2)	C21-C22	1.41(2)
C2-C12	1.429(19)	C21-H21	0.95
C3-C4	1.40(2)	C22-C23	1.36(2)
С3-Н3	0.95	С22-Н22	0.95
C4-C5	1.38(2)	C23-C24	1.43(2)
C4-H4	0.95	С23-Н23	0.95
C5-C13	1.43(2)	C25-N1	1.461(19)
C5-C6	1.45(2)	C25-C26	1.58(2)
C6-C7	1.40(2)	C25-H25A	0.99
C6-C12	1.420(19)	C25-H25B	0.99
C7-C8	1.36(2)	C26-C27	1.551(19)
С7-Н7	0.95	С26-Н26А	0.99
C8-C9	1.39(2)	С26-Н26В	0.99
С8-Н8	0.95	C27-C28	1.49(2)
C9-C10	1.35(2)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.38(2)	C28-C29	1.53(2)
C10-C11	1.51(2)	C28-H28A	0.99
C11-O2	1.239(17)	C28-H28B	0.99
C11-N1	1.387(18)	C29-C30	1.55(2)
C13-C14	1.21(2)	С29-Н29А	0.99
C14-C15	1.42(2)	С29-Н29В	0.99
C15-C16	1.36(2)	C30-C31	1.53(2)
C15-C24	1.46(2)	С30-Н30А	0.99
C16-C17	1.38(2)	С30-Н30В	0.99
С16-Н16	0.95	C31-C32	1.53(2)
C17-C18	1.39(2)	C31-H31A	0.99
C17-H17	0.95	C31-H31B	0.99
C18-O3	1.352(17)	C32-H32A	0.98
C18-C19	1.42(2)	C32-H32B	0.98
C19-C24	1.397(19)	C32-H32C	0.98

Table **8Y.3**. Bond lengths [Å] and angles [°] for **8Y.** 

C33-O3	1.457(17)	C46-C47	1.41(2)
C33-C34	1.55(2)	C46-C52	1.411(19)
C33-H33A	0.99	C47-C48	1.41(2)
С33-Н33В	0.99	C47-H47	0.95
C34-C35	1.493(19)	C48-C49	1.40(2)
C34-H34A	0.99	C48-H48	0.95
C34-H34B	0.99	C49-C50	1.36(2)
C35-C36	1.51(2)	C49-H49	0.95
C35-H35A	0.99	C50-C52	1.420(19)
C35-H35B	0.99	C50-C51	1.49(2)
C36-C37	1.55(2)	C51-O5	1.243(18)
C36-H36A	0.99	C51-N2	1.379(19)
C36-H36B	0.99	C53-C54	1.207(19)
C37-C38	1.54(2)	C54-C55	1.424(19)
С37-Н37А	0.99	C55-C56	1.36(2)
С37-Н37В	0.99	C55-C64	1.45(2)
C38-C39	1.51(2)	C56-C57	1.40(2)
C38-H38A	0.99	С56-Н56	0.95
C38-H38B	0.99	C57-C58	1.38(2)
C39-C40	1.51(2)	С57-Н57	0.95
С39-Н39А	0.99	C58-O6	1.355(17)
С39-Н39В	0.99	C58-C59	1.430(19)
C40-H40A	0.98	C59-C60	1.42(2)
C40-H40B	0.98	C59-C64	1.437(18)
C40-H40C	0.98	C60-C61	1.38(2)
C41-O4	1.216(17)	С60-Н60	0.95
C41-N2	1.419(19)	C61-C62	1.39(2)
C41-C42	1.49(2)	C61-H61	0.95
C42-C43	1.36(2)	C62-C63	1.38(2)
C42-C52	1.41(2)	С62-Н62	0.95
C43-C44	1.41(2)	C63-C64	1.40(2)
С43-Н43	0.95	С63-Н63	0.95
C44-C45	1.38(2)	C65-N2	1.494(17)
C44-H44	0.95	C65-C66	1.52(2)
C45-C53	1.429(19)	С65-Н65А	0.99
C45-C46	1.45(2)	C65-H65B	0.99

C66-C67	1.50(2)	С73-Н73А	0.99
C66-H66A	0.99	С73-Н73В	0.99
С66-Н66В	0.99	C74-C75	1.51(2)
C67-C68	1.51(2)	C74-H74A	0.99
С67-Н67А	0.99	C74-H74B	0.99
С67-Н67В	0.99	C75-C76	1.54(2)
C68-C69	1.56(2)	С75-Н75А	0.99
C68-H68A	0.99	C75-H75B	0.99
C68-H68B	0.99	C76-C77	1.53(2)
C69-C70	1.55(2)	С76-Н76А	0.99
С69-Н69А	0.99	C76-H76B	0.99
С69-Н69В	0.99	C77-C78	1.53(2)
C70-C71	1.54(2)	С77-Н77А	0.99
С70-Н70А	0.99	С77-Н77В	0.99
С70-Н70В	0.99	C78-C79	1.49(2)
C71-C72	1.55(2)	C78-H78A	0.99
C71-H71A	0.99	C78-H78B	0.99
C71-H71B	0.99	C79-C80	1.52(2)
С72-Н72А	0.98	С79-Н79А	0.99
С72-Н72В	0.98	С79-Н79В	0.99
С72-Н72С	0.98	C80-H80A	0.98
C73-O6	1.475(16)	C80-H80B	0.98
C73-C74	1.49(2)	C80-H80C	0.98
01-C1-N1	118.8(14)	C4-C5-C13	122.0(16)
01-C1-C2	122.8(14)	C4-C5-C6	119.3(14)
N1-C1-C2	118.3(13)	C13-C5-C6	118.6(15)
C3-C2-C12	119.3(14)	C7-C6-C12	119.3(14)
C3-C2-C1	121.1(14)	C7-C6-C5	122.4(13)
C12-C2-C1	119.6(13)	C12-C6-C5	118.3(14)
C2-C3-C4	119.8(15)	C8-C7-C6	119.4(14)
С2-С3-Н3	120.1	С8-С7-Н7	120.3
С4-С3-Н3	120.1	С6-С7-Н7	120.3
C5-C4-C3	122.2(15)	C7-C8-C9	121.7(16)
С5-С4-Н4	118.9	С7-С8-Н8	119.2
С3-С4-Н4	118.9	С9-С8-Н8	119.2

C10-C9-C8	118.8(15)	С23-С22-Н22	118.5
С10-С9-Н9	120.6	С21-С22-Н22	118.5
С8-С9-Н9	120.6	C22-C23-C24	118.5(14)
C9-C10-C12	122.5(13)	С22-С23-Н23	120.7
C9-C10-C11	117.4(13)	С24-С23-Н23	120.7
C12-C10-C11	119.9(13)	C19-C24-C23	120.5(13)
O2-C11-N1	121.8(14)	C19-C24-C15	117.6(13)
O2-C11-C10	121.1(13)	C23-C24-C15	121.8(13)
N1-C11-C10	117.1(13)	N1-C25-C26	108.9(12)
C10-C12-C6	118.2(13)	N1-C25-H25A	109.9
C10-C12-C2	121.0(13)	С26-С25-Н25А	109.9
C6-C12-C2	120.9(14)	N1-C25-H25B	109.9
C14-C13-C5	175.2(19)	С26-С25-Н25В	109.9
C13-C14-C15	178.4(18)	H25A-C25-H25B	108.3
C16-C15-C14	120.8(15)	C27-C26-C25	110.2(12)
C16-C15-C24	118.6(13)	С27-С26-Н26А	109.6
C14-C15-C24	120.5(14)	С25-С26-Н26А	109.6
C15-C16-C17	123.6(15)	С27-С26-Н26В	109.6
С15-С16-Н16	118.2	С25-С26-Н26В	109.6
С17-С16-Н16	118.2	H26A-C26-H26B	108.1
C16-C17-C18	119.5(14)	C28-C27-C26	114.3(14)
С16-С17-Н17	120.3	С28-С27-Н27А	108.7
С18-С17-Н17	120.3	С26-С27-Н27А	108.7
O3-C18-C17	125.7(14)	С28-С27-Н27В	108.7
O3-C18-C19	115.4(13)	С26-С27-Н27В	108.7
C17-C18-C19	118.8(13)	H27A-C27-H27B	107.6
C24-C19-C18	121.8(14)	C27-C28-C29	112.1(14)
C24-C19-C20	117.5(13)	C27-C28-H28A	109.2
C18-C19-C20	120.7(13)	C29-C28-H28A	109.2
C21-C20-C19	120.6(13)	С27-С28-Н28В	109.2
С21-С20-Н20	119.7	С29-С28-Н28В	109.2
С19-С20-Н20	119.7	H28A-C28-H28B	107.9
C20-C21-C22	119.7(16)	C28-C29-C30	114.4(14)
C20-C21-H21	120.2	С28-С29-Н29А	108.7
С22-С21-Н21	120.2	С30-С29-Н29А	108.7
C23-C22-C21	122.9(15)	С28-С29-Н29В	108.7

С30-С29-Н29В	108.7	С36-С35-Н35В	108.7
H29A-C29-H29B	107.6	H35A-C35-H35B	107.6
C31-C30-C29	114.0(14)	C35-C36-C37	113.4(14)
С31-С30-Н30А	108.7	С35-С36-Н36А	108.9
С29-С30-Н30А	108.7	С37-С36-Н36А	108.9
С31-С30-Н30В	108.7	С35-С36-Н36В	108.9
С29-С30-Н30В	108.7	С37-С36-Н36В	108.9
H30A-C30-H30B	107.6	H36A-C36-H36B	107.7
C30-C31-C32	114.6(15)	C38-C37-C36	114.0(14)
С30-С31-Н31А	108.6	С38-С37-Н37А	108.7
С32-С31-Н31А	108.6	С36-С37-Н37А	108.7
С30-С31-Н31В	108.6	С38-С37-Н37В	108.7
С32-С31-Н31В	108.6	С36-С37-Н37В	108.7
H31A-C31-H31B	107.6	H37A-C37-H37B	107.6
С31-С32-Н32А	109.5	C39-C38-C37	111.8(14)
С31-С32-Н32В	109.5	С39-С38-Н38А	109.3
H32A-C32-H32B	109.5	С37-С38-Н38А	109.3
С31-С32-Н32С	109.5	С39-С38-Н38В	109.3
H32A-C32-H32C	109.5	С37-С38-Н38В	109.3
H32B-C32-H32C	109.5	H38A-C38-H38B	107.9
O3-C33-C34	104.7(12)	C38-C39-C40	114.7(15)
O3-C33-H33A	110.8	С38-С39-Н39А	108.6
С34-С33-Н33А	110.8	С40-С39-Н39А	108.6
O3-C33-H33B	110.8	С38-С39-Н39В	108.6
С34-С33-Н33В	110.8	С40-С39-Н39В	108.6
H33A-C33-H33B	108.9	H39A-C39-H39B	107.6
C35-C34-C33	112.6(13)	С39-С40-Н40А	109.5
С35-С34-Н34А	109.1	С39-С40-Н40В	109.5
С33-С34-Н34А	109.1	H40A-C40-H40B	109.5
С35-С34-Н34В	109.1	С39-С40-Н40С	109.5
С33-С34-Н34В	109.1	H40A-C40-H40C	109.5
H34A-C34-H34B	107.8	H40B-C40-H40C	109.5
C34-C35-C36	114.1(14)	O4-C41-N2	121.5(14)
С34-С35-Н35А	108.7	O4-C41-C42	121.8(14)
С36-С35-Н35А	108.7	N2-C41-C42	116.8(13)
C34-C35-H35B	108.7	C43-C42-C52	120.0(14)

C43-C42-C41	120.3(14)	C54-C55-C64	121.7(14)
C52-C42-C41	119.7(13)	C55-C56-C57	122.7(14)
C42-C43-C44	121.8(15)	С55-С56-Н56	118.6
С42-С43-Н43	119.1	С57-С56-Н56	118.6
С44-С43-Н43	119.1	C58-C57-C56	120.3(14)
C45-C44-C43	119.4(16)	С58-С57-Н57	119.8
C45-C44-H44	120.3	С56-С57-Н57	119.8
C43-C44-H44	120.3	O6-C58-C57	126.0(13)
C44-C45-C53	119.2(14)	O6-C58-C59	114.2(13)
C44-C45-C46	120.5(13)	C57-C58-C59	119.8(13)
C53-C45-C46	120.3(13)	C60-C59-C58	121.6(13)
C47-C46-C52	120.1(14)	C60-C59-C64	119.0(13)
C47-C46-C45	121.9(13)	C58-C59-C64	119.4(13)
C52-C46-C45	118.0(13)	C61-C60-C59	120.4(13)
C48-C47-C46	119.5(14)	С61-С60-Н60	119.8
С48-С47-Н47	120.2	С59-С60-Н60	119.8
С46-С47-Н47	120.2	C60-C61-C62	119.7(14)
C49-C48-C47	120.2(15)	С60-С61-Н61	120.2
С49-С48-Н48	119.9	С62-С61-Н61	120.2
С47-С48-Н48	119.9	C63-C62-C61	121.5(15)
C50-C49-C48	120.0(15)	С63-С62-Н62	119.3
С50-С49-Н49	120.0	С61-С62-Н62	119.3
С48-С49-Н49	120.0	C62-C63-C64	120.6(15)
C49-C50-C52	122.0(14)	С62-С63-Н63	119.7
C49-C50-C51	118.8(14)	С64-С63-Н63	119.7
C52-C50-C51	119.1(13)	C63-C64-C59	118.6(14)
O5-C51-N2	119.6(14)	C63-C64-C55	122.5(13)
O5-C51-C50	122.7(14)	C59-C64-C55	118.8(13)
N2-C51-C50	117.6(13)	N2-C65-C66	112.7(12)
C46-C52-C42	120.3(14)	N2-C65-H65A	109.0
C46-C52-C50	118.1(13)	С66-С65-Н65А	109.0
C42-C52-C50	121.6(13)	N2-C65-H65B	109.0
C54-C53-C45	177.5(16)	С66-С65-Н65В	109.0
C53-C54-C55	176.3(16)	H65A-C65-H65B	107.8
C56-C55-C54	119.5(14)	C67-C66-C65	111.0(13)
C56-C55-C64	118.8(13)	C67-C66-H66A	109.4

С65-С66-Н66А	109.4	H72A-C72-H72B	109.5
С67-С66-Н66В	109.4	С71-С72-Н72С	109.5
С65-С66-Н66В	109.4	H72A-C72-H72C	109.5
H66A-C66-H66B	108.0	H72B-C72-H72C	109.5
C66-C67-C68	111.3(13)	O6-C73-C74	108.2(13)
С66-С67-Н67А	109.4	O6-C73-H73A	110.1
С68-С67-Н67А	109.4	С74-С73-Н73А	110.1
С66-С67-Н67В	109.4	O6-C73-H73B	110.1
С68-С67-Н67В	109.4	С74-С73-Н73В	110.1
H67A-C67-H67B	108.0	H73A-C73-H73B	108.4
C67-C68-C69	111.2(14)	C73-C74-C75	113.9(14)
C67-C68-H68A	109.4	С73-С74-Н74А	108.8
C69-C68-H68A	109.4	С75-С74-Н74А	108.8
C67-C68-H68B	109.4	С73-С74-Н74В	108.8
C69-C68-H68B	109.4	С75-С74-Н74В	108.8
H68A-C68-H68B	108.0	H74A-C74-H74B	107.7
C70-C69-C68	112.1(15)	C74-C75-C76	114.6(14)
С70-С69-Н69А	109.2	С74-С75-Н75А	108.6
С68-С69-Н69А	109.2	С76-С75-Н75А	108.6
С70-С69-Н69В	109.2	С74-С75-Н75В	108.6
С68-С69-Н69В	109.2	С76-С75-Н75В	108.6
H69A-C69-H69B	107.9	H75A-C75-H75B	107.6
C71-C70-C69	111.1(15)	C77-C76-C75	114.1(14)
С71-С70-Н70А	109.4	С77-С76-Н76А	108.7
С69-С70-Н70А	109.4	С75-С76-Н76А	108.7
С71-С70-Н70В	109.4	С77-С76-Н76В	108.7
С69-С70-Н70В	109.4	С75-С76-Н76В	108.7
H70A-C70-H70B	108.0	H76A-C76-H76B	107.6
C70-C71-C72	112.1(15)	C76-C77-C78	115.1(14)
C70-C71-H71A	109.2	С76-С77-Н77А	108.5
C72-C71-H71A	109.2	С78-С77-Н77А	108.5
С70-С71-Н71В	109.2	С76-С77-Н77В	108.5
С72-С71-Н71В	109.2	С78-С77-Н77В	108.5
H71A-C71-H71B	107.9	H77A-C77-H77B	107.5
С71-С72-Н72А	109.5	C79-C78-C77	111.6(15)
С71-С72-Н72В	109.5	С79-С78-Н78А	109.3

С77-С78-Н78А	109.3	H80A-C80-H80B	109.5
С79-С78-Н78В	109.3	С79-С80-Н80С	109.5
С77-С78-Н78В	109.3	H80A-C80-H80C	109.5
H78A-C78-H78B	108.0	H80B-C80-H80C	109.5
C78-C79-C80	114.4(16)	C11-N1-C1	123.9(13)
С78-С79-Н79А	108.7	C11-N1-C25	115.3(13)
С80-С79-Н79А	108.7	C1-N1-C25	120.8(13)
С78-С79-Н79В	108.7	C51-N2-C41	125.1(12)
С80-С79-Н79В	108.7	C51-N2-C65	118.0(13)
Н79А-С79-Н79В	107.6	C41-N2-C65	116.8(12)
С79-С80-Н80А	109.5	C18-O3-C33	116.6(12)
С79-С80-Н80В	109.5	C58-O6-C73	117.5(11)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	27(7)	63(9)	42(7)	-7(7)	-1(6)	-5(6)
C2	27(6)	54(8)	34(7)	-5(6)	6(5)	7(6)
C3	37(7)	55(8)	59(8)	6(7)	-3(7)	-4(7)
C4	35(7)	54(8)	39(7)	-3(7)	10(6)	-3(6)
C5	41(7)	53(8)	41(7)	2(7)	9(6)	0(7)
C6	22(6)	49(8)	47(7)	7(7)	2(6)	0(6)
C7	22(6)	60(9)	51(8)	1(7)	5(6)	5(6)
C8	31(7)	62(9)	53(8)	1(7)	-6(6)	5(7)
С9	34(7)	61(9)	46(7)	-9(7)	4(6)	0(7)
C10	22(6)	50(8)	40(7)	-3(7)	4(6)	-8(6)
C11	33(7)	57(8)	36(7)	-5(7)	1(6)	2(6)
C12	22(6)	50(8)	41(7)	-10(6)	4(6)	0(6)
C13	39(8)	60(9)	56(8)	4(7)	4(7)	3(7)
C14	26(7)	54(8)	49(7)	-1(7)	6(6)	1(6)
C15	28(6)	44(8)	50(7)	3(7)	10(6)	-1(6)
C16	40(7)	45(8)	40(7)	0(7)	10(6)	3(6)
C17	27(6)	56(8)	30(6)	-2(6)	8(6)	2(6)
C18	22(6)	44(8)	49(7)	5(7)	2(6)	1(6)
C19	27(6)	55(8)	37(7)	3(7)	2(6)	-1(6)
C20	22(6)	54(8)	45(7)	-4(7)	6(6)	1(6)
C21	42(7)	49(8)	46(7)	1(7)	8(6)	7(7)
C22	38(7)	59(8)	43(7)	-1(7)	-4(6)	0(7)
C23	28(6)	44(8)	47(7)	5(7)	-3(6)	3(6)
C24	32(7)	44(8)	32(7)	1(6)	4(6)	3(6)
C25	21(6)	69(9)	64(8)	5(8)	0(6)	7(6)
C26	29(6)	67(9)	59(8)	9(7)	17(6)	10(7)
C27	25(6)	74(9)	57(8)	-9(7)	3(6)	-4(7)
C28	30(7)	81(10)	66(9)	-1(8)	-5(6)	-8(7)
C29	20(6)	70(9)	59(8)	-11(7)	0(6)	3(6)
C30	33(7)	69(9)	58(8)	0(7)	-2(6)	2(7)

Table **8Y.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **8Y.** The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C31	28(7)	90(10)	61(8)	2(8)	2(6)	1(7)
C32	34(8)	105(14)	75(11)	-10(11)	14(8)	-6(9)
C33	32(7)	58(8)	54(8)	-6(7)	1(6)	-7(7)
C34	25(6)	68(9)	62(8)	-18(7)	-4(6)	11(7)
C35	32(7)	67(9)	58(8)	-17(7)	-2(6)	-4(7)
C36	40(7)	70(9)	71(9)	-1(8)	7(7)	0(7)
C37	35(7)	68(9)	72(9)	-4(8)	6(7)	-4(7)
C38	37(7)	79(10)	75(9)	-5(8)	-2(7)	5(7)
C39	38(7)	86(10)	74(9)	5(8)	0(7)	-3(7)
C40	47(9)	99(14)	88(12)	3(12)	15(9)	-6(10)
C41	31(7)	51(8)	45(7)	-16(7)	1(6)	2(6)
C42	30(7)	54(8)	39(7)	-4(7)	7(6)	-2(6)
C43	18(6)	52(8)	43(7)	4(7)	-7(5)	-3(6)
C44	32(7)	65(9)	53(8)	-3(7)	5(6)	1(7)
C45	24(6)	46(8)	35(6)	7(6)	2(5)	-5(6)
C46	20(6)	44(8)	39(7)	-5(6)	0(5)	1(6)
C47	28(6)	47(8)	45(7)	1(7)	2(6)	-4(6)
C48	32(6)	55(8)	39(7)	1(7)	-1(6)	-5(6)
C49	30(7)	63(9)	46(7)	2(7)	7(6)	3(7)
C50	32(7)	48(8)	28(6)	2(6)	6(5)	4(6)
C51	28(7)	62(9)	51(8)	-4(7)	6(6)	3(7)
C52	23(6)	48(8)	46(7)	8(7)	2(6)	3(6)
C53	17(6)	56(8)	39(7)	-1(6)	6(5)	2(6)
C54	29(7)	49(8)	49(7)	1(7)	0(6)	6(6)
C55	18(6)	53(8)	33(6)	6(6)	5(5)	-4(6)
C56	27(6)	49(8)	44(7)	0(7)	10(6)	0(6)
C57	28(6)	64(9)	39(7)	5(7)	8(6)	1(6)
C58	24(6)	47(8)	36(7)	6(6)	2(6)	-3(6)
C59	26(6)	53(8)	28(6)	6(6)	1(5)	-1(6)
C60	26(6)	58(9)	43(7)	7(7)	7(6)	1(6)
C61	30(7)	50(8)	43(7)	-6(7)	6(6)	4(6)
C62	33(7)	72(9)	38(7)	0(7)	-1(6)	14(7)
C63	32(7)	52(8)	62(8)	1(7)	5(6)	3(7)
C64	20(6)	53(8)	49(7)	0(7)	8(6)	-5(6)
C65	25(6)	74(9)	48(7)	-3(7)	7(6)	8(7)
C66	32(7)	65(9)	53(8)	5(7)	12(6)	6(7)

C67	30(7)	76(9)	68(8)	1(8)	5(6)	13(7)
C68	41(7)	71(9)	68(8)	-7(8)	7(7)	6(7)
C69	45(8)	77(10)	71(9)	-20(8)	22(7)	3(7)
C70	42(7)	80(10)	70(9)	-11(8)	10(7)	0(7)
C71	45(8)	79(10)	75(9)	-4(8)	11(7)	3(7)
C72	49(10)	94(14)	94(13)	-16(11)	24(9)	-15(10)
C73	38(7)	67(9)	45(7)	-8(7)	-6(6)	-10(7)
C74	27(6)	67(9)	64(8)	4(7)	0(6)	-5(7)
C75	32(7)	76(9)	61(8)	2(8)	8(6)	-2(7)
C76	31(7)	66(9)	65(8)	0(7)	8(6)	-3(7)
C77	32(7)	70(9)	56(8)	9(7)	12(6)	-13(7)
C78	33(7)	82(10)	63(8)	7(8)	13(6)	-1(7)
C79	51(8)	75(10)	68(9)	-4(8)	8(7)	-5(8)
C80	48(9)	99(14)	84(12)	8(11)	23(9)	-2(10)
N1	21(5)	67(8)	48(6)	-11(6)	3(5)	-2(5)
N2	19(5)	70(8)	44(6)	5(6)	9(5)	-5(6)
01	31(5)	82(9)	60(7)	-6(7)	3(5)	-9(6)
02	34(6)	92(10)	57(7)	-3(7)	4(5)	-6(6)
O3	24(5)	74(7)	42(5)	-6(5)	4(4)	10(5)
O4	28(5)	78(8)	49(6)	-6(6)	8(5)	-7(6)
05	28(5)	87(9)	66(7)	-8(7)	8(5)	1(6)
06	22(4)	65(6)	41(5)	-6(5)	2(4)	-3(5)

	Х	у	Z	U(eq)
H3	5911	5454	6108	61
H4	5513	5323	6400	51
H7	5113	2576	3961	53
H8	5222	1824	2611	59
Н9	5615	2085	2294	56
H16	4600	2307	4580	50
H17	4198	1963	4695	45
H20	4108	3877	7546	48
H21	4351	5251	8616	54
H22	4757	5557	8472	57
H23	4910	5033	7176	48
H25A	6421	3598	3106	62
H25B	6505	4556	4015	62
H26A	6249	6464	2559	61
H26B	6346	7406	3457	61
H27A	6627	8084	2511	62
H27B	6749	6594	3153	62
H28A	6532	5811	1461	71
H28B	6670	4381	2100	71
H29A	7030	6011	2027	60
H29B	6892	7433	1386	60
H30A	6961	3719	944	65
H30B	6822	5136	304	65
H31A	7318	5415	883	72
H31B	7177	6776	217	72
H32A	7251	3068	-177	106
H32B	7405	4682	-512	106
H32C	7129	4516	-846	106
H33A	3852	858	5169	58
H33B	3810	2943	4914	58

Table **8Y.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **8Y.** 

H34A	3582	1267	6301	63
H34B	3523	3238	5922	63
H35A	3418	-19	5002	63
H35B	3367	1936	4593	63
H36A	3013	893	4982	72
H36B	3095	2470	5648	72
H37A	3136	-1316	6037	70
H37B	3242	205	6697	70
H38A	2848	1277	6832	77
H38B	2742	-248	6172	77
H39A	3003	-1039	7799	80
H39B	2875	-2498	7152	80
H40A	2634	70	8106	116
H40B	2644	-2052	8284	116
H40C	2501	-1288	7417	116
H43	4141	6791	4784	46
H44	4534	7291	4479	60
H47	4894	9934	7027	48
H48	4762	10652	8384	51
H49	4362	10235	8615	55
H56	5418	10278	6381	47
H57	5828	10501	6327	52
H60	5946	8516	3545	50
H61	5704	7212	2403	49
H62	5296	6937	2495	58
Н63	5135	7508	3785	58
H65A	3518	7219	6685	59
H65B	3562	8262	7591	59
H66A	3685	4562	7350	60
H66B	3731	5605	8257	60
H67A	3273	4901	7372	69
Н67В	3314	6050	8250	69
H68A	3480	3497	8998	72
H68B	3445	2345	8121	72
H69A	3013	2924	8101	76
H69B	3120	1561	8840	76

H70A	3146	4041	9870	77
H70B	3018	5310	9127	77
H71A	2797	2166	9792	79
H71B	2669	3454	9058	79
H72A	2813	4727	10791	117
H72B	2547	4081	10491	117
H72C	2653	5827	10061	117
H73A	6194	9232	6260	61
H73B	6224	11263	5934	61
H74A	6486	8256	5400	63
H74B	6592	9758	6070	63
H75A	6562	11923	4978	67
H75B	6436	10511	4304	67
H76A	6923	10320	5018	65
H76B	6799	8799	4399	65
H77A	6887	12415	3887	63
H77B	6736	11025	3266	63
H78A	7233	10640	3830	70
H78B	7084	9177	3243	70
H79A	7167	12772	2734	78
H79B	7004	11381	2153	78
H80A	7505	10987	2579	114
H80B	7380	11539	1643	114
H80C	7344	9559	2015	114

End of Crystallographic material for 8Y.

#### **CRYSTALLOGRAPHIC MATERIAL FOR 1BO**

Crystallographic Material for 1BO.

X-ray Experimental.

Table **1BO.**1. Crystallographic Data for **1BO**.

Table **1BO.2**. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **1BO**.

Table **1BO.3**. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of **1BO**.

Table **1BO.4**. Anisotropic thermal parameters for the non-hydrogen atoms of **1BO**.

Table **1BO.5**. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **1**.

Table **1BO.6**. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **1BO**.

X-ray Experimental for complex  $C_{26}H_{17}NO_3$  (**1BO**) Crystals grew as long, very thin orange needles by slow evaporation from CHCl<sub>3</sub>. The data crystal was cut from a larger crystal and had approximate dimensions; 0.45 x 0.030 x 0.018 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda$ = 1.5418Å) with collimating mirror monochromators. A total of 375 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 32 seconds per frame with a detector offset of +/- 41.6° and 90.5 seconds per frame with a detector offset of 110.7°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.37a.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.099*P)^2]$ and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.354, with R(F) equal to 0.117 and a goodness of fit, S, = 1.10. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- 1) CrysAlisPro V 1.171.40.37a (2019). Rigaku Oxford Diffraction, Tokyo, Japan.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
- 4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 1BO.1. Crystal data and structure refine	ment for <b>1BO</b> .			
Empirical formula	C26 H17 N O3	C26 H17 N O3		
Formula weight	391.40			
Temperature	100(2) K			
Wavelength	1.54184 Å			
Crystal system	orthorhombic			
Space group	P n a 21			
Unit cell dimensions	a = 17.809(4) Å	α= 90°.		
	b = 26.103(6) Å	β= 90°.		
	c = 3.8515(15)  Å	$\gamma = 90^{\circ}$ .		
Volume	1790.4(9) Å <sup>3</sup>			
Ζ	4			
Density (calculated)	1.452 Mg/m <sup>3</sup>			
Absorption coefficient	0.767 mm <sup>-1</sup>			
F(000)	816			
Crystal size	0.450 x 0.030 x 0.018 m	nm <sup>3</sup>		
Theta range for data collection	3.004 to 75.312°.			
Index ranges	-11<=h<=21, -19<=k<=	32, -3<=l<=4		
Reflections collected	3667			
Independent reflections	2417 [R(int) = 0.1310]			
Completeness to theta = $67.684^{\circ}$	98.9 %			
Absorption correction	Gaussian and multi-scar	1		
Max. and min. transmission	1.00 and 0.433			
Refinement method	Full-matrix least-square	s on F <sup>2</sup>		
Data / restraints / parameters	2417 / 181 / 273			
Goodness-of-fit on F <sup>2</sup>	1.096			
Final R indices [I>2sigma(I)]	R1 = 0.1172, wR2 = 0.2	640		
R indices (all data) $R1 = 0.2026$ , wR2 = 0.3540				
Absolute structure parameter	-1.6(10)			
Extinction coefficient n/a				
Largest diff. peak and hole 0.474 and -0.437 e.Å <sup>-3</sup>				

	х	У	Z	U(eq)
C1	1428(6)	5130(4)	2280(40)	30(3)
C2	2128(6)	5416(4)	3140(40)	28(3)
C3	2194(6)	5912(5)	2200(40)	33(3)
C4	2853(6)	6194(4)	2980(50)	34(3)
C5	3449(6)	5973(4)	4680(40)	29(3)
C6	3380(6)	5445(4)	5690(50)	31(3)
C7	3974(7)	5189(5)	7490(50)	41(4)
C8	3892(7)	4687(5)	8470(50)	40(3)
C9	3221(5)	4415(5)	7690(40)	32(3)
C10	2649(6)	4659(4)	6020(40)	28(3)
C11	1959(6)	4369(4)	5160(40)	30(3)
C12	2710(5)	5169(4)	4930(40)	27(3)
C13	4113(6)	6261(5)	5440(50)	35(3)
C14	4662(6)	6507(4)	5990(50)	31(3)
C15	5330(6)	6807(4)	6600(40)	28(3)
C16	5948(6)	6573(5)	8110(40)	34(3)
C17	6633(6)	6843(4)	8550(40)	31(3)
C18	6675(6)	7338(5)	7580(50)	30(3)
C19	6036(6)	7606(4)	6130(40)	29(3)
C20	6064(6)	8121(5)	5270(50)	36(3)
C21	5457(6)	8361(4)	3820(50)	34(3)
C22	4792(7)	8086(5)	3280(50)	39(3)
C23	4755(6)	7580(4)	4120(40)	31(3)
C24	5366(6)	7317(4)	5630(40)	29(3)
C25	716(6)	4337(5)	2430(50)	36(3)
C26	7964(6)	7386(5)	9270(50)	43(4)
N1	1396(5)	4626(4)	3390(40)	33(3)
01	916(4)	5326(3)	670(40)	45(3)
02	1872(4)	3923(3)	6040(40)	38(3)
03	7306(4)	7632(3)	7910(30)	35(2)

Table **1BO.2**. Atomic coordinates (  $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **1BO**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C1-O1	1.216(17)	C15-C16	1.387(17)
C1-N1	1.385(15)	C16-C17	1.420(14)
C1-C2	1.491(15)	C16-H16	0.95
C2-C3	1.349(16)	C17-C18	1.347(17)
C2-C12	1.402(18)	C17-H17	0.95
C3-C4	1.418(16)	C18-O3	1.368(12)
С3-Н3	0.95	C18-C19	1.446(17)
C4-C5	1.374(19)	C19-C20	1.387(17)
С4-Н4	0.95	C19-C24	1.425(14)
C5-C13	1.432(16)	C20-C21	1.367(17)
C5-C6	1.437(16)	C20-H20	0.95
C6-C12	1.424(15)	C21-C22	1.402(15)
C6-C7	1.429(19)	C21-H21	0.95
C7-C8	1.373(18)	C22-C23	1.362(17)
С7-Н7	0.95	C22-H22	0.95
C8-C9	1.423(16)	C23-C24	1.413(17)
С8-Н8	0.95	С23-Н23	0.95
C9-C10	1.362(18)	C25-N1	1.473(15)
С9-Н9	0.95	C25-H25A	0.98
C10-C12	1.400(16)	C25-H25B	0.98
C10-C11	1.481(15)	C25-H25C	0.98
C11-O2	1.222(14)	C26-O3	1.434(16)
C11-N1	1.385(17)	C26-H26A	0.98
C13-C14	1.189(16)	C26-H26B	0.98
C14-C15	1.444(15)	C26-H26C	0.98
C15-C24	1.383(16)		
01-C1-N1	121.9(11)	С2-С3-Н3	119.5
O1-C1-C2	121.9(12)	С4-С3-Н3	119.5
N1-C1-C2	116.2(12)	C5-C4-C3	121.5(12)
C3-C2-C12	120.6(11)	С5-С4-Н4	119.3
C3-C2-C1	119.6(12)	С3-С4-Н4	119.3
C12-C2-C1	119.8(11)	C4-C5-C13	121.0(12)
C2-C3-C4	120.9(13)	C4-C5-C6	117.8(10)

Table **1BO.3**. Bond lengths [Å] and angles  $[\circ]$  for **1BO**.

C13-C5-C6	121.2(12)	O3-C18-C19	114.3(11)
C12-C6-C7	118.9(11)	C20-C19-C24	120.7(11)
C12-C6-C5	120.0(12)	C20-C19-C18	122.2(10)
C7-C6-C5	121.0(11)	C24-C19-C18	117.1(11)
C8-C7-C6	120.0(12)	C21-C20-C19	121.0(11)
С8-С7-Н7	120.0	С21-С20-Н20	119.5
С6-С7-Н7	120.0	С19-С20-Н20	119.5
C7-C8-C9	120.5(14)	C20-C21-C22	119.6(12)
С7-С8-Н8	119.7	C20-C21-H21	120.2
С9-С8-Н8	119.7	С22-С21-Н21	120.2
C10-C9-C8	119.6(12)	C23-C22-C21	120.1(12)
С10-С9-Н9	120.2	С23-С22-Н22	119.9
С8-С9-Н9	120.2	С21-С22-Н22	119.9
C9-C10-C12	121.9(11)	C22-C23-C24	122.2(11)
C9-C10-C11	119.1(11)	С22-С23-Н23	118.9
C12-C10-C11	118.8(12)	С24-С23-Н23	118.9
O2-C11-N1	120.3(11)	C15-C24-C23	122.9(11)
O2-C11-C10	122.0(13)	C15-C24-C19	120.8(11)
N1-C11-C10	117.7(10)	C23-C24-C19	116.4(11)
C10-C12-C2	121.9(10)	N1-C25-H25A	109.5
C10-C12-C6	118.9(12)	N1-C25-H25B	109.5
C2-C12-C6	119.2(11)	H25A-C25-H25B	109.5
C14-C13-C5	178.2(19)	N1-C25-H25C	109.5
C13-C14-C15	179.0(19)	H25A-C25-H25C	109.5
C24-C15-C16	120.0(10)	H25B-C25-H25C	109.5
C24-C15-C14	121.1(11)	O3-C26-H26A	109.5
C16-C15-C14	118.8(11)	O3-C26-H26B	109.5
C15-C16-C17	120.8(11)	H26A-C26-H26B	109.5
С15-С16-Н16	119.6	O3-C26-H26C	109.5
С17-С16-Н16	119.6	H26A-C26-H26C	109.5
C18-C17-C16	119.4(12)	H26B-C26-H26C	109.5
С18-С17-Н17	120.3	C1-N1-C11	125.6(10)
С16-С17-Н17	120.3	C1-N1-C25	116.2(11)
C17-C18-O3	123.9(12)	C11-N1-C25	118.1(10)
C17-C18-C19	121.8(10)	C18-O3-C26	117.0(11)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	14(5)	31(5)	45(8)	-1(6)	10(5)	-6(4)
C2	15(5)	30(5)	38(7)	-3(5)	8(5)	-6(4)
C3	21(5)	34(5)	45(7)	-4(6)	3(6)	-2(5)
C4	25(5)	27(5)	50(8)	-9(6)	4(6)	4(4)
C5	14(5)	30(5)	45(7)	-4(5)	7(5)	-6(4)
C6	18(5)	30(5)	45(7)	-8(6)	1(6)	0(4)
C7	22(5)	48(6)	52(8)	-2(7)	6(6)	-3(5)
C8	34(6)	35(5)	49(8)	-3(6)	11(6)	6(5)
C9	12(5)	37(5)	46(7)	9(6)	13(6)	2(4)
C10	13(5)	28(5)	43(7)	0(5)	19(5)	-2(4)
C11	18(5)	28(5)	45(8)	-2(5)	16(5)	-3(4)
C12	8(4)	28(5)	44(7)	0(5)	9(5)	-1(4)
C13	16(5)	47(6)	42(7)	-3(6)	6(6)	-1(5)
C14	23(5)	32(5)	39(7)	2(5)	3(6)	-1(4)
C15	12(5)	28(5)	45(7)	-1(5)	1(5)	-3(4)
C16	23(5)	32(5)	46(7)	-7(6)	5(6)	-5(5)
C17	16(5)	29(5)	48(7)	-3(6)	0(6)	-4(4)
C18	7(4)	37(5)	47(7)	-5(6)	7(5)	-6(4)
C19	15(5)	31(5)	42(7)	0(5)	2(5)	-3(4)
C20	18(5)	35(5)	54(8)	2(6)	-2(6)	1(4)
C21	23(5)	27(5)	51(8)	-4(5)	2(6)	-4(4)
C22	22(5)	46(6)	49(8)	2(6)	0(6)	2(5)
C23	16(5)	38(6)	40(7)	6(6)	0(5)	-6(4)
C24	15(5)	31(5)	40(7)	-6(6)	-3(5)	-2(4)
C25	15(5)	44(7)	50(9)	13(6)	19(6)	-2(5)
C26	20(6)	62(8)	47(9)	-19(8)	6(7)	-5(6)
N1	17(4)	31(4)	50(7)	4(5)	1(5)	-4(4)
01	17(4)	42(5)	76(8)	4(6)	-3(5)	-2(4)
O2	19(4)	33(4)	63(7)	7(5)	5(5)	-4(3)
O3	8(3)	39(4)	58(6)	-5(5)	0(4)	-1(3)

Table **1BO.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **1BO**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

	х	У	Z	U(eq)
H3	1793	6074	1002	40
H4	2884	6543	2308	41
H7	4426	5367	7998	49
H8	4286	4520	9688	47
Н9	3172	4065	8319	38
H16	5912	6227	8862	40
H17	7059	6676	9508	37
H20	6511	8310	5679	43
H21	5487	8712	3191	40
H22	4365	8253	2327	47
H23	4304	7397	3666	38
H25A	461	4219	4540	55
H25B	857	4040	1011	55
H25C	378	4559	1104	55
H26A	7887	7306	11725	64
H26B	8396	7616	9024	64
H26C	8059	7070	7973	64

Table **1BO.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **1BO**.

01-C1-C2-C3	2(2)	C5-C6-C12-C2	1(2)
N1-C1-C2-C3	-178.7(15)	C24-C15-C16-C17	-3(2)
01-C1-C2-C12	-178.5(14)	C14-C15-C16-C17	175.8(15)
N1-C1-C2-C12	1(2)	C15-C16-C17-C18	2(2)
C12-C2-C3-C4	0(2)	C16-C17-C18-O3	179.6(15)
C1-C2-C3-C4	180.0(15)	C16-C17-C18-C19	0(2)
C2-C3-C4-C5	1(2)	C17-C18-C19-C20	177.3(18)
C3-C4-C5-C13	179.8(16)	O3-C18-C19-C20	-2(2)
C3-C4-C5-C6	-1(2)	C17-C18-C19-C24	-2(2)
C4-C5-C6-C12	0(2)	O3-C18-C19-C24	178.3(14)
C13-C5-C6-C12	179.5(15)	C24-C19-C20-C21	-2(3)
C4-C5-C6-C7	-179.7(16)	C18-C19-C20-C21	178.4(16)
C13-C5-C6-C7	0(2)	C19-C20-C21-C22	1(3)
C12-C6-C7-C8	-1(2)	C20-C21-C22-C23	-1(3)
C5-C6-C7-C8	179.1(17)	C21-C22-C23-C24	2(3)
C6-C7-C8-C9	1(3)	C16-C15-C24-C23	-179.3(15)
C7-C8-C9-C10	-2(2)	C14-C15-C24-C23	2(2)
C8-C9-C10-C12	3(2)	C16-C15-C24-C19	1(2)
C8-C9-C10-C11	178.7(15)	C14-C15-C24-C19	-177.9(15)
C9-C10-C11-O2	4(2)	C22-C23-C24-C15	177.8(18)
C12-C10-C11-O2	179.9(15)	C22-C23-C24-C19	-2(2)
C9-C10-C11-N1	-178.5(15)	C20-C19-C24-C15	-177.9(16)
C12-C10-C11-N1	-2.2(19)	C18-C19-C24-C15	2(2)
C9-C10-C12-C2	178.3(15)	C20-C19-C24-C23	2(2)
C11-C10-C12-C2	2(2)	C18-C19-C24-C23	-178.1(14)
C9-C10-C12-C6	-3(2)	01-C1-N1-C11	178.2(15)
C11-C10-C12-C6	-178.7(14)	C2-C1-N1-C11	-1(2)
C3-C2-C12-C10	178.0(16)	01-C1-N1-C25	2(2)
C1-C2-C12-C10	-2(2)	C2-C1-N1-C25	-177.7(13)
C3-C2-C12-C6	-1(2)	O2-C11-N1-C1	179.6(16)
C1-C2-C12-C6	179.4(16)	C10-C11-N1-C1	2(2)
C7-C6-C12-C10	1(2)	O2-C11-N1-C25	-4(2)
C5-C6-C12-C10	-178.3(15)	C10-C11-N1-C25	178.4(14)
C7-C6-C12-C2	-179.3(15)	C17-C18-O3-C26	2(2)

Table **1BO.6**. Torsion angles [°] for **1BO.** 

# C19-C18-O3-C26 -178.7(13)

End of **1BO** crystallographic info

### **CRYSTALLOGRAPHIC MATERIAL FOR 60**

Crystallographic Material for 6O.

X-ray Experimental.

Table **6O**.1. Crystallographic Data for **6O**.

Table 60.2. Fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for the non-hydrogen atoms of 60.

Table 60.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 60

Table 60.4. Anisotropic thermal parameters for the non-hydrogen atoms of 60.

Table 60.5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of 60.

Table **60**.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **60**.

X-ray Experimental for C<sub>36</sub>H<sub>37</sub>NO<sub>3</sub>: (**60**) Crystals grew as very, long orange laths by vapor:vapor diffusion from (30% Toluene, 70% Xylenes) in a jar of MeCN. The data crystal was cut from a larger crystal and had approximate dimensions; 0.41 x 0.037 x 0.020 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 762 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 15 seconds per frame for frames collected with a detector offset of +/- 41.6° and 60 seconds per frame with frames collected with a detector offset of +/- 112.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix leastsquares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The absolute structure could not be reliably determined using either the method of Flack<sup>6</sup> or the Hooft y-parameter method.<sup>7</sup>

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.0395*P)^2]$ and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.120, with R(F) equal to 0.0509 and a goodness of fit, S, = 1.00. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>8</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>9</sup> All figures were generated using SHELXTL/PC.<sup>10</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

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- 6) Flack, H. D. (1983). Acta Cryst A39, 876-881.
- 7) Hooft, R. W. W., Straver, L. H. and Spek, A. L. (2008). J. Appl. Cryst. 41, 96-103.
- 8) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 9) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 10) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 60.1. Crystal data and structure refinement for 60.			
Identification code	shelx		
Empirical formula	C36 H37 N O3		
Formula weight	531.66		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	C c		
Unit cell dimensions	a = 4.6867(4)  Å	<i>α</i> = 90°.	
	b = 38.869(4) Å	β= 96.175(10)°.	
	c = 15.557(2) Å	$\gamma = 90^{\circ}$ .	
Volume	2817.5(5) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.253 Mg/m <sup>3</sup>		
Absorption coefficient	0.617 mm <sup>-1</sup>		
F(000)	1136		
Crystal size	$0.410 \ x \ 0.037 \ x \ 0.020 \ mm^3$		
Theta range for data collection	2.273 to 68.306°.		
Index ranges	-5<=h<=3, -42<=k<=46, -17<=l<=18		
Reflections collected	5693		
Independent reflections	2975 [R(int) = 0.0535]		
Completeness to theta = $67.684^{\circ}$	97.0 %		
Absorption correction	Semi-empirical from equivalen	ts	
Max. and min. transmission	1.00 and 0.750		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	2975 / 2 / 363		
Goodness-of-fit on F <sup>2</sup>	1.003		
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1070		
R indices (all data)	R1 = 0.0791, wR2 = 0.1196		
Absolute structure parameter	0.3(4)		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.232 and -0.232 e.Å <sup>-3</sup>		

	Х	у	Z	U(eq)
C1	-2524(8)	5808(1)	6029(3)	17(1)
C2	-544(8)	5537(1)	5784(3)	14(1)
C3	1174(8)	5366(1)	6419(3)	20(1)
C4	3082(8)	5107(1)	6196(3)	20(1)
C5	3251(8)	5022(1)	5348(4)	18(1)
C6	1471(8)	5194(1)	4669(3)	18(1)
C7	1506(9)	5112(1)	3783(3)	19(1)
C8	-231(9)	5282(1)	3158(3)	21(1)
С9	-2106(9)	5546(1)	3384(3)	21(1)
C10	-2193(8)	5627(1)	4242(3)	16(1)
C11	-4172(8)	5904(1)	4467(3)	18(1)
C12	-432(8)	5454(1)	4897(3)	16(1)
C13	5203(9)	4766(1)	5124(3)	19(1)
C14	6872(9)	4550(1)	4927(3)	18(1)
C15	8856(8)	4296(1)	4691(3)	18(1)
C16	9180(8)	4235(1)	3835(3)	20(1)
C17	11116(9)	3984(1)	3580(3)	18(1)
C18	12672(8)	3794(1)	4208(3)	18(1)
C19	12456(8)	3849(1)	5109(3)	19(1)
C20	14161(8)	3661(1)	5761(3)	20(1)
C21	13944(9)	3725(1)	6620(4)	22(1)
C22	11981(9)	3973(1)	6861(3)	22(1)
C23	10315(9)	4159(1)	6240(3)	21(1)
C24	10529(8)	4104(1)	5354(3)	16(1)
C25	-6125(8)	6253(1)	5582(3)	17(1)
C26	-4513(9)	6596(1)	5600(3)	21(1)
C27	-6412(9)	6904(1)	5777(3)	20(1)
C28	-4806(9)	7244(1)	5733(3)	22(1)
C29	-6605(10)	7564(1)	5888(4)	24(1)
C30	-4885(11)	7893(2)	5828(4)	34(1)
C31	14873(9)	3463(1)	3152(3)	24(1)

Table **60.**2. Atomic coordinates ( $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for 1. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	16561(9)	3129(1)	3143(3)	23(1)
C33	14825(10)	2815(1)	3354(4)	25(1)
C34	16383(10)	2473(2)	3292(3)	26(1)
C35	14502(11)	2162(2)	3435(4)	31(1)
C36	16007(14)	1817(2)	3346(4)	38(1)
N1	-4236(7)	5969(1)	5353(3)	17(1)
01	-2683(6)	5893(1)	6777(2)	25(1)
O2	-5660(7)	6066(1)	3925(2)	28(1)
O3	14491(6)	3531(1)	4039(2)	22(1)

C1-O1	1.221(7)	C19-C20	1.425(7)
C1-N1	1.400(6)	C20-C21	1.374(8)
C1-C2	1.479(7)	С20-Н20	0.95
C2-C3	1.377(7)	C21-C22	1.411(7)
C2-C12	1.424(7)	C21-H21	0.95
C3-C4	1.414(7)	C22-C23	1.381(8)
С3-Н3	0.95	C22-H22	0.95
C4-C5	1.372(7)	C23-C24	1.409(7)
С4-Н4	0.95	С23-Н23	0.95
C5-C13	1.420(7)	C25-N1	1.482(6)
C5-C6	1.438(7)	C25-C26	1.532(7)
C6-C7	1.416(7)	C25-H25A	0.99
C6-C12	1.418(7)	C25-H25B	0.99
C7-C8	1.370(7)	C26-C27	1.532(7)
С7-Н7	0.95	C26-H26A	0.99
C8-C9	1.418(7)	C26-H26B	0.99
С8-Н8	0.95	C27-C28	1.526(7)
C9-C10	1.376(7)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.412(7)	C28-C29	1.536(7)
C10-C11	1.486(7)	C28-H28A	0.99
C11-O2	1.213(6)	C28-H28B	0.99
C11-N1	1.405(7)	C29-C30	1.521(8)
C13-C14	1.208(7)	С29-Н29А	0.99
C14-C15	1.431(7)	C29-H29B	0.99
C15-C16	1.376(7)	С30-Н30А	0.98
C15-C24	1.437(7)	C30-H30B	0.98
C16-C17	1.417(7)	C30-H30C	0.98
С16-Н16	0.95	C31-O3	1.435(6)
C17-C18	1.371(7)	C31-C32	1.521(7)
C17-H17	0.95	C31-H31A	0.99
C18-O3	1.375(6)	C31-H31B	0.99
C18-C19	1.432(7)	C32-C33	1.524(8)
C19-C24	1.420(7)	C32-H32A	0.99

Table **60.3**. Bond lengths [Å] and angles  $[\circ]$  for **60**.

С32-Н32В	0.99	C35-C36	1.528(8)
C33-C34	1.525(7)	C35-H35A	0.99
С33-Н33А	0.99	С35-Н35В	0.99
С33-Н33В	0.99	С36-Н36А	0.98
C34-C35	1.525(8)	С36-Н36В	0.98
C34-H34A	0.99	С36-Н36С	0.98
C34-H34B	0.99		
01-C1-N1	120.3(4)	C9-C10-C11	118.7(4)
01-C1-C2	122.9(4)	C12-C10-C11	120.4(4)
N1-C1-C2	116.7(4)	O2-C11-N1	121.2(4)
C3-C2-C12	120.4(4)	O2-C11-C10	122.6(5)
C3-C2-C1	119.6(4)	N1-C11-C10	116.2(4)
C12-C2-C1	120.1(4)	C10-C12-C6	119.7(5)
C2-C3-C4	120.3(5)	C10-C12-C2	120.7(4)
С2-С3-Н3	119.9	C6-C12-C2	119.6(4)
С4-С3-Н3	119.9	C14-C13-C5	179.3(5)
C5-C4-C3	120.8(5)	C13-C14-C15	179.8(6)
С5-С4-Н4	119.6	C16-C15-C14	120.6(5)
С3-С4-Н4	119.6	C16-C15-C24	119.8(4)
C4-C5-C13	120.8(5)	C14-C15-C24	119.6(5)
C4-C5-C6	120.3(4)	C15-C16-C17	122.0(5)
C13-C5-C6	118.9(5)	С15-С16-Н16	119.0
C7-C6-C12	118.4(5)	C17-C16-H16	119.0
C7-C6-C5	123.0(4)	C18-C17-C16	118.7(5)
C12-C6-C5	118.6(5)	C18-C17-H17	120.7
C8-C7-C6	121.1(4)	С16-С17-Н17	120.7
С8-С7-Н7	119.5	C17-C18-O3	124.0(5)
С6-С7-Н7	119.5	C17-C18-C19	121.9(4)
C7-C8-C9	120.6(5)	O3-C18-C19	114.1(4)
С7-С8-Н8	119.7	C24-C19-C20	119.4(5)
С9-С8-Н8	119.7	C24-C19-C18	118.8(4)
C10-C9-C8	119.4(5)	C20-C19-C18	121.8(4)
С10-С9-Н9	120.3	C21-C20-C19	120.4(4)
С8-С9-Н9	120.3	С21-С20-Н20	119.8
C9-C10-C12	120.9(4)	С19-С20-Н20	119.8
C20-C21-C22	120.1(5)	C30-C29-C28	111.6(4)
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С20-С21-Н21	120.0	С30-С29-Н29А	109.3
C22-C21-H21	120.0	С28-С29-Н29А	109.3
C23-C22-C21	120.5(5)	С30-С29-Н29В	109.3
С23-С22-Н22	119.7	С28-С29-Н29В	109.3
С21-С22-Н22	119.7	H29A-C29-H29B	108.0
C22-C23-C24	120.8(5)	С29-С30-Н30А	109.5
С22-С23-Н23	119.6	С29-С30-Н30В	109.5
С24-С23-Н23	119.6	H30A-C30-H30B	109.5
C23-C24-C19	118.9(5)	С29-С30-Н30С	109.5
C23-C24-C15	122.2(4)	H30A-C30-H30C	109.5
C19-C24-C15	118.9(4)	H30B-C30-H30C	109.5
N1-C25-C26	110.3(3)	O3-C31-C32	106.5(4)
N1-C25-H25A	109.6	O3-C31-H31A	110.4
С26-С25-Н25А	109.6	C32-C31-H31A	110.4
N1-C25-H25B	109.6	O3-C31-H31B	110.4
С26-С25-Н25В	109.6	С32-С31-Н31В	110.4
H25A-C25-H25B	108.1	H31A-C31-H31B	108.6
C25-C26-C27	112.8(3)	C31-C32-C33	113.1(4)
С25-С26-Н26А	109.0	C31-C32-H32A	109.0
С27-С26-Н26А	109.0	С33-С32-Н32А	109.0
С25-С26-Н26В	109.0	С31-С32-Н32В	109.0
С27-С26-Н26В	109.0	С33-С32-Н32В	109.0
H26A-C26-H26B	107.8	H32A-C32-H32B	107.8
C28-C27-C26	111.6(4)	C32-C33-C34	114.6(4)
С28-С27-Н27А	109.3	С32-С33-Н33А	108.6
С26-С27-Н27А	109.3	С34-С33-Н33А	108.6
С28-С27-Н27В	109.3	С32-С33-Н33В	108.6
С26-С27-Н27В	109.3	С34-С33-Н33В	108.6
H27A-C27-H27B	108.0	H33A-C33-H33B	107.6
C27-C28-C29	114.4(4)	C35-C34-C33	113.1(4)
С27-С28-Н28А	108.7	C35-C34-H34A	109.0
С29-С28-Н28А	108.7	С33-С34-Н34А	109.0
С27-С28-Н28В	108.7	С35-С34-Н34В	109.0
С29-С28-Н28В	108.7	C33-C34-H34B	109.0
H28A-C28-H28B	107.6	H34A-C34-H34B	107.8

C34-C35-C36	113.7(5)	H36A-C36-H36B	109.5
С34-С35-Н35А	108.8	С35-С36-Н36С	109.5
С36-С35-Н35А	108.8	Н36А-С36-Н36С	109.5
С34-С35-Н35В	108.8	Н36В-С36-Н36С	109.5
С36-С35-Н35В	108.8	C1-N1-C11	125.8(4)
H35A-C35-H35B	107.7	C1-N1-C25	117.6(4)
С35-С36-Н36А	109.5	C11-N1-C25	116.5(4)
С35-С36-Н36В	109.5	C18-O3-C31	117.6(4)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	10(2)	19(3)	22(3)	2(2)	-2(2)	0(2)
C2	10(2)	14(2)	18(2)	-1(2)	1(2)	0(2)
C3	12(2)	28(3)	20(2)	-2(2)	0(2)	0(2)
C4	14(2)	19(3)	26(3)	3(2)	1(2)	3(2)
C5	9(2)	18(3)	28(3)	-3(2)	4(2)	1(2)
C6	15(2)	13(2)	25(2)	2(2)	4(2)	-3(2)
C7	18(2)	18(3)	21(2)	-1(2)	4(2)	3(2)
C8	23(2)	24(3)	18(2)	-4(2)	5(2)	-3(2)
C9	22(2)	18(3)	23(3)	2(2)	4(2)	0(2)
C10	13(2)	14(2)	22(2)	0(2)	3(2)	0(2)
C11	16(2)	16(2)	22(2)	-3(2)	-3(2)	0(2)
C12	13(2)	16(3)	20(2)	1(2)	5(2)	-2(2)
C13	17(2)	18(3)	21(2)	2(2)	1(2)	-2(2)
C14	15(2)	17(2)	23(2)	-2(2)	4(2)	-3(2)
C15	13(2)	17(2)	24(3)	-1(2)	2(2)	0(2)
C16	15(2)	20(3)	25(3)	1(2)	0(2)	0(2)
C17	22(2)	18(3)	15(2)	-1(2)	2(2)	-1(2)
C18	14(2)	18(3)	22(3)	-3(2)	5(2)	2(2)
C19	12(2)	16(2)	28(3)	-1(2)	2(2)	-2(2)
C20	14(2)	20(3)	24(3)	2(2)	-1(2)	0(2)
C21	19(2)	19(3)	27(3)	3(2)	-4(2)	2(2)
C22	23(2)	27(3)	17(2)	-1(2)	4(2)	-2(2)
C23	18(2)	22(3)	23(3)	-4(2)	4(2)	-1(2)
C24	14(2)	15(2)	21(2)	-3(2)	0(2)	-3(2)
C25	16(2)	17(3)	20(2)	-3(2)	5(2)	2(2)
C26	15(2)	23(3)	25(3)	-2(2)	1(2)	1(2)
C27	21(2)	20(3)	20(2)	0(2)	3(2)	-1(2)
C28	20(2)	24(3)	21(2)	-3(2)	0(2)	2(2)
C29	25(2)	17(3)	31(3)	-1(2)	6(2)	0(2)
C30	34(3)	20(3)	47(3)	0(3)	-2(3)	2(2)
C31	23(2)	24(3)	25(3)	-5(2)	6(2)	5(2)

Table **60.**4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **60.** The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	19(2)	27(3)	22(3)	-3(2)	5(2)	4(2)
C33	25(2)	24(3)	26(3)	-4(2)	7(2)	5(2)
C34	26(2)	30(3)	23(3)	-3(2)	5(2)	9(2)
C35	38(3)	24(3)	32(3)	0(2)	10(2)	12(2)
C36	56(3)	23(3)	36(3)	3(3)	13(3)	12(3)
N1	17(2)	13(2)	21(2)	-4(2)	5(2)	1(2)
01	26(2)	29(2)	18(2)	-2(2)	3(1)	5(2)
02	30(2)	30(2)	21(2)	-2(2)	-2(2)	9(2)
O3	22(1)	23(2)	21(2)	-2(2)	0(1)	6(1)

	х	у	Z	U(eq)
H3	1078	5422	7009	24
H4	4261	4991	6640	24
H7	2753	4937	3620	23
H8	-177	5224	2567	26
H9	-3294	5664	2948	25
H16	8074	4365	3402	24
H17	11331	3949	2986	22
H20	15455	3490	5601	24
H21	15116	3602	7052	27
H22	11804	4012	7456	27
H23	9009	4326	6411	25
H25A	-6777	6208	6156	21
H25B	-7841	6265	5152	21
H26A	-3745	6631	5038	26
H26B	-2864	6587	6054	26
H27A	-8127	6906	5346	24
H27B	-7071	6879	6357	24
H28A	-4109	7264	5156	27
H28B	-3105	7240	6169	27
H29A	-8310	7570	5454	29
H29B	-7284	7548	6468	29
H30A	-3136	7881	6234	51
H30B	-6043	8090	5975	51
H30C	-4367	7920	5238	51
H31A	15943	3654	2911	28
H31B	12990	3440	2803	28
H32A	18284	3146	3568	27
H32B	17218	3099	2564	27
H33A	13034	2809	2954	30
H33B	14278	2840	3948	30

Table 60.5. Hydrogen coordinates (  $x\;10^4$  ) and isotropic displacement parameters (Å  $^2x\;10\;^3$  ) for 60.

H34A	17070	2454	2714	31
H34B	18085	2469	3728	31
H35A	12768	2171	3012	37
H35B	13868	2177	4021	37
H36A	16495	1791	2752	57
H36B	14726	1630	3479	57
H36C	17764	1809	3748	57

01-C1-C2-C3 1.4(7)C1-C2-C12-C6 -179.9(4) N1-C1-C2-C3 -179.3(4) C14-C15-C16-C17 -179.7(4)01-C1-C2-C12 -179.0(4) C24-C15-C16-C17 0.5(7)N1-C1-C2-C12 0.4(6) C15-C16-C17-C18 1.0(7)C12-C2-C3-C4 C16-C17-C18-O3 0.4(7) 176.2(4) C1-C2-C3-C4 -179.9(4) C16-C17-C18-C19 -1.9(7)C2-C3-C4-C5 -0.1(7)C17-C18-C19-C24 1.2(7)C3-C4-C5-C13 178.9(4) O3-C18-C19-C24 -177.0(4)-177.4(4) C3-C4-C5-C6 -0.3(7)C17-C18-C19-C20 C4-C5-C6-C7 O3-C18-C19-C20 -178.8(4) 4.4(6) C13-C5-C6-C7 2.1(7)C24-C19-C20-C21 0.1(7)C4-C5-C6-C12 0.5(6) C18-C19-C20-C21 178.7(4) C13-C5-C6-C12 -178.7(4) C19-C20-C21-C22 1.3(7)C12-C6-C7-C8 C20-C21-C22-C23 0.7(7)-1.6(7)C5-C6-C7-C8 179.9(4) C21-C22-C23-C24 0.3(7) C6-C7-C8-C9 0.1(7) C22-C23-C24-C19 1.1(7)C7-C8-C9-C10 -0.6(7)C22-C23-C24-C15 -179.2(4)C8-C9-C10-C12 C20-C19-C24-C23 0.2(7)-1.3(6)C8-C9-C10-C11 180.0(4) C18-C19-C24-C23 -179.9(4) C9-C10-C11-O2 -1.9(7)C20-C19-C24-C15 179.0(4) C18-C19-C24-C15 C12-C10-C11-O2 177.8(5) 0.3(6)C9-C10-C11-N1 178.0(4) C16-C15-C24-C23 179.1(4) C12-C10-C11-N1 C14-C15-C24-C23 -2.2(6)-0.7(7)C9-C10-C12-C6 0.6(7) C16-C15-C24-C19 -1.2(7)C11-C10-C12-C6 -179.2(4) C14-C15-C24-C19 179.1(4) C9-C10-C12-C2 -179.5(4)N1-C25-C26-C27 176.4(4) C11-C10-C12-C2 0.8(6) C25-C26-C27-C28 -176.2(4)C7-C6-C12-C10 C26-C27-C28-C29 -1.0(6)179.0(4) C5-C6-C12-C10 C27-C28-C29-C30 179.7(4) -179.6(5)C7-C6-C12-C2 179.1(4) O3-C31-C32-C33 70.3(5) C5-C6-C12-C2 -0.2(6)C31-C32-C33-C34 176.2(4) C3-C2-C12-C10 179.8(4) C32-C33-C34-C35 -175.3(5)C1-C2-C12-C10 0.2(6) C33-C34-C35-C36 178.1(5) C3-C2-C12-C6 -0.2(6)01-C1-N1-C11 177.3(4)

Table **60.**6. Torsion angles [°] for **60**.

C2-C1-N1-C11	-2.1(6)	C10-C11-N1-C25	177.8(4)
01-C1-N1-C25	2.5(6)	C26-C25-N1-C1	88.2(5)
C2-C1-N1-C25	-176.9(4)	C26-C25-N1-C11	-87.1(5)
O2-C11-N1-C1	-177.1(4)	C17-C18-O3-C31	3.0(7)
C10-C11-N1-C1	3.0(6)	C19-C18-O3-C31	-178.8(4)
O2-C11-N1-C25	-2.2(6)	C32-C31-O3-C18	-170.9(4)

End of **6O** data.

## **CRYSTALLOGRAPHIC MATERIAL FOR 70**

Crystallographic Material for 7O.

X-ray Experimental.

Table **70.**1. Crystallographic Data for **70.** 

Table **70.**2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **70**.

Table **70.3**. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of **70**.

Table 70.4. Anisotropic thermal parameters for the non-hydrogen atoms of 70.

Table **70.5**. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **70**.

Table **70.6**. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **70**.

X-ray Experimental for complex  $C_{38}H_{41}NO_3$ : (**70**) Crystals grew as very long, orange laths by precipitation from a 1.0 mM solution of **7** in Acetone. The data crystal was cut from a longer crystal and had approximate dimensions; 0.28 x 0.089 x 0.031 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$ radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1007 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 26 seconds per frame with a detector offset of +/- 41.9° and 90 seconds per frame with a detector offset of +/- 110.4°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>4</sup> The structure was solved by direct methods using SHELXT<sup>5</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>5</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.098*P)^2]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.176, with R(F) equal to 0.0626 and a goodness of fit, S, = 1.02. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere. **References** 

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_{W}(F^{2}) &= \{ \Sigma w (|F_{0}|^{2} |F_{c}|^{2})^{2} / \Sigma w (|F_{0}|)^{4} \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_{0}| |F_{c}|) / \Sigma |F_{0}| \} \text{ for reflections with } F_{0} > 4(\sigma(F_{0})). \\ S &= [\Sigma w (|F_{0}|^{2} |F_{c}|^{2})^{2} / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

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Table 70.1. Crystal data and structure re	finement for 70.	
Empirical formula	C38 H41 N O3	
Formula weight	559.72	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	C c	
Unit cell dimensions	a = 4.6766(7) Å	<i>α</i> = 90°.
	b = 41.435(3) Å	β= 94.880(10)°.
	c = 15.4245(15)  Å	$\gamma = 90^{\circ}$ .
Volume	2978.0(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.248 Mg/m <sup>3</sup>	
Absorption coefficient	0.608 mm <sup>-1</sup>	
F(000)	1200	
Crystal size	0.28 x 0.089 x 0.031 mm	n <sup>3</sup>
Theta range for data collection	3.581 to 76.009°.	
Index ranges	-5<=h<=5, -47<=k<=51	, <b>-</b> 18<=l<=19
Reflections collected	8683	
Independent reflections	4179 [R(int) = 0.0878]	
Completeness to theta = $67.684^{\circ}$	100.0 %	
Absorption correction	Semi-empirical from eq	uivalents
Max. and min. transmission	1.00 and 0.457	
Refinement method	Full-matrix least-square	s on F <sup>2</sup>
Data / restraints / parameters	4179 / 578 / 381	
Goodness-of-fit on F <sup>2</sup>	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0626, $wR2 = 0.1$	627
R indices (all data)	R1 = 0.0774, wR2 = 0.1	758
Absolute structure parameter	0.0(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.318 and -0.351 e.Å <sup>-3</sup>	

	х	У	Z	U(eq)
C1	-4827(9)	5838(1)	6958(3)	17(1)
C2	-2880(9)	5578(1)	6725(3)	17(1)
C3	-2793(10)	5492(1)	5865(3)	20(1)
C4	-940(10)	5247(1)	5623(3)	21(1)
C5	816(10)	5091(1)	6245(3)	20(1)
C6	804(9)	5175(1)	7132(3)	17(1)
C7	2602(9)	5017(1)	7805(3)	18(1)
C8	2466(10)	5105(1)	8666(3)	20(1)
С9	570(10)	5351(1)	8896(3)	20(1)
C10	-1185(9)	5505(1)	8261(3)	17(1)
C11	-3154(9)	5762(1)	8510(3)	18(1)
C12	-1098(9)	5418(1)	7373(3)	17(1)
C13	4557(9)	4772(1)	7587(3)	19(1)
C14	6234(9)	4568(1)	7389(3)	18(1)
C15	8221(9)	4328(1)	7168(3)	18(1)
C16	8650(10)	4266(1)	6304(3)	20(1)
C17	10592(10)	4029(1)	6070(3)	19(1)
C18	12088(9)	3847(1)	6706(3)	17(1)
C19	11793(9)	3909(1)	7606(3)	16(1)
C20	13416(10)	3736(1)	8267(3)	21(1)
C21	13116(10)	3798(1)	9132(3)	23(1)
C22	11165(10)	4037(1)	9364(3)	24(1)
C23	9571(10)	4207(1)	8734(3)	20(1)
C24	9837(9)	4149(1)	7840(3)	16(1)
C25	-6722(9)	6180(1)	8081(3)	18(1)
C26	-5019(10)	6494(1)	8082(3)	22(1)
C27	-6853(10)	6792(1)	8245(3)	20(1)
C28	-5092(10)	7102(1)	8227(3)	22(1)
C29	-6890(10)	7409(1)	8291(3)	21(1)
C30	-5088(11)	7716(1)	8265(3)	26(1)
C31	-6924(12)	8021(1)	8289(4)	32(1)

Table **70.**2. Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters (Å<sup>2</sup>x  $10^3$ ) for **70.** U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	14430(10)	3541(1)	5654(3)	21(1)
C33	16275(10)	3240(1)	5647(3)	21(1)
C34	14580(10)	2929(1)	5783(3)	22(1)
C35	16411(10)	2625(1)	5754(3)	21(1)
C36	14641(10)	2315(1)	5802(3)	22(1)
C37	16421(11)	2007(1)	5790(3)	25(1)
C38	14612(12)	1702(1)	5831(3)	30(1)
N1	-4880(8)	5906(1)	7851(2)	17(1)
01	-6348(8)	5987(1)	6424(2)	27(1)
O2	-3263(7)	5847(1)	9268(2)	25(1)
O3	13906(7)	3603(1)	6543(2)	21(1)

C1-O1	1.211(6)	C19-C24	1.419(6)
C1-N1	1.409(5)	C20-C21	1.377(6)
C1-C2	1.476(6)	C20-H20	0.95
C2-C3	1.378(6)	C21-C22	1.411(6)
C2-C12	1.409(6)	C21-H21	0.95
C3-C4	1.404(6)	C22-C23	1.369(7)
С3-Н3	0.95	C22-H22	0.95
C4-C5	1.371(7)	C23-C24	1.415(6)
С4-Н4	0.95	C23-H23	0.95
C5-C6	1.412(6)	C25-N1	1.485(5)
С5-Н5	0.95	C25-C26	1.526(5)
C6-C12	1.414(6)	C25-H25A	0.99
C6-C7	1.437(6)	C25-H25B	0.99
C7-C8	1.385(6)	C26-C27	1.536(5)
C7-C13	1.424(6)	C26-H26A	0.99
C8-C9	1.416(6)	C26-H26B	0.99
С8-Н8	0.95	C27-C28	1.529(6)
C9-C10	1.378(6)	C27-H27A	0.99
С9-Н9	0.95	C27-H27B	0.99
C10-C12	1.420(6)	C28-C29	1.530(6)
C10-C11	1.480(5)	C28-H28A	0.99
C11-O2	1.226(6)	C28-H28B	0.99
C11-N1	1.380(6)	C29-C30	1.529(6)
C13-C14	1.212(6)	C29-H29A	0.99
C14-C15	1.422(6)	C29-H29B	0.99
C15-C16	1.388(6)	C30-C31	1.529(6)
C15-C24	1.436(6)	C30-H30A	0.99
C16-C17	1.407(6)	C30-H30B	0.99
С16-Н16	0.95	C31-H31A	0.98
C17-C18	1.378(6)	C31-H31B	0.98
С17-Н17	0.95	C31-H31C	0.98
C18-O3	1.359(5)	C32-O3	1.437(5)
C18-C19	1.430(6)	C32-C33	1.516(6)
C19-C20	1.414(6)	C32-H32A	0.99

Table 70. Bond lengths [Å] and angles  $[\circ]$  for 70.

С32-Н32В	0.99	C36-C37	1.528(6)
C33-C34	1.535(6)	C36-H36A	0.99
С33-Н33А	0.99	C36-H36B	0.99
С33-Н33В	0.99	C37-C38	1.524(6)
C34-C35	1.528(6)	С37-Н37А	0.99
C34-H34A	0.99	С37-Н37В	0.99
C34-H34B	0.99	C38-H38A	0.98
C35-C36	1.532(6)	C38-H38B	0.98
С35-Н35А	0.99	C38-H38C	0.98
С35-Н35В	0.99		
01-C1-N1	120.3(4)	С10-С9-Н9	119.9
O1-C1-C2	123.1(4)	С8-С9-Н9	119.9
N1-C1-C2	116.6(4)	C9-C10-C12	120.3(4)
C3-C2-C12	119.9(4)	C9-C10-C11	119.6(4)
C3-C2-C1	119.5(4)	C12-C10-C11	120.1(4)
C12-C2-C1	120.6(4)	O2-C11-N1	120.5(4)
C2-C3-C4	120.7(4)	O2-C11-C10	122.2(4)
С2-С3-Н3	119.6	N1-C11-C10	117.3(4)
С4-С3-Н3	119.6	C2-C12-C6	119.6(4)
C5-C4-C3	120.1(4)	C2-C12-C10	120.2(4)
С5-С4-Н4	119.9	C6-C12-C10	120.2(4)
С3-С4-Н4	119.9	C14-C13-C7	178.7(4)
C4-C5-C6	120.7(4)	C13-C14-C15	179.2(5)
С4-С5-Н5	119.7	C16-C15-C14	120.6(4)
С6-С5-Н5	119.7	C16-C15-C24	119.2(4)
C5-C6-C12	119.0(4)	C14-C15-C24	120.2(4)
C5-C6-C7	122.4(4)	C15-C16-C17	121.6(4)
C12-C6-C7	118.6(4)	C15-C16-H16	119.2
C8-C7-C13	119.8(4)	C17-C16-H16	119.2
C8-C7-C6	120.0(4)	C18-C17-C16	120.0(4)
C13-C7-C6	120.2(4)	С18-С17-Н17	120.0
C7-C8-C9	120.8(4)	С16-С17-Н17	120.0
С7-С8-Н8	119.6	O3-C18-C17	124.2(4)
С9-С8-Н8	119.6	O3-C18-C19	115.2(4)
C10-C9-C8	120.1(4)	C17-C18-C19	120.6(4)

C20-C19-C24	119.4(4)	C27-C28-C29	113.4(4)
C20-C19-C18	121.4(4)	C27-C28-H28A	108.9
C24-C19-C18	119.3(4)	C29-C28-H28A	108.9
C21-C20-C19	120.7(4)	C27-C28-H28B	108.9
С21-С20-Н20	119.7	C29-C28-H28B	108.9
С19-С20-Н20	119.7	H28A-C28-H28B	107.7
C20-C21-C22	119.9(4)	C30-C29-C28	112.5(4)
С20-С21-Н21	120.0	С30-С29-Н29А	109.1
С22-С21-Н21	120.0	С28-С29-Н29А	109.1
C23-C22-C21	120.3(4)	С30-С29-Н29В	109.1
С23-С22-Н22	119.8	С28-С29-Н29В	109.1
С21-С22-Н22	119.8	H29A-C29-H29B	107.8
C22-C23-C24	121.1(4)	C31-C30-C29	112.0(4)
С22-С23-Н23	119.4	С31-С30-Н30А	109.2
С24-С23-Н23	119.4	С29-С30-Н30А	109.2
C23-C24-C19	118.6(4)	С31-С30-Н30В	109.2
C23-C24-C15	122.1(4)	С29-С30-Н30В	109.2
C19-C24-C15	119.3(4)	H30A-C30-H30B	107.9
N1-C25-C26	109.8(3)	C30-C31-H31A	109.5
N1-C25-H25A	109.7	C30-C31-H31B	109.5
С26-С25-Н25А	109.7	H31A-C31-H31B	109.5
N1-C25-H25B	109.7	С30-С31-Н31С	109.5
С26-С25-Н25В	109.7	H31A-C31-H31C	109.5
H25A-C25-H25B	108.2	H31B-C31-H31C	109.5
C25-C26-C27	112.8(3)	O3-C32-C33	107.4(3)
С25-С26-Н26А	109.0	O3-C32-H32A	110.2
С27-С26-Н26А	109.0	С33-С32-Н32А	110.2
С25-С26-Н26В	109.0	O3-C32-H32B	110.2
С27-С26-Н26В	109.0	С33-С32-Н32В	110.2
H26A-C26-H26B	107.8	H32A-C32-H32B	108.5
C28-C27-C26	111.4(3)	C32-C33-C34	112.8(4)
С28-С27-Н27А	109.4	С32-С33-Н33А	109.0
С26-С27-Н27А	109.4	С34-С33-Н33А	109.0
С28-С27-Н27В	109.4	С32-С33-Н33В	109.0
С26-С27-Н27В	109.4	С34-С33-Н33В	109.0
H27A-C27-H27B	108.0	H33A-C33-H33B	107.8

C35-C34-C33	113.0(4)	H36A-C36-H36B	107.7
C35-C34-H34A	109.0	C38-C37-C36	112.8(4)
C33-C34-H34A	109.0	С38-С37-Н37А	109.0
C35-C34-H34B	109.0	С36-С37-Н37А	109.0
C33-C34-H34B	109.0	С38-С37-Н37В	109.0
H34A-C34-H34B	107.8	С36-С37-Н37В	109.0
C34-C35-C36	112.5(4)	Н37А-С37-Н37В	107.8
С34-С35-Н35А	109.1	С37-С38-Н38А	109.5
С36-С35-Н35А	109.1	С37-С38-Н38В	109.5
С34-С35-Н35В	109.1	H38A-C38-H38B	109.5
С36-С35-Н35В	109.1	С37-С38-Н38С	109.5
H35A-C35-H35B	107.8	H38A-C38-H38C	109.5
C37-C36-C35	113.8(4)	H38B-C38-H38C	109.5
С37-С36-Н36А	108.8	C11-N1-C1	125.1(4)
С35-С36-Н36А	108.8	C11-N1-C25	118.0(3)
С37-С36-Н36В	108.8	C1-N1-C25	116.5(3)
С35-С36-Н36В	108.8	C18-O3-C32	118.1(3)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	26(2)	12(2)	13(2)	-2(1)	-4(2)	-3(2)
C2	24(2)	11(2)	14(2)	-4(1)	-2(2)	-3(1)
C3	27(2)	16(2)	17(2)	1(2)	-5(2)	-1(2)
C4	32(2)	16(2)	14(2)	-4(2)	-3(2)	-1(2)
C5	30(2)	12(2)	17(2)	-2(1)	1(2)	0(2)
C6	21(2)	11(2)	18(2)	-1(1)	-2(2)	-2(1)
C7	22(2)	11(2)	19(2)	0(1)	-1(2)	-3(2)
C8	25(2)	16(2)	18(2)	3(2)	-7(2)	2(2)
C9	25(2)	16(2)	18(2)	0(2)	-4(2)	-2(2)
C10	22(2)	11(2)	17(2)	0(1)	0(2)	-1(2)
C11	25(2)	12(2)	17(2)	1(1)	-4(2)	-1(2)
C12	21(2)	10(2)	19(2)	-1(1)	-2(2)	-2(1)
C13	22(2)	16(2)	18(2)	1(2)	-2(2)	-2(2)
C14	20(2)	13(2)	20(2)	2(1)	-5(2)	0(2)
C15	21(2)	12(2)	20(2)	-2(2)	-2(2)	0(1)
C16	26(2)	12(2)	20(2)	0(1)	-7(2)	3(2)
C17	29(2)	14(2)	14(2)	-2(1)	-2(2)	0(2)
C18	21(2)	10(2)	20(2)	-3(1)	-3(2)	-2(1)
C19	22(2)	9(2)	17(2)	-2(1)	-5(2)	-4(1)
C20	27(2)	14(2)	21(2)	-1(2)	-4(2)	2(2)
C21	28(2)	20(2)	19(2)	2(2)	-5(2)	0(2)
C22	33(2)	20(2)	17(2)	-1(2)	0(2)	-2(2)
C23	26(2)	14(2)	20(2)	-6(2)	0(2)	-1(2)
C24	22(2)	10(2)	17(2)	-2(1)	-5(2)	-3(1)
C25	22(2)	13(2)	18(2)	-1(1)	-3(2)	5(2)
C26	25(2)	12(2)	28(2)	-2(2)	-1(2)	2(2)
C27	26(2)	13(2)	21(2)	-2(2)	-6(2)	5(2)
C28	33(2)	13(2)	20(2)	0(2)	-2(2)	1(2)
C29	27(2)	13(2)	22(2)	-2(2)	-6(2)	3(2)
C30	33(2)	16(2)	26(2)	1(2)	-6(2)	2(2)
C31	44(3)	13(2)	36(3)	-2(2)	-12(2)	1(2)

Table 70.4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for 70. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	31(2)	16(2)	15(2)	-2(2)	-2(2)	2(2)
C33	28(2)	14(2)	21(2)	-3(2)	-2(2)	0(2)
C34	29(2)	14(2)	21(2)	-2(2)	-3(2)	-1(2)
C35	29(2)	16(2)	18(2)	1(1)	-4(2)	1(2)
C36	30(2)	17(2)	18(2)	1(2)	-3(2)	2(2)
C37	32(2)	18(2)	24(2)	0(2)	-4(2)	4(2)
C38	44(3)	14(2)	31(3)	1(2)	-4(2)	2(2)
N1	22(2)	11(1)	16(2)	-1(1)	-3(1)	0(1)
01	38(2)	21(2)	18(2)	1(1)	-9(1)	9(1)
02	37(2)	20(1)	18(2)	-4(1)	-2(1)	5(1)
O3	33(2)	15(1)	16(2)	-3(1)	0(1)	6(1)

	х	у	Z	U(eq)
H3	-3999	5600	5430	24
H4	-904	5190	5028	25
H5	2054	4925	6078	23
H8	3659	5000	9108	24
H9	508	5411	9489	24
H16	7608	4388	5860	24
H17	10872	3994	5475	23
H20	14727	3575	8114	25
H21	14222	3681	9571	27
H22	10957	4079	9960	28
H23	8264	4366	8899	24
H25A	-7400	6143	8664	21
H25B	-8422	6194	7654	21
H26A	-4203	6518	7514	26
H26B	-3402	6482	8539	26
H27A	-8486	6803	7793	24
H27B	-7641	6771	8818	24
H28A	-4129	7109	7680	26
H28B	-3582	7099	8718	26
H29A	-8408	7413	7803	25
H29B	-7839	7404	8841	25
H30A	-3625	7717	8768	31
H30B	-4072	7717	7728	31
H31A	-7759	8034	8850	47
H31B	-8466	8013	7818	47
H31C	-5725	8211	8215	47
H32A	15435	3726	5411	26
H32B	12594	3507	5297	26
H33A	17861	3258	6112	26
H33B	17134	3227	5083	26

Table 70.5. Hydrogen coordinates (  $x\ 10^4$  ) and isotropic displacement parameters (Å  $^2x\ 10\ ^3$  ) for 70.

H34A	13761	2941	6353	26
H34B	12964	2915	5326	26
H35A	17913	2629	6247	25
H35B	17382	2624	5208	25
H36A	13642	2319	6343	27
H36B	13158	2311	5305	27
H37A	17430	2002	5251	30
H37B	17893	2009	6290	30
H38A	13249	1690	5313	45
H38B	13558	1708	6354	45
H38C	15867	1512	5854	45

01-C1-C2-C3	-1.2(6)	C11-C10-C12-C6	179.3(4)
N1-C1-C2-C3	178.0(4)	C14-C15-C16-C17	-179.7(4)
O1-C1-C2-C12	178.2(4)	C24-C15-C16-C17	1.2(6)
N1-C1-C2-C12	-2.6(5)	C15-C16-C17-C18	1.0(7)
C12-C2-C3-C4	-0.1(6)	C16-C17-C18-O3	176.8(4)
C1-C2-C3-C4	179.4(4)	C16-C17-C18-C19	-3.1(6)
C2-C3-C4-C5	-0.2(7)	O3-C18-C19-C20	3.2(6)
C3-C4-C5-C6	-0.5(6)	C17-C18-C19-C20	-176.9(4)
C4-C5-C6-C12	1.4(6)	O3-C18-C19-C24	-177.0(3)
C4-C5-C6-C7	179.8(4)	C17-C18-C19-C24	2.9(6)
C5-C6-C7-C8	-178.9(4)	C24-C19-C20-C21	-0.1(6)
C12-C6-C7-C8	-0.5(6)	C18-C19-C20-C21	179.8(4)
C5-C6-C7-C13	2.0(6)	C19-C20-C21-C22	0.2(7)
C12-C6-C7-C13	-179.6(4)	C20-C21-C22-C23	-0.2(7)
C13-C7-C8-C9	179.0(4)	C21-C22-C23-C24	-0.1(7)
C6-C7-C8-C9	-0.1(6)	C22-C23-C24-C19	0.3(6)
C7-C8-C9-C10	0.5(6)	C22-C23-C24-C15	-179.0(4)
C8-C9-C10-C12	-0.3(6)	C20-C19-C24-C23	-0.2(6)
C8-C9-C10-C11	-179.9(4)	C18-C19-C24-C23	180.0(4)
C9-C10-C11-O2	0.8(6)	C20-C19-C24-C15	179.1(4)
C12-C10-C11-O2	-178.8(4)	C18-C19-C24-C15	-0.7(5)
C9-C10-C11-N1	-179.5(4)	C16-C15-C24-C23	178.0(4)
C12-C10-C11-N1	0.8(5)	C14-C15-C24-C23	-1.2(6)
C3-C2-C12-C6	1.1(6)	C16-C15-C24-C19	-1.3(6)
C1-C2-C12-C6	-178.4(4)	C14-C15-C24-C19	179.5(4)
C3-C2-C12-C10	-179.8(4)	N1-C25-C26-C27	175.5(3)
C1-C2-C12-C10	0.8(6)	C25-C26-C27-C28	-179.1(4)
C5-C6-C12-C2	-1.7(6)	C26-C27-C28-C29	173.9(4)
C7-C6-C12-C2	179.9(4)	C27-C28-C29-C30	-179.5(4)
C5-C6-C12-C10	179.1(4)	C28-C29-C30-C31	177.5(4)
C7-C6-C12-C10	0.7(6)	O3-C32-C33-C34	75.0(4)
C9-C10-C12-C2	-179.5(4)	C32-C33-C34-C35	178.6(4)
C11-C10-C12-C2	0.1(6)	C33-C34-C35-C36	-174.5(3)
C9-C10-C12-C6	-0.3(6)	C34-C35-C36-C37	-179.1(4)

Table **70.**6. Torsion angles [°] for **70.** 

C35-C36-C37-C38	-179.6(4)	O1-C1-N1-C25	-4.0(6)
O2-C11-N1-C1	176.7(4)	C2-C1-N1-C25	176.8(3)
C10-C11-N1-C1	-2.9(6)	C26-C25-N1-C11	85.7(4)
O2-C11-N1-C25	3.8(6)	C26-C25-N1-C1	-87.9(4)
C10-C11-N1-C25	-175.9(3)	C17-C18-O3-C32	3.6(6)
01-C1-N1-C11	-177.0(4)	C19-C18-O3-C32	-176.5(3)
C2-C1-N1-C11	3.8(6)	C33-C32-O3-C18	-174.6(3)

End of crystallographic data for 70.

## **CRYSTALLOGRAPHIC MATERIAL FOR 90**

Crystallographic Material for 90.

X-ray Experimental.

Table 90.1. Crystallographic Data for 90.

Table **90.**2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **90.** 

Table 90.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 90.

Table 90.4. Anisotropic thermal parameters for the non-hydrogen atoms of 90.

Table **90.5**. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **90.** 

Table 90.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of 90.

X-ray Experimental for complex C<sub>42</sub>H<sub>49</sub>NO<sub>3</sub> (**90**): Crystals grew as long, orange laths by vapor diffusion (solvent = p-xylenes, precipitant = acetonitrile). The data crystal was cut from a larger crystal and had approximate dimensions; 0.29 x 0.09 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1015 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 30 seconds per frame with a detector offset of +/- 41.9° and 80 seconds per frame with a detector offset of +/-110.4°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1329*P)^2 + (0.9071*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.212, with R(F) equal to 0.0684 and a goodness of fit, S, = 1.06. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

## 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

ruble 90.1. Orystar data and structure refinement	101 90.		
Empirical formula	C42 H49 N O3		
Formula weight	615.82		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	C c		
Unit cell dimensions	a = 4.6726(4)  Å	α= 90°.	
	b = 46.582(3)  Å	β= 94.233(7)°.	
	c = 15.3879(11) Å	$\gamma = 90^{\circ}$ .	
Volume	3340.1(4) Å <sup>3</sup>		
Z	4		
Density (calculated)	1.225 Mg/m <sup>3</sup>		
Absorption coefficient	0.586 mm <sup>-1</sup>		
F(000)	1328		
Crystal size	0.290 x 0.090 x 0.030 mm <sup>3</sup>		
Theta range for data collection	3.449 to 75.634°.		
Index ranges	-5<=h<=5, -49<=k<=58, -18<=	=1<=19	
Reflections collected	9974		
Independent reflections	4830 [R(int) = 0.0689]		
Completeness to theta = $67.684^{\circ}$	99.9 %		
Absorption correction	Semi-empirical from equivalen	ıts	
Max. and min. transmission	1.00 and 0.591		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	4830 / 278 / 417		
Goodness-of-fit on F <sup>2</sup>	1.061		
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1928		
R indices (all data)	R1 = 0.0774, wR2 = 0.2119		
Absolute structure parameter	-0.3(4)		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.314 and -0.353 e.Å <sup>-3</sup>		

Table **90**.1. Crystal data and structure refinement for **90**.

	Х	у	Z	U(eq)
C1	-2950(9)	5680(1)	6030(3)	20(1)
C2	-957(9)	5450(1)	5781(3)	20(1)
C3	775(10)	5314(1)	6405(3)	23(1)
C4	2676(10)	5095(1)	6187(3)	23(1)
C5	2820(10)	5016(1)	5322(3)	21(1)
C6	1043(9)	5154(1)	4655(3)	19(1)
C7	1061(10)	5076(1)	3759(3)	23(1)
C8	-721(11)	5214(1)	3144(3)	24(1)
С9	-2594(10)	5434(1)	3378(3)	22(1)
C10	-2644(10)	5513(1)	4240(3)	19(1)
C11	-4632(10)	5744(1)	4476(3)	19(1)
C12	-879(9)	5372(1)	4892(3)	17(1)
C13	4796(10)	4796(1)	5100(3)	21(1)
C14	6455(10)	4614(1)	4906(3)	21(1)
C15	8438(9)	4400(1)	4688(3)	19(1)
C16	8877(10)	4342(1)	3826(3)	22(1)
C17	10823(10)	4128(1)	3588(3)	22(1)
C18	12307(9)	3972(1)	4217(3)	19(1)
C19	12023(10)	4024(1)	5124(3)	19(1)
C20	13658(10)	3876(1)	5782(3)	24(1)
C21	13359(10)	3936(1)	6643(3)	25(1)
C22	11392(10)	4146(1)	6874(3)	23(1)
C23	9805(10)	4299(1)	6255(3)	22(1)
C24	10061(9)	4241(1)	5358(3)	18(1)
C25	-6517(10)	6051(1)	5604(3)	21(1)
C26	-4836(10)	6329(1)	5597(3)	23(1)
C27	-6676(10)	6595(1)	5762(3)	22(1)
C28	-4930(10)	6870(1)	5742(3)	23(1)
C29	-6726(11)	7143(1)	5809(3)	23(1)
C30	-4909(10)	7416(1)	5783(3)	23(1)
C31	-6673(11)	7692(1)	5804(3)	23(1)

Table **90**.2. Atomic coordinates ( $x \ 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **90**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	-4859(11)	7963(1)	5774(3)	26(1)
C33	-6641(12)	8237(1)	5782(4)	33(1)
C34	14656(10)	3694(1)	3170(3)	22(1)
C35	16511(10)	3427(1)	3160(3)	24(1)
C36	14828(10)	3153(1)	3295(3)	24(1)
C37	16673(11)	2880(1)	3274(3)	22(1)
C38	14896(11)	2604(1)	3318(3)	25(1)
C39	16690(11)	2330(1)	3287(3)	24(1)
C40	14889(11)	2056(1)	3310(3)	25(1)
C41	16644(11)	1781(1)	3296(3)	27(1)
C42	14814(12)	1510(1)	3333(3)	32(1)
N1	-4677(8)	5808(1)	5372(2)	19(1)
01	-3065(8)	5757(1)	6787(2)	27(1)
O2	-6124(8)	5876(1)	3942(2)	29(1)
O3	14133(7)	3752(1)	4059(2)	23(1)

C1-O1	1.225(6)	C19-C24	1.426(6)
C1-N1	1.382(6)	C20-C21	1.371(6)
C1-C2	1.487(6)	С20-Н20	0.95
C2-C3	1.365(6)	C21-C22	1.408(6)
C2-C12	1.418(6)	C21-H21	0.95
C3-C4	1.409(6)	C22-C23	1.364(7)
С3-Н3	0.95	С22-Н22	0.95
C4-C5	1.389(6)	C23-C24	1.420(6)
С4-Н4	0.95	С23-Н23	0.95
C5-C6	1.426(6)	C25-N1	1.482(5)
C5-C13	1.435(6)	C25-C26	1.516(6)
C6-C12	1.421(6)	C25-H25A	0.99
C6-C7	1.426(6)	C25-H25B	0.99
C7-C8	1.374(7)	C26-C27	1.540(5)
С7-Н7	0.95	C26-H26A	0.99
C8-C9	1.408(6)	C26-H26B	0.99
С8-Н8	0.95	C27-C28	1.518(6)
C9-C10	1.379(6)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.410(6)	C28-C29	1.533(6)
C10-C11	1.486(6)	C28-H28A	0.99
C11-O2	1.205(6)	C28-H28B	0.99
C11-N1	1.410(5)	C29-C30	1.532(6)
C13-C14	1.205(6)	С29-Н29А	0.99
C14-C15	1.416(6)	С29-Н29В	0.99
C15-C16	1.384(6)	C30-C31	1.527(6)
C15-C24	1.439(6)	С30-Н30А	0.99
C16-C17	1.413(6)	С30-Н30В	0.99
C16-H16	0.95	C31-C32	1.524(6)
C17-C18	1.362(6)	C31-H31A	0.99
C17-H17	0.95	C31-H31B	0.99
C18-O3	1.364(5)	C32-C33	1.525(6)
C18-C19	1.433(6)	C32-H32A	0.99
C19-C20	1.406(6)	C32-H32B	0.99

Table 90.3. Bond lengths [Å] and angles [°] for 90.

С33-Н33А	0.98	C38-C39	1.527(6)
С33-Н33В	0.98	C38-H38A	0.99
С33-Н33С	0.98	C38-H38B	0.99
C34-O3	1.432(5)	C39-C40	1.533(6)
C34-C35	1.517(6)	С39-Н39А	0.99
C34-H34A	0.99	С39-Н39В	0.99
C34-H34B	0.99	C40-C41	1.522(6)
C35-C36	1.521(6)	C40-H40A	0.99
С35-Н35А	0.99	C40-H40B	0.99
С35-Н35В	0.99	C41-C42	1.527(7)
C36-C37	1.539(6)	C41-H41A	0.99
С36-Н36А	0.99	C41-H41B	0.99
С36-Н36В	0.99	C42-H42A	0.98
C37-C38	1.535(6)	C42-H42B	0.98
С37-Н37А	0.99	C42-H42C	0.98
С37-Н37В	0.99		
01-C1-N1	120.4(4)	С8-С7-Н7	120.0
01-C1-C2	122.0(4)	С6-С7-Н7	120.0
N1-C1-C2	117.6(4)	C7-C8-C9	121.3(4)
C3-C2-C12	120.3(4)	С7-С8-Н8	119.4
C3-C2-C1	120.2(4)	С9-С8-Н8	119.4
C12-C2-C1	119.6(4)	C10-C9-C8	119.7(4)
C2-C3-C4	121.3(4)	С10-С9-Н9	120.1
С2-С3-Н3	119.3	С8-С9-Н9	120.1
С4-С3-Н3	119.3	C9-C10-C12	120.6(4)
C5-C4-C3	119.8(4)	C9-C10-C11	119.0(4)
С5-С4-Н4	120.1	C12-C10-C11	120.4(4)
С3-С4-Н4	120.1	O2-C11-N1	120.8(4)
C4-C5-C6	120.2(4)	O2-C11-C10	122.8(4)
C4-C5-C13	119.7(4)	N1-C11-C10	116.4(4)
C6-C5-C13	120.1(4)	C10-C12-C2	120.8(4)
C12-C6-C5	119.0(4)	C10-C12-C6	119.7(4)
C12-C6-C7	118.6(4)	C2-C12-C6	119.5(4)
C5-C6-C7	122.4(4)	C14-C13-C5	179.3(5)
C8-C7-C6	120.0(4)	C13-C14-C15	179.1(5)

C16-C15-C14	120.7(4)	C25-C26-C27	113.0(4)
C16-C15-C24	118.5(4)	C25-C26-H26A	109.0
C14-C15-C24	120.8(4)	C27-C26-H26A	109.0
C15-C16-C17	122.0(4)	C25-C26-H26B	109.0
С15-С16-Н16	119.0	C27-C26-H26B	109.0
С17-С16-Н16	119.0	H26A-C26-H26B	107.8
C18-C17-C16	119.8(4)	C28-C27-C26	111.5(4)
С18-С17-Н17	120.1	C28-C27-H27A	109.3
С16-С17-Н17	120.1	C26-C27-H27A	109.3
C17-C18-O3	124.5(4)	C28-C27-H27B	109.3
C17-C18-C19	121.4(4)	С26-С27-Н27В	109.3
O3-C18-C19	114.0(4)	H27A-C27-H27B	108.0
C20-C19-C24	119.5(4)	C27-C28-C29	113.6(4)
C20-C19-C18	122.1(4)	C27-C28-H28A	108.8
C24-C19-C18	118.4(4)	C29-C28-H28A	108.8
C21-C20-C19	120.4(4)	C27-C28-H28B	108.8
С21-С20-Н20	119.8	C29-C28-H28B	108.8
С19-С20-Н20	119.8	H28A-C28-H28B	107.7
C20-C21-C22	120.1(4)	C30-C29-C28	112.4(4)
C20-C21-H21	120.0	С30-С29-Н29А	109.1
C22-C21-H21	120.0	C28-C29-H29A	109.1
C23-C22-C21	121.3(4)	С30-С29-Н29В	109.1
С23-С22-Н22	119.4	C28-C29-H29B	109.1
С21-С22-Н22	119.4	H29A-C29-H29B	107.9
C22-C23-C24	119.9(4)	C31-C30-C29	113.3(4)
С22-С23-Н23	120.1	С31-С30-Н30А	108.9
С24-С23-Н23	120.1	С29-С30-Н30А	108.9
C23-C24-C19	118.8(4)	С31-С30-Н30В	108.9
C23-C24-C15	121.3(4)	С29-С30-Н30В	108.9
C19-C24-C15	119.9(4)	H30A-C30-H30B	107.7
N1-C25-C26	110.0(4)	C32-C31-C30	113.2(4)
N1-C25-H25A	109.7	C32-C31-H31A	108.9
С26-С25-Н25А	109.7	C30-C31-H31A	108.9
N1-C25-H25B	109.7	C32-C31-H31B	108.9
С26-С25-Н25В	109.7	C30-C31-H31B	108.9
H25A-C25-H25B	108.2	H31A-C31-H31B	107.8

C31-C32-C33	112.9(4)	H37A-C37-H37B	107.8
C31-C32-H32A	109.0	C39-C38-C37	113.4(4)
С33-С32-Н32А	109.0	С39-С38-Н38А	108.9
С31-С32-Н32В	109.0	С37-С38-Н38А	108.9
С33-С32-Н32В	109.0	С39-С38-Н38В	108.9
H32A-C32-H32B	107.8	С37-С38-Н38В	108.9
С32-С33-Н33А	109.5	H38A-C38-H38B	107.7
С32-С33-Н33В	109.5	C38-C39-C40	113.0(4)
H33A-C33-H33B	109.5	С38-С39-Н39А	109.0
С32-С33-Н33С	109.5	С40-С39-Н39А	109.0
H33A-C33-H33C	109.5	С38-С39-Н39В	109.0
H33B-C33-H33C	109.5	С40-С39-Н39В	109.0
O3-C34-C35	107.6(3)	H39A-C39-H39B	107.8
O3-C34-H34A	110.2	C41-C40-C39	113.9(4)
C35-C34-H34A	110.2	C41-C40-H40A	108.8
O3-C34-H34B	110.2	С39-С40-Н40А	108.8
С35-С34-Н34В	110.2	C41-C40-H40B	108.8
H34A-C34-H34B	108.5	С39-С40-Н40В	108.8
C34-C35-C36	112.6(4)	H40A-C40-H40B	107.7
С34-С35-Н35А	109.1	C40-C41-C42	113.0(4)
С36-С35-Н35А	109.1	C40-C41-H41A	109.0
С34-С35-Н35В	109.1	C42-C41-H41A	109.0
С36-С35-Н35В	109.1	C40-C41-H41B	109.0
H35A-C35-H35B	107.8	C42-C41-H41B	109.0
C35-C36-C37	113.3(4)	H41A-C41-H41B	107.8
С35-С36-Н36А	108.9	C41-C42-H42A	109.5
С37-С36-Н36А	108.9	C41-C42-H42B	109.5
С35-С36-Н36В	108.9	H42A-C42-H42B	109.5
С37-С36-Н36В	108.9	C41-C42-H42C	109.5
H36A-C36-H36B	107.7	H42A-C42-H42C	109.5
C38-C37-C36	112.7(4)	H42B-C42-H42C	109.5
С38-С37-Н37А	109.0	C1-N1-C11	125.2(4)
С36-С37-Н37А	109.0	C1-N1-C25	118.1(3)
С38-С37-Н37В	109.0	C11-N1-C25	116.5(4)
С36-С37-Н37В	109.0	C18-O3-C34	117.8(3)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	21(2)	16(2)	23(2)	0(2)	-1(2)	-3(2)
C2	20(2)	14(2)	26(2)	1(2)	3(2)	-3(2)
C3	24(2)	26(2)	18(2)	1(2)	1(2)	-1(2)
C4	25(2)	19(2)	24(2)	2(2)	-3(2)	1(2)
C5	21(2)	19(2)	24(2)	3(2)	4(2)	-3(2)
C6	17(2)	19(2)	23(2)	1(2)	5(2)	-3(2)
C7	29(2)	16(2)	23(2)	-1(1)	4(2)	0(2)
C8	26(2)	25(2)	21(2)	-2(2)	4(2)	-1(2)
C9	22(2)	21(2)	22(2)	1(2)	-4(2)	-1(2)
C10	21(2)	15(2)	21(2)	-2(1)	1(2)	-2(2)
C11	23(2)	13(2)	21(2)	-2(1)	-2(2)	-3(2)
C12	19(2)	11(2)	22(2)	0(1)	1(2)	-2(1)
C13	24(2)	21(2)	20(2)	3(2)	-1(2)	0(2)
C14	23(2)	17(2)	22(2)	2(1)	-4(2)	0(2)
C15	19(2)	14(2)	24(2)	-3(1)	0(2)	0(2)
C16	21(2)	22(2)	21(2)	2(2)	-6(2)	3(2)
C17	25(2)	20(2)	21(2)	-4(2)	-1(2)	2(2)
C18	18(2)	14(2)	23(2)	-5(1)	-1(2)	-1(2)
C19	22(2)	10(2)	24(2)	-3(1)	1(2)	-4(2)
C20	23(2)	21(2)	27(2)	0(2)	-1(2)	5(2)
C21	25(2)	25(2)	23(2)	2(2)	-4(2)	2(2)
C22	27(2)	24(2)	19(2)	-3(2)	1(2)	-3(2)
C23	24(2)	20(2)	24(2)	-5(2)	3(2)	-2(2)
C24	19(2)	16(2)	20(2)	-4(1)	1(2)	-2(2)
C25	22(2)	17(2)	26(2)	2(2)	1(2)	4(2)
C26	21(2)	19(2)	30(2)	-2(2)	-1(2)	2(2)
C27	23(2)	19(2)	24(2)	0(2)	1(2)	3(2)
C28	25(2)	20(2)	23(2)	0(2)	0(2)	0(2)
C29	27(2)	19(2)	24(2)	0(2)	-1(2)	3(2)
C30	24(2)	22(2)	22(2)	0(2)	-2(2)	0(2)
C31	26(2)	22(2)	22(2)	0(2)	1(2)	3(2)

Table **90.** Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **90.** The anisotropicdisplacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	28(2)	20(2)	30(2)	1(2)	-3(2)	1(2)
C33	35(3)	24(2)	37(3)	2(2)	-8(2)	2(2)
C34	25(2)	22(2)	19(2)	0(2)	-2(2)	0(2)
C35	23(2)	21(2)	27(2)	-3(2)	2(2)	2(2)
C36	24(2)	24(2)	23(2)	-2(2)	3(2)	0(2)
C37	24(2)	20(2)	23(2)	-1(2)	2(2)	-2(2)
C38	25(2)	24(2)	26(2)	2(2)	2(2)	-2(2)
C39	26(2)	19(2)	26(2)	1(2)	1(2)	-2(2)
C40	24(2)	26(2)	26(2)	1(2)	2(2)	-2(2)
C41	30(2)	24(2)	27(2)	3(2)	2(2)	1(2)
C42	34(3)	26(2)	37(3)	3(2)	-2(2)	3(2)
N1	21(2)	18(2)	18(2)	-1(1)	3(1)	-2(1)
01	32(2)	25(1)	22(2)	-2(1)	0(1)	7(1)
02	34(2)	30(2)	22(2)	2(1)	-2(1)	7(1)
O3	27(2)	21(1)	21(2)	-2(1)	0(1)	6(1)

	Х	У	Z	U(eq)
H3	697	5369	6998	27
H4	3855	5002	6632	27
H7	2304	4929	3588	27
H8	-689	5161	2549	29
H9	-3818	5526	2945	26
H16	7839	4448	3380	26
H17	11095	4095	2990	27
H20	14980	3732	5629	29
H21	14481	3835	7084	29
H22	11165	4182	7472	28
H23	8531	4444	6423	27
H25A	-7200	6019	6190	26
H25B	-8214	6063	5180	26
H26A	-4015	6350	5025	28
H26B	-3221	6320	6050	28
H27A	-8300	6605	5312	26
H27B	-7477	6577	6338	26
H28A	-3957	6875	5192	27
H28B	-3427	6866	6230	27
H29A	-8232	7147	5322	28
H29B	-7691	7139	6361	28
H30A	-3464	7415	6287	28
H30B	-3865	7414	5246	28
H31A	-8122	7692	5301	28
H31B	-7711	7694	6342	28
H32A	-3799	7960	5241	31
H32B	-3430	7964	6282	31
H33A	-7995	8242	5264	49
H33B	-5368	8404	5778	49
H33C	-7705	8241	6307	49

Table **90**.5. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) For **90**.
H34A	15652	3858	2918	27
H34B	12819	3662	2821	27
H35A	18083	3442	3625	28
H35B	17388	3415	2595	28
H36A	13238	3139	2835	29
H36B	13972	3164	3864	29
H37A	17688	2878	2732	27
H37B	18140	2883	3772	27
H38A	13898	2605	3864	30
H38B	13413	2602	2824	30
H39A	18142	2330	3790	28
H39B	17725	2331	2749	28
H40A	13824	2057	3842	30
H40B	13460	2056	2801	30
H41A	18092	1781	3800	32
H41B	17682	1777	2759	32
H42A	13640	1521	3834	49
H42B	16068	1341	3393	49
H42C	13561	1494	2796	49

01-C1-C2-C3	1.3(6)	C7-C6-C12-C2	179.1(4)
N1-C1-C2-C3	-179.2(4)	C14-C15-C16-C17	-179.5(4)
01-C1-C2-C12	-178.9(4)	C24-C15-C16-C17	1.1(7)
N1-C1-C2-C12	0.5(5)	C15-C16-C17-C18	0.7(7)
C12-C2-C3-C4	0.1(6)	C16-C17-C18-O3	176.9(4)
C1-C2-C3-C4	179.8(4)	C16-C17-C18-C19	-2.3(6)
C2-C3-C4-C5	0.4(7)	C17-C18-C19-C20	-176.3(4)
C3-C4-C5-C6	-0.2(6)	O3-C18-C19-C20	4.4(6)
C3-C4-C5-C13	178.8(4)	C17-C18-C19-C24	2.1(6)
C4-C5-C6-C12	-0.4(6)	O3-C18-C19-C24	-177.2(3)
C13-C5-C6-C12	-179.5(4)	C24-C19-C20-C21	0.5(6)
C4-C5-C6-C7	-178.5(4)	C18-C19-C20-C21	178.9(4)
C13-C5-C6-C7	2.4(6)	C19-C20-C21-C22	0.4(7)
C12-C6-C7-C8	1.1(6)	C20-C21-C22-C23	-1.7(7)
C5-C6-C7-C8	179.2(4)	C21-C22-C23-C24	1.9(7)
C6-C7-C8-C9	-0.2(7)	C22-C23-C24-C19	-0.9(6)
C7-C8-C9-C10	0.3(7)	C22-C23-C24-C15	-179.4(4)
C8-C9-C10-C12	-1.3(6)	C20-C19-C24-C23	-0.3(6)
C8-C9-C10-C11	179.9(4)	C18-C19-C24-C23	-178.7(4)
C9-C10-C11-O2	-3.3(6)	C20-C19-C24-C15	178.2(4)
C12-C10-C11-O2	177.9(4)	C18-C19-C24-C15	-0.3(6)
C9-C10-C11-N1	177.3(4)	C16-C15-C24-C23	177.1(4)
C12-C10-C11-N1	-1.5(6)	C14-C15-C24-C23	-2.2(6)
C9-C10-C12-C2	-179.0(4)	C16-C15-C24-C19	-1.3(6)
C11-C10-C12-C2	-0.2(6)	C14-C15-C24-C19	179.3(4)
C9-C10-C12-C6	2.2(6)	N1-C25-C26-C27	175.5(3)
C11-C10-C12-C6	-179.0(4)	C25-C26-C27-C28	-179.4(4)
C3-C2-C12-C10	-179.6(4)	C26-C27-C28-C29	174.1(4)
C1-C2-C12-C10	0.7(6)	C27-C28-C29-C30	-179.8(3)
C3-C2-C12-C6	-0.7(6)	C28-C29-C30-C31	177.2(3)
C1-C2-C12-C6	179.5(4)	C29-C30-C31-C32	-179.8(4)
C5-C6-C12-C10	179.7(4)	C30-C31-C32-C33	179.1(4)
C7-C6-C12-C10	-2.1(6)	O3-C34-C35-C36	75.9(4)
C5-C6-C12-C2	0.9(6)	C34-C35-C36-C37	179.2(4)

Table **90**.6. Torsion angles  $[^{\circ}]$  for **90**.

C35-C36-C37-C38	-174.2(4)	O2-C11-N1-C1	-176.5(4)
C36-C37-C38-C39	179.3(3)	C10-C11-N1-C1	2.9(6)
C37-C38-C39-C40	-178.6(4)	O2-C11-N1-C25	-3.2(6)
C38-C39-C40-C41	-178.9(4)	C10-C11-N1-C25	176.2(3)
C39-C40-C41-C42	179.1(4)	C26-C25-N1-C1	85.6(4)
O1-C1-N1-C11	177.1(4)	C26-C25-N1-C11	-88.2(4)
C2-C1-N1-C11	-2.4(6)	C17-C18-O3-C34	3.8(6)
01-C1-N1-C25	3.8(6)	C19-C18-O3-C34	-177.0(3)
C2-C1-N1-C25	-175.6(3)	C35-C34-O3-C18	-174.8(3)

End crystallographic info for 90.

#### **CRYSTALLOGRAPHIC MATERIAL FOR 100**

Crystallographic Material for 10o.

X-ray Experimental.

Table 100.1. Crystallographic Data for 100.

Table 100.2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of 100.

Table 100.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 100.

Table 100.4. Anisotropic thermal parameters for the non-hydrogen atoms of 100.

Table 100.5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of 100.

Table 100.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of 100.

X-ray Experimental for complex  $C_{44}H_{53}NO_3$  (100): Crystals grew as long, orange laths by vapor diffusion (solvent = p-xylenes, precipitant = acetonitrile). The data crystal was cut from a larger crystal and had approximate dimensions; 0.28 x 0.06 x 0.02 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 581 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 25 seconds per frame with a detector offset of +/- 40.3° and 75 seconds per frame with a detector offset of +/-110.0°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1829^*P)^2 + (0.4842^*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.295, with R(F) equal to 0.0947 and a goodness of fit, S, = 1.04. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
- 4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

# 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 100.1 Crystal data and structure refinement for 100.			
Identification code	shelx		
Empirical formula	C44 H53 N O3		
Formula weight	643.87		
Temperature	100(2) K		
Wavelength	1.54184 ≈		
Crystal system	monoclinic		
Space group	C c		
Unit cell dimensions	$a = 4.6678(13) \approx$	$\alpha = 90\infty$ .	
	$b = 49.083(9) \approx$	β= 112.97(3)∞.	
	$c = 16.707(4) \approx$	$\gamma = 90\infty$ .	
Volume	3524.4(16) ≈ <sup>3</sup>		
Z	4		
Density (calculated)	1.213 Mg/m <sup>3</sup>		
Absorption coefficient	0.576 mm <sup>-1</sup>		
F(000)	1392		
Crystal size	$0.280 \ge 0.062 \ge 0.023 \text{ mm}^3$		
Theta range for data collection	3.391 to 74.798∞.		
Index ranges	-5<=h<=5, -55<=k<=60, -10<=l<=20		
Reflections collected	5696		
Independent reflections	3928 [R(int) = 0.0658]		
Completeness to theta = $67.684\infty$	98.4 %		
Absorption correction	Semi-empirical from equivalen	ts	
Max. and min. transmission	1.00 and 0.564		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	3928 / 290 / 435		
Goodness-of-fit on F <sup>2</sup>	1.045		
Final R indices [I>2sigma(I)]	R1 = 0.0947, wR2 = 0.2648		
R indices (all data)	R1 = 0.1159, wR2 = 0.2952		
Absolute structure parameter	-0.5(7)		
Extinction coefficient	n/a		
Largest diff. peak and hole	$0.671 \text{ and } -0.442 \text{ e.} \approx^3$		

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	Х	у	Z	U(eq)
C1	-4104(18)	8206(1)	4479(5)	24(1)
C2	-2379(17)	7994(1)	4233(5)	22(1)
C3	-3175(18)	7931(2)	3373(5)	25(1)
C4	-1540(18)	7726(2)	3135(5)	26(2)
C5	872(19)	7590(1)	3765(5)	26(2)
C6	1748(17)	7647(1)	4660(5)	20(1)
C7	4190(17)	7508(1)	5329(5)	22(1)
C8	4872(18)	7577(2)	6187(5)	26(2)
С9	3182(17)	7782(2)	6422(5)	24(1)
C10	821(17)	7915(1)	5774(4)	21(1)
C11	-923(16)	8127(1)	6032(5)	22(1)
C12	44(16)	7855(1)	4892(5)	21(1)
C13	5958(17)	7308(2)	5112(5)	24(1)
C14	7444(19)	7140(2)	4913(5)	26(2)
C15	9172(17)	6939(1)	4690(5)	23(1)
C16	8705(17)	6894(2)	3826(5)	25(2)
C17	10427(17)	6698(2)	3589(5)	23(1)
C18	12561(17)	6542(1)	4215(5)	23(1)
C19	13215(17)	6585(1)	5113(5)	23(1)
C20	15507(18)	6434(2)	5775(5)	28(2)
C21	16145(18)	6481(2)	6634(5)	29(2)
C22	14393(19)	6674(2)	6871(5)	29(2)
C23	12134(18)	6824(1)	6245(5)	25(2)
C24	11494(16)	6785(1)	5353(5)	22(1)
C25	-5003(18)	8478(2)	5596(5)	28(2)
C26	-3389(18)	8752(1)	5618(5)	25(2)
C27	-5176(18)	8992(2)	5790(5)	26(2)
C28	-3508(18)	9263(1)	5766(5)	25(2)
C29	-5277(18)	9514(1)	5875(5)	24(1)
C30	-3611(19)	9776(1)	5807(5)	27(2)
C31	-5270(19)	10037(2)	5890(5)	27(2)

Table 2.100. Atomic coordinates (x 10<sup>4</sup>) and equivalent isotropic displacement parameters ( $\approx^2 x 10^3$ ) for 100. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	-3562(19)	10292(2)	5791(5)	29(2)
C33	-5200(20)	10556(2)	5868(6)	31(2)
C34	-3470(20)	10810(2)	5760(7)	40(2)
C35	13781(18)	6286(2)	3171(5)	27(2)
C36	15609(19)	6026(2)	3158(5)	30(2)
C37	14066(19)	5771(2)	3342(5)	28(2)
C38	15720(20)	5509(2)	3299(5)	31(2)
C39	14030(20)	5254(2)	3411(5)	29(2)
C40	15550(20)	4988(2)	3335(5)	29(2)
C41	13770(20)	4737(2)	3433(5)	32(2)
C42	15205(19)	4466(2)	3335(5)	29(2)
C43	13350(20)	4220(2)	3431(5)	32(2)
C44	14760(30)	3952(2)	3316(6)	42(2)
N1	-3338(15)	8260(1)	5363(4)	22(1)
O1	-6155(14)	8341(1)	3935(4)	34(1)
O2	-321(14)	8194(1)	6785(3)	31(1)
O3	14249(13)	6336(1)	4051(3)	28(1)

C1-O1	1.227(10)
C1-N1	1.402(9)
C1-C2	1.471(9)
C2-C3	1.370(10)
C2-C12	1.408(10)
C3-C4	1.413(10)
С3-Н3	0.9500
C4-C5	1.375(11)
C4-H4	0.9500
C5-C6	1.417(10)
С5-Н5	0.9500
C6-C7	1.423(10)
C6-C12	1.437(9)
C7-C8	1.383(10)
C7-C13	1.416(10)
C8-C9	1.425(10)
С8-Н8	0.9500
C9-C10	1.372(10)
С9-Н9	0.9500
C10-C12	1.403(9)
C10-C11	1.487(9)
C11-O2	1.222(9)
C11-N1	1.401(9)
C13-C14	1.204(11)
C14-C15	1.414(10)
C15-C16	1.391(10)
C15-C24	1.427(11)
C16-C17	1.408(10)
C16-H16	0.9500
C17-C18	1.363(11)
C17-H17	0.9500
C18-O3	1.373(9)
C18-C19	1.426(10)
C19-C20	1.413(11)

Table 100.3. Bond lengths  $[\approx]$  and angles  $[\infty]$  for 100.

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C19-C24	1.422(10)
C20-C21	1.367(11)
С20-Н20	0.9500
C21-C22	1.405(11)
С21-Н21	0.9500
C22-C23	1.372(12)
С22-Н22	0.9500
C23-C24	1.413(10)
С23-Н23	0.9500
C25-N1	1.463(9)
C25-C26	1.534(10)
С25-Н25А	0.9900
С25-Н25В	0.9900
C26-C27	1.534(9)
C26-H26A	0.9900
С26-Н26В	0.9900
C27-C28	1.549(10)
С27-Н27А	0.9900
С27-Н27В	0.9900
C28-C29	1.534(10)
C28-H28A	0.9900
C28-H28B	0.9900
C29-C30	1.528(9)
С29-Н29А	0.9900
С29-Н29В	0.9900
C30-C31	1.532(10)
С30-Н30А	0.9900
С30-Н30В	0.9900
C31-C32	1.529(11)
С31-Н31А	0.9900
C31-H31B	0.9900
C32-C33	1.535(10)
С32-Н32А	0.9900
С32-Н32В	0.9900
C33-C34	1.529(11)
С33-Н33А	0.9900

С33-Н33В	0.9900
C34-H34A	0.9800
C34-H34B	0.9800
C34-H34C	0.9800
C35-O3	1.422(8)
C35-C36	1.540(10)
С35-Н35А	0.9900
С35-Н35В	0.9900
C36-C37	1.534(11)
С36-Н36А	0.9900
С36-Н36В	0.9900
C37-C38	1.517(10)
С37-Н37А	0.9900
С37-Н37В	0.9900
C38-C39	1.525(11)
С38-Н38А	0.9900
С38-Н38В	0.9900
C39-C40	1.515(10)
С39-Н39А	0.9900
С39-Н39В	0.9900
C40-C41	1.531(11)
C40-H40A	0.9900
C40-H40B	0.9900
C41-C42	1.527(10)
C41-H41A	0.9900
C41-H41B	0.9900
C42-C43	1.530(11)
C42-H42A	0.9900
C42-H42B	0.9900
C43-C44	1.519(11)
С43-Н43А	0.9900
С43-Н43В	0.9900
C44-H44A	0.9800
C44-H44B	0.9800
C44-H44C	0.9800

01-C1-N1	118.9(6)
01-C1-C2	122.0(7)
N1-C1-C2	119.1(7)
C3-C2-C12	121.2(6)
C3-C2-C1	119.9(7)
C12-C2-C1	118.9(6)
C2-C3-C4	120.0(7)
С2-С3-Н3	120.0
С4-С3-Н3	120.0
C5-C4-C3	120.1(7)
С5-С4-Н4	120.0
С3-С4-Н4	120.0
C4-C5-C6	121.7(7)
С4-С5-Н5	119.2
С6-С5-Н5	119.2
C5-C6-C7	123.1(6)
C5-C6-C12	117.6(7)
C7-C6-C12	119.2(6)
C8-C7-C13	120.9(7)
C8-C7-C6	119.0(7)
C13-C7-C6	120.0(6)
C7-C8-C9	122.0(7)
С7-С8-Н8	119.0
С9-С8-Н8	119.0
C10-C9-C8	118.7(7)
С10-С9-Н9	120.7
С8-С9-Н9	120.7
C9-C10-C12	121.9(6)
C9-C10-C11	117.8(6)
C12-C10-C11	120.3(6)
O2-C11-N1	119.1(6)
O2-C11-C10	123.8(7)
N1-C11-C10	117.1(6)
C10-C12-C2	121.3(6)
C10-C12-C6	119.2(7)
C2-C12-C6	119.5(6)

C14-C13-C7	178.9(8)
C13-C14-C15	178.8(8)
C16-C15-C14	120.7(7)
C16-C15-C24	119.0(7)
C14-C15-C24	120.2(7)
C15-C16-C17	121.8(7)
С15-С16-Н16	119.1
С17-С16-Н16	119.1
C18-C17-C16	119.6(6)
С18-С17-Н17	120.2
С16-С17-Н17	120.2
C17-C18-O3	124.3(6)
C17-C18-C19	121.1(6)
O3-C18-C19	114.5(6)
C20-C19-C24	118.7(7)
C20-C19-C18	122.1(7)
C24-C19-C18	119.1(7)
C21-C20-C19	121.4(7)
С21-С20-Н20	119.3
С19-С20-Н20	119.3
C20-C21-C22	119.8(7)
С20-С21-Н21	120.1
С22-С21-Н21	120.1
C23-C22-C21	120.3(7)
С23-С22-Н22	119.8
С21-С22-Н22	119.8
C22-C23-C24	121.0(7)
С22-С23-Н23	119.5
С24-С23-Н23	119.5
C23-C24-C19	118.6(7)
C23-C24-C15	122.1(7)
C19-C24-C15	119.2(6)
N1-C25-C26	110.0(6)
N1-C25-H25A	109.7
С26-С25-Н25А	109.7
N1-C25-H25B	109.7

С26-С25-Н25В	109.7
H25A-C25-H25B	108.2
C27-C26-C25	112.3(6)
С27-С26-Н26А	109.1
С25-С26-Н26А	109.1
С27-С26-Н26В	109.1
С25-С26-Н26В	109.1
H26A-C26-H26B	107.9
C26-C27-C28	109.8(6)
С26-С27-Н27А	109.7
С28-С27-Н27А	109.7
С26-С27-Н27В	109.7
С28-С27-Н27В	109.7
Н27А-С27-Н27В	108.2
C29-C28-C27	112.8(6)
С29-С28-Н28А	109.0
С27-С28-Н28А	109.0
С29-С28-Н28В	109.0
С27-С28-Н28В	109.0
H28A-C28-H28B	107.8
C30-C29-C28	110.7(6)
С30-С29-Н29А	109.5
С28-С29-Н29А	109.5
С30-С29-Н29В	109.5
С28-С29-Н29В	109.5
H29A-C29-H29B	108.1
C29-C30-C31	113.9(6)
С29-С30-Н30А	108.8
С31-С30-Н30А	108.8
С29-С30-Н30В	108.8
С31-С30-Н30В	108.8
H30A-C30-H30B	107.7
C32-C31-C30	111.9(6)
С32-С31-Н31А	109.2
С30-С31-Н31А	109.2
С32-С31-Н31В	109.2

C30-C31-H31B	109.2
H31A-C31-H31B	107.9
C31-C32-C33	112.7(6)
С31-С32-Н32А	109.0
С33-С32-Н32А	109.0
С31-С32-Н32В	109.0
С33-С32-Н32В	109.0
H32A-C32-H32B	107.8
C34-C33-C32	112.0(7)
С34-С33-Н33А	109.2
С32-С33-Н33А	109.2
С34-С33-Н33В	109.2
С32-С33-Н33В	109.2
Н33А-С33-Н33В	107.9
С33-С34-Н34А	109.5
С33-С34-Н34В	109.5
H34A-C34-H34B	109.5
С33-С34-Н34С	109.5
H34A-C34-H34C	109.5
H34B-C34-H34C	109.5
O3-C35-C36	107.1(6)
O3-C35-H35A	110.3
С36-С35-Н35А	110.3
O3-C35-H35B	110.3
С36-С35-Н35В	110.3
H35A-C35-H35B	108.5
C37-C36-C35	111.6(6)
С37-С36-Н36А	109.3
С35-С36-Н36А	109.3
С37-С36-Н36В	109.3
С35-С36-Н36В	109.3
H36A-C36-H36B	108.0
C38-C37-C36	113.4(7)
С38-С37-Н37А	108.9
С36-С37-Н37А	108.9
С38-С37-Н37В	108.9

С36-С37-Н37В	108.9
Н37А-С37-Н37В	107.7
C37-C38-C39	113.2(7)
С37-С38-Н38А	108.9
С39-С38-Н38А	108.9
С37-С38-Н38В	108.9
С39-С38-Н38В	108.9
H38A-C38-H38B	107.8
C40-C39-C38	114.6(7)
С40-С39-Н39А	108.6
С38-С39-Н39А	108.6
С40-С39-Н39В	108.6
С38-С39-Н39В	108.6
Н39А-С39-Н39В	107.6
C39-C40-C41	113.3(7)
С39-С40-Н40А	108.9
C41-C40-H40A	108.9
С39-С40-Н40В	108.9
С41-С40-Н40В	108.9
H40A-C40-H40B	107.7
C42-C41-C40	114.2(7)
С42-С41-Н41А	108.7
C40-C41-H41A	108.7
С42-С41-Н41В	108.7
C40-C41-H41B	108.7
H41A-C41-H41B	107.6
C41-C42-C43	112.6(7)
C41-C42-H42A	109.1
С43-С42-Н42А	109.1
С41-С42-Н42В	109.1
С43-С42-Н42В	109.1
H42A-C42-H42B	107.8
C44-C43-C42	112.2(7)
С44-С43-Н43А	109.2
С42-С43-Н43А	109.2
С44-С43-Н43В	109.2

С42-С43-Н43В	109.2
H43A-C43-H43B	107.9
C43-C44-H44A	109.5
C43-C44-H44B	109.5
H44A-C44-H44B	109.5
C43-C44-H44C	109.5
H44A-C44-H44C	109.5
H44B-C44-H44C	109.5
C11-N1-C1	123.2(6)
C11-N1-C25	118.3(6)
C1-N1-C25	118.4(6)
C18-O3-C35	117.7(6)

Symmetry transformations used to generate equivalent atoms:

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	28(3)	27(3)	18(3)	-5(3)	11(3)	-3(3)
C2	30(4)	24(3)	14(3)	-4(2)	11(3)	3(3)
C3	31(4)	29(3)	18(3)	1(3)	12(3)	1(3)
C4	29(4)	37(4)	16(3)	-1(3)	12(3)	0(3)
C5	35(4)	24(3)	22(3)	0(3)	12(3)	0(3)
C6	24(3)	22(3)	18(3)	1(2)	14(3)	-1(2)
C7	26(3)	25(3)	20(3)	0(3)	13(3)	-2(3)
C8	25(3)	31(3)	22(3)	-2(3)	10(3)	1(3)
С9	22(3)	27(3)	23(3)	-3(3)	10(3)	0(3)
C10	27(3)	22(3)	18(3)	-2(3)	12(3)	1(3)
C11	22(3)	25(3)	18(3)	-3(3)	7(3)	1(3)
C12	21(3)	25(3)	21(3)	-6(3)	12(3)	-3(2)
C13	20(3)	32(3)	21(3)	1(3)	11(3)	-2(3)
C14	32(4)	26(3)	22(3)	0(3)	12(3)	-2(3)
C15	21(3)	26(3)	22(3)	-3(3)	8(3)	-1(3)
C16	23(3)	32(3)	19(3)	-1(3)	8(3)	3(3)
C17	25(3)	28(3)	17(3)	-4(3)	9(3)	-3(3)
C18	27(4)	21(3)	20(3)	-6(3)	8(3)	0(2)
C19	30(4)	19(3)	19(3)	-3(2)	11(3)	-2(2)
C20	30(4)	28(3)	22(3)	-2(3)	7(3)	2(3)
C21	31(4)	34(3)	20(3)	4(3)	7(3)	1(3)
C22	30(4)	41(4)	18(3)	-3(3)	11(3)	-4(3)
C23	30(4)	28(3)	20(3)	-6(3)	11(3)	-3(3)
C24	25(3)	24(3)	18(3)	-5(3)	9(3)	-6(3)
C25	27(4)	27(3)	29(4)	-2(3)	8(3)	2(3)
C26	28(3)	24(3)	25(3)	-4(3)	11(3)	3(3)
C27	23(3)	30(3)	25(3)	2(3)	9(3)	1(3)
C28	28(4)	27(3)	20(3)	0(3)	10(3)	1(3)
C29	24(3)	27(3)	21(3)	-3(3)	8(3)	-1(2)
C30	29(4)	29(3)	22(3)	-4(3)	10(3)	-4(3)
C31	29(4)	32(3)	21(3)	-4(3)	13(3)	-2(3)

Table 100.4. Anisotropic displacement parameters ( $\approx^2 x \ 10^3$ ) for 100. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	30(4)	30(3)	22(3)	3(3)	5(3)	4(3)
C33	35(4)	26(3)	32(4)	-1(3)	12(3)	4(3)
C34	42(5)	28(3)	47(5)	3(4)	16(4)	-2(3)
C35	30(4)	34(4)	14(3)	-5(3)	5(3)	3(3)
C36	33(4)	35(4)	22(3)	-8(3)	10(3)	1(3)
C37	30(4)	34(4)	19(3)	-4(3)	8(3)	3(3)
C38	37(4)	29(3)	22(3)	2(3)	9(3)	5(3)
C39	31(4)	31(3)	21(3)	0(3)	5(3)	6(3)
C40	36(4)	30(3)	20(3)	1(3)	8(3)	5(3)
C41	36(4)	36(4)	19(3)	-1(3)	7(3)	5(3)
C42	30(4)	35(4)	22(3)	-4(3)	10(3)	6(3)
C43	36(4)	40(4)	22(3)	2(3)	13(3)	3(3)
C44	58(6)	36(4)	34(5)	-2(4)	18(4)	7(4)
N1	30(3)	19(2)	14(3)	-2(2)	5(2)	0(2)
01	38(3)	37(3)	17(2)	0(2)	0(2)	10(2)
02	34(3)	38(3)	16(2)	-5(2)	6(2)	4(2)
O3	34(3)	31(2)	18(2)	-2(2)	9(2)	7(2)

	х	у	Z	U(eq)
H3	-4825	8026	2937	31
H4	-2107	7681	2540	32
H5	1978	7455	3595	32
H8	6518	7485	6633	31
H9	3680	7825	7015	29
H16	7184	6998	3385	30
H17	10103	6674	2995	28
H20	16628	6296	5621	33
H21	17768	6384	7070	35
H22	14775	6701	7467	35
H23	10982	6955	6414	31
H25A	-5044	8440	6173	34
H25B	-7178	8486	5165	34
H26A	-1266	8746	6079	30
H26B	-3193	8781	5055	30
H27A	-5288	8970	6367	31
H27B	-7326	8996	5344	31
H28A	-1402	9261	6236	30
H28B	-3263	9276	5205	30
H29A	-7412	9514	5420	29
H29B	-5436	9507	6448	29
H30A	-3403	9777	5239	32
H30B	-1487	9775	6268	32
H31A	-7412	10037	5438	32
H31B	-5417	10040	6465	32
H32A	-3405	10288	5217	34
H32B	-1422	10291	6243	34
H33A	-7340	10557	5418	38
H33B	-5336	10562	6444	38
H34A	-1334	10807	6196	60

Table 100.5. Hydrogen coordinates (  $x\ 10^4$ ) and isotropic displacement parameters ( $\approx^2\!x\ 10\ ^3$ ) for 100.

H34B	-4539	10973	5838	60
H34C	-3441	10811	5177	60
H35A	14546	6442	2933	32
H35B	11539	6260	2813	32
H36A	15732	6008	2583	36
H36B	17756	6042	3602	36
H37A	14018	5787	3927	34
H37B	11888	5761	2914	34
H38A	17843	5512	3760	37
H38B	15920	5499	2732	37
H39A	13908	5262	3988	35
H39B	11879	5257	2966	35
H40A	17688	4983	3788	35
H40B	15706	4981	2761	35
H41A	13660	4742	4013	38
H41B	11612	4746	2992	38
H42A	17353	4455	3780	35
H42B	15322	4460	2757	35
H43A	13262	4224	4014	39
H43B	11187	4233	2992	39
H44A	14901	3949	2746	64
H44B	13451	3801	3355	64
H44C	16851	3933	3773	64

Table 100.6.	Torsion	angles	$\infty$	for <b>100</b> .	
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O1-C1-C2-C3 N1-C1-C2-C3 O1-C1-C2-C12 N1-C1-C2-C12	-3.9(12) 177.6(7) 177.0(7) -1.5(10) -0.4(11) -179.4(7) -0.7(11)
N1-C1-C2-C3 O1-C1-C2-C12 N1-C1-C2-C12	177.6(7) 177.0(7) -1.5(10) -0.4(11) -179.4(7) -0.7(11)
01-C1-C2-C12 N1-C1-C2-C12	177.0(7) -1.5(10) -0.4(11) -179.4(7) -0.7(11)
N1-C1-C2-C12	-1.5(10) -0.4(11) -179.4(7) -0.7(11)
	-0.4(11) -179.4(7) -0.7(11)
C12-C2-C3-C4	-179.4(7) -0.7(11)
C1-C2-C3-C4	-0.7(11)
C2-C3-C4-C5	()
C3-C4-C5-C6	1.3(12)
C4-C5-C6-C7	178.7(7)
C4-C5-C6-C12	-0.7(11)
C5-C6-C7-C8	-179.7(7)
C12-C6-C7-C8	-0.3(10)
C5-C6-C7-C13	2.6(11)
C12-C6-C7-C13	-178.0(6)
C13-C7-C8-C9	178.3(7)
C6-C7-C8-C9	0.7(11)
C7-C8-C9-C10	-0.4(11)
C8-C9-C10-C12	-0.3(11)
C8-C9-C10-C11	179.8(6)
C9-C10-C11-O2	1.9(11)
C12-C10-C11-O2	-178.1(7)
C9-C10-C11-N1	-179.6(7)
C12-C10-C11-N1	0.4(10)
C9-C10-C12-C2	-179.8(7)
C11-C10-C12-C2	0.1(10)
C9-C10-C12-C6	0.6(10)
C11-C10-C12-C6	-179.5(6)
C3-C2-C12-C10	-178.6(7)
C1-C2-C12-C10	0.4(10)
C3-C2-C12-C6	1.0(11)
C1-C2-C12-C6	180.0(6)
C5-C6-C12-C10	179.2(6)
C7-C6-C12-C10	-0.3(9)
C5-C6-C12-C2	-0.4(10)

C7-C6-C12-C2	-179.9(7)
C14-C15-C16-C17	179.1(7)
C24-C15-C16-C17	1.0(11)
C15-C16-C17-C18	1.6(11)
C16-C17-C18-O3	176.6(7)
C16-C17-C18-C19	-3.7(11)
C17-C18-C19-C20	-177.4(7)
O3-C18-C19-C20	2.3(10)
C17-C18-C19-C24	3.2(11)
O3-C18-C19-C24	-177.1(6)
C24-C19-C20-C21	-1.8(11)
C18-C19-C20-C21	178.8(7)
C19-C20-C21-C22	3.3(12)
C20-C21-C22-C23	-2.8(12)
C21-C22-C23-C24	0.7(12)
C22-C23-C24-C19	0.8(11)
C22-C23-C24-C15	-179.6(7)
C20-C19-C24-C23	-0.3(10)
C18-C19-C24-C23	179.2(6)
C20-C19-C24-C15	-179.9(7)
C18-C19-C24-C15	-0.5(10)
C16-C15-C24-C23	178.8(7)
C14-C15-C24-C23	0.8(11)
C16-C15-C24-C19	-1.6(10)
C14-C15-C24-C19	-179.6(6)
N1-C25-C26-C27	175.6(6)
C25-C26-C27-C28	-177.6(6)
C26-C27-C28-C29	176.3(6)
C27-C28-C29-C30	-177.5(6)
C28-C29-C30-C31	178.8(6)
C29-C30-C31-C32	-178.3(6)
C30-C31-C32-C33	179.7(6)
C31-C32-C33-C34	-179.5(7)
O3-C35-C36-C37	71.7(8)
C35-C36-C37-C38	177.6(6)
C36-C37-C38-C39	-175.4(6)

C37-C38-C39-C40	177.6(6)
C38-C39-C40-C41	-179.0(6)
C39-C40-C41-C42	178.4(6)
C40-C41-C42-C43	-179.6(6)
C41-C42-C43-C44	179.0(7)
O2-C11-N1-C1	177.0(7)
C10-C11-N1-C1	-1.6(10)
O2-C11-N1-C25	1.2(10)
C10-C11-N1-C25	-177.3(6)
01-C1-N1-C11	-176.4(7)
C2-C1-N1-C11	2.2(10)
01-C1-N1-C25	-0.7(11)
C2-C1-N1-C25	177.9(6)
C26-C25-N1-C11	89.4(8)
C26-C25-N1-C1	-86.5(8)
C17-C18-O3-C35	1.3(11)
C19-C18-O3-C35	-178.4(6)
C36-C35-O3-C18	-173.0(6)

Symmetry transformations used to generate equivalent atoms:

End of crystallographic info for 10o.

#### **CRYSTALLOGRAPHIC MATERIAL FOR 120**

Crystallographic Material for 120.

X-ray Experimental.

Table 120.1. Crystallographic Data for 120.

Table 120.2. Fractional coordinates and equivalent isotropic thermal parameters  $(Å^2)$  for the non-hydrogen atoms of 120.

Table 120.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of 120.

Table 120.4. Anisotropic thermal parameters for the non-hydrogen atoms of 120.

Table 120.5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of 120.

Table **120**.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **120**.

X-ray Experimental for complex  $C_{48}H_{61}NO_3$  (120): Crystals grew as very thin, orange laths by vapor diffusion (p-xylenes, acetonitrile) The data crystal had approximate dimensions; 0.21 x 0.05 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 448 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 45 seconds per frame with a detector offset of 0.0° and 74 seconds per frame with a detector offset of +/- 72.3°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.46.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.0422*P)^2]$ and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.200, with R(F) equal to 0.0817 and a goodness of fit, S, = 1.00. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.46.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
- 4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

# 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Empirical formula	C48 H61 N O3			
Formula weight	699.97			
Temperature	100(2) K			
Wavelength	1.54184 Å			
Crystal system	monoclinic			
Space group	C c			
Unit cell dimensions	a = 4.6653(8) Å	<i>α</i> = 90°.		
	b = 54.243(7) Å	β= 96.006(15)°.		
	c = 15.4813(18) Å	$\gamma = 90^{\circ}$ .		
Volume	3896.2(10) Å <sup>3</sup>			
Z	4			
Density (calculated)	1.193 Mg/m <sup>3</sup>			
Absorption coefficient	0.559 mm <sup>-1</sup>			
F(000)	1520			
Crystal size	0.210 x 0.050 x 0.030 n	0.210 x 0.050 x 0.030 mm <sup>3</sup>		
Theta range for data collection	5.747 to 56.765°.			
Index ranges	-4<=h<=5, -46<=k<=58, -12<=l<=16			
Reflections collected	5754			
Independent reflections	3982 [R(int) = 0.1110]			
Completeness to theta = $56.765^{\circ}$	93.7 %			
Absorption correction	Semi-empirical from eq	uivalents		
Max. and min. transmission	1.00 and 0.181			
Refinement method	Full-matrix least-square	es on F <sup>2</sup>		
Data / restraints / parameters	3982 / 314 / 471			
Goodness-of-fit on F <sup>2</sup>	0.995			
Final R indices [I>2sigma(I)]	R1 = 0.0817, w $R2 = 0.1564$			
R indices (all data)	R1 = 0.1484, $wR2 = 0.2003$			
Absolute structure parameter	0.1(10)			
Extinction coefficient	n/a			
Largest diff. peak and hole	0.263 and -0.269 e.Å <sup>-3</sup>			

Table 120. Crystal data and structure refinement for 120.

	X	у	Z	U(eq)
C1	-4150(20)	5639(2)	4473(8)	31(3)
C2	-2170(20)	5446(2)	4247(7)	26(3)
C3	-2130(20)	5387(2)	3374(7)	28(3)
C4	-210(30)	5202(2)	3138(8)	36(3)
C5	1510(30)	5079(2)	3767(7)	30(3)
C6	1510(20)	5136(2)	4647(8)	29(3)
C7	3260(30)	5010(2)	5338(8)	28(3)
C8	3110(20)	5074(2)	6189(7)	32(3)
С9	1140(20)	5258(2)	6413(8)	37(3)
C10	-570(20)	5377(2)	5788(7)	24(3)
C11	-2560(20)	5568(2)	6033(8)	29(3)
C12	-460(20)	5322(2)	4900(7)	23(3)
C13	5240(20)	4827(2)	5114(7)	29(3)
C14	6940(20)	4672(2)	4904(7)	26(3)
C15	8950(20)	4493(2)	4677(7)	31(3)
C16	9300(20)	4447(2)	3830(8)	31(3)
C17	11300(20)	4266(2)	3588(7)	28(3)
C18	12790(20)	4134(2)	4230(7)	28(3)
C19	12550(20)	4168(2)	5121(7)	27(3)
C20	14130(20)	4039(2)	5793(8)	34(3)
C21	13890(20)	4081(2)	6633(8)	36(3)
C22	11940(30)	4258(2)	6862(8)	36(3)
C23	10330(20)	4390(2)	6241(7)	33(3)
C24	10570(20)	4354(2)	5361(7)	28(3)
C25	-6190(20)	5890(2)	5598(7)	28(3)
C26	-4680(20)	6132(2)	5621(8)	33(3)
C27	-6630(30)	6349(2)	5796(8)	35(3)
C28	-5050(20)	6592(2)	5773(8)	38(3)
C29	-6900(30)	6821(2)	5907(8)	36(3)
C30	-5190(30)	7060(2)	5836(8)	34(3)
C31	-6960(30)	7293(2)	5925(8)	37(3)

Table **120**.2. Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters  $(Å^2x \ 10^3)$  for **120**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	-5190(30)	7528(2)	5830(8)	39(3)
C33	-6880(30)	7765(2)	5900(8)	37(3)
C34	-5050(20)	7996(2)	5797(8)	35(3)
C35	-6670(30)	8239(2)	5872(8)	44(4)
C36	-4780(30)	8464(2)	5761(9)	53(4)
C37	15090(30)	3898(2)	3173(7)	35(3)
C38	16910(30)	3668(2)	3163(8)	39(3)
C39	15300(30)	3436(2)	3364(8)	34(3)
C40	17030(30)	3198(2)	3299(8)	33(3)
C41	15230(30)	2966(2)	3420(8)	35(3)
C42	16870(30)	2725(2)	3347(8)	34(3)
C43	15030(30)	2497(2)	3434(8)	36(3)
C44	16600(30)	2254(2)	3350(8)	36(3)
C45	14750(30)	2027(2)	3443(8)	34(3)
C46	16250(30)	1780(2)	3332(7)	35(3)
C47	14310(30)	1556(2)	3436(8)	40(3)
C48	15780(30)	1311(2)	3309(8)	51(4)
N1	-4292(19)	5685(2)	5370(6)	26(2)
O1	-2690(18)	5629(1)	6800(5)	39(2)
O2	-5689(19)	5754(2)	3938(5)	47(2)
O3	14648(17)	3946(1)	4056(5)	37(2)

C1-O2	1.214(13)	C19-C24	1.443(15)
C1-N1	1.420(14)	C20-C21	1.337(14)
C1-C2	1.462(15)	С20-Н20	0.95
C2-C3	1.391(14)	C21-C22	1.393(16)
C2-C12	1.391(14)	C21-H21	0.95
C3-C4	1.416(15)	C22-C23	1.361(15)
С3-Н3	0.95	С22-Н22	0.95
C4-C5	1.369(15)	C23-C24	1.393(15)
С4-Н4	0.95	С23-Н23	0.95
C5-C6	1.396(15)	C25-N1	1.489(13)
С5-Н5	0.95	C25-C26	1.491(14)
C6-C7	1.447(15)	C25-H25A	0.99
C6-C12	1.451(14)	C25-H25B	0.99
C7-C8	1.371(15)	C26-C27	1.527(15)
C7-C13	1.427(16)	C26-H26A	0.99
C8-C9	1.426(15)	С26-Н26В	0.99
С8-Н8	0.95	C27-C28	1.515(15)
C9-C10	1.349(14)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.411(13)	C28-C29	1.535(15)
C10-C11	1.471(14)	C28-H28A	0.99
C11-O1	1.240(12)	C28-H28B	0.99
C11-N1	1.390(13)	C29-C30	1.530(15)
C13-C14	1.218(14)	С29-Н29А	0.99
C14-C15	1.423(16)	С29-Н29В	0.99
C15-C16	1.360(15)	C30-C31	1.526(15)
C15-C24	1.444(15)	С30-Н30А	0.99
C16-C17	1.433(14)	С30-Н30В	0.99
С16-Н16	0.95	C31-C32	1.532(16)
C17-C18	1.357(14)	C31-H31A	0.99
C17-H17	0.95	C31-H31B	0.99
C18-O3	1.382(13)	C32-C33	1.519(15)
C18-C19	1.408(15)	C32-H32A	0.99
C19-C20	1.400(14)	C32-H32B	0.99

Table 120.3. Bond lengths [Å] and angles  $[\circ]$  for 120.

C33-C34	1.534(15)	C41-C42	1.524(14)
С33-Н33А	0.99	C41-H41A	0.99
С33-Н33В	0.99	C41-H41B	0.99
C34-C35	1.531(15)	C42-C43	1.523(14)
C34-H34A	0.99	C42-H42A	0.99
C34-H34B	0.99	C42-H42B	0.99
C35-C36	1.525(16)	C43-C44	1.520(14)
С35-Н35А	0.99	C43-H43A	0.99
С35-Н35В	0.99	C43-H43B	0.99
С36-Н36А	0.98	C44-C45	1.516(15)
С36-Н36В	0.98	C44-H44A	0.99
С36-Н36С	0.98	C44-H44B	0.99
C37-O3	1.429(13)	C45-C46	1.527(14)
C37-C38	1.508(15)	C45-H45A	0.99
С37-Н37А	0.99	C45-H45B	0.99
С37-Н37В	0.99	C46-C47	1.533(14)
C38-C39	1.516(15)	C46-H46A	0.99
C38-H38A	0.99	C46-H46B	0.99
C38-H38B	0.99	C47-C48	1.519(15)
C39-C40	1.532(14)	C47-H47A	0.99
С39-Н39А	0.99	C47-H47B	0.99
С39-Н39В	0.99	C48-H48A	0.98
C40-C41	1.535(15)	C48-H48B	0.98
C40-H40A	0.99	C48-H48C	0.98
C40-H40B	0.99		
O2-C1-N1	119.3(11)	С5-С4-Н4	120.0
O2-C1-C2	123.5(11)	C3-C4-H4	120.0
N1-C1-C2	117.1(10)	C4-C5-C6	121.8(11)
C3-C2-C12	122.1(11)	С4-С5-Н5	119.1
C3-C2-C1	117.9(10)	С6-С5-Н5	119.1
C12-C2-C1	119.9(10)	C5-C6-C7	124.2(11)
C2-C3-C4	119.0(10)	C5-C6-C12	118.8(10)
С2-С3-Н3	120.5	C7-C6-C12	116.9(11)
С4-С3-Н3	120.5	C8-C7-C13	120.7(11)
C5-C4-C3	120.0(11)	C8-C7-C6	120.6(11)

C13-C7-C6	118.5(11)	C20-C21-C22	119.3(12)
C7-C8-C9	120.7(11)	С20-С21-Н21	120.4
С7-С8-Н8	119.6	C22-C21-H21	120.4
С9-С8-Н8	119.6	C23-C22-C21	120.7(12)
C10-C9-C8	120.4(12)	С23-С22-Н22	119.7
С10-С9-Н9	119.8	C21-C22-H22	119.7
С8-С9-Н9	119.8	C22-C23-C24	121.5(12)
C9-C10-C12	121.4(11)	С22-С23-Н23	119.2
C9-C10-C11	119.5(11)	С24-С23-Н23	119.2
C12-C10-C11	119.1(9)	C23-C24-C19	117.9(10)
01-C11-N1	120.3(10)	C23-C24-C15	123.8(11)
O1-C11-C10	122.0(10)	C19-C24-C15	118.3(10)
N1-C11-C10	117.7(10)	N1-C25-C26	111.8(10)
C2-C12-C10	122.1(10)	N1-C25-H25A	109.2
C2-C12-C6	118.0(11)	С26-С25-Н25А	109.2
C10-C12-C6	119.9(10)	N1-C25-H25B	109.2
C14-C13-C7	178.6(12)	С26-С25-Н25В	109.2
C13-C14-C15	178.7(13)	H25A-C25-H25B	107.9
C16-C15-C14	120.7(11)	C25-C26-C27	113.1(10)
C16-C15-C24	120.5(11)	С25-С26-Н26А	109.0
C14-C15-C24	118.8(11)	С27-С26-Н26А	109.0
C15-C16-C17	121.5(11)	С25-С26-Н26В	109.0
С15-С16-Н16	119.2	С27-С26-Н26В	109.0
С17-С16-Н16	119.2	H26A-C26-H26B	107.8
C18-C17-C16	118.0(11)	C28-C27-C26	111.4(10)
С18-С17-Н17	121.0	С28-С27-Н27А	109.3
С16-С17-Н17	121.0	С26-С27-Н27А	109.3
C17-C18-O3	122.0(10)	С28-С27-Н27В	109.3
C17-C18-C19	124.1(10)	С26-С27-Н27В	109.3
O3-C18-C19	113.9(9)	H27A-C27-H27B	108.0
C20-C19-C18	124.8(11)	C27-C28-C29	114.8(10)
C20-C19-C24	117.5(11)	С27-С28-Н28А	108.6
C18-C19-C24	117.7(10)	С29-С28-Н28А	108.6
C21-C20-C19	123.1(12)	С27-С28-Н28В	108.6
С21-С20-Н20	118.5	С29-С28-Н28В	108.6
С19-С20-Н20	118.5	H28A-C28-H28B	107.5

C30-C29-C28	111.7(10)	C36-C35-C34	112.5(11)
С30-С29-Н29А	109.3	С36-С35-Н35А	109.1
С28-С29-Н29А	109.3	С34-С35-Н35А	109.1
С30-С29-Н29В	109.3	С36-С35-Н35В	109.1
С28-С29-Н29В	109.3	C34-C35-H35B	109.1
H29A-C29-H29B	107.9	H35A-C35-H35B	107.8
C31-C30-C29	113.9(10)	С35-С36-Н36А	109.5
С31-С30-Н30А	108.8	С35-С36-Н36В	109.5
С29-С30-Н30А	108.8	H36A-C36-H36B	109.5
С31-С30-Н30В	108.8	С35-С36-Н36С	109.5
С29-С30-Н30В	108.8	H36A-C36-H36C	109.5
H30A-C30-H30B	107.7	H36B-C36-H36C	109.5
C30-C31-C32	112.3(10)	O3-C37-C38	107.4(9)
С30-С31-Н31А	109.2	O3-C37-H37A	110.2
С32-С31-Н31А	109.2	С38-С37-Н37А	110.2
С30-С31-Н31В	109.2	ОЗ-С37-Н37В	110.2
С32-С31-Н31В	109.2	С38-С37-Н37В	110.2
H31A-C31-H31B	107.9	H37A-C37-H37B	108.5
C33-C32-C31	114.2(11)	C37-C38-C39	113.0(10)
С33-С32-Н32А	108.7	С37-С38-Н38А	109.0
С31-С32-Н32А	108.7	С39-С38-Н38А	109.0
С33-С32-Н32В	108.7	С37-С38-Н38В	109.0
С31-С32-Н32В	108.7	С39-С38-Н38В	109.0
H32A-C32-H32B	107.6	H38A-C38-H38B	107.8
C32-C33-C34	112.9(11)	C38-C39-C40	114.3(10)
С32-С33-Н33А	109.0	С38-С39-Н39А	108.7
С34-С33-Н33А	109.0	С40-С39-Н39А	108.7
С32-С33-Н33В	109.0	С38-С39-Н39В	108.7
С34-С33-Н33В	109.0	С40-С39-Н39В	108.7
H33A-C33-H33B	107.8	H39A-C39-H39B	107.6
C35-C34-C33	114.3(10)	C39-C40-C41	112.6(10)
С35-С34-Н34А	108.7	С39-С40-Н40А	109.1
С33-С34-Н34А	108.7	С41-С40-Н40А	109.1
С35-С34-Н34В	108.7	С39-С40-Н40В	109.1
С33-С34-Н34В	108.7	С41-С40-Н40В	109.1
H34A-C34-H34B	107.6	H40A-C40-H40B	107.8

C42-C41-C40	114.0(10)	C46-C45-H45A	108.5
C42-C41-H41A	108.8	C44-C45-H45B	108.5
C40-C41-H41A	108.8	C46-C45-H45B	108.5
C42-C41-H41B	108.8	H45A-C45-H45B	107.5
C40-C41-H41B	108.8	C45-C46-C47	113.7(10)
H41A-C41-H41B	107.7	С45-С46-Н46А	108.8
C43-C42-C41	113.5(10)	С47-С46-Н46А	108.8
C43-C42-H42A	108.9	С45-С46-Н46В	108.8
C41-C42-H42A	108.9	С47-С46-Н46В	108.8
C43-C42-H42B	108.9	H46A-C46-H46B	107.7
C41-C42-H42B	108.9	C48-C47-C46	113.7(11)
H42A-C42-H42B	107.7	С48-С47-Н47А	108.8
C44-C43-C42	114.7(10)	С46-С47-Н47А	108.8
C44-C43-H43A	108.6	С48-С47-Н47В	108.8
С42-С43-Н43А	108.6	С46-С47-Н47В	108.8
С44-С43-Н43В	108.6	H47A-C47-H47B	107.7
С42-С43-Н43В	108.6	C47-C48-H48A	109.5
H43A-C43-H43B	107.6	C47-C48-H48B	109.5
C45-C44-C43	114.2(10)	H48A-C48-H48B	109.5
C45-C44-H44A	108.7	С47-С48-Н48С	109.5
C43-C44-H44A	108.7	H48A-C48-H48C	109.5
C45-C44-H44B	108.7	H48B-C48-H48C	109.5
C43-C44-H44B	108.7	C11-N1-C1	124.0(10)
H44A-C44-H44B	107.6	C11-N1-C25	118.6(9)
C44-C45-C46	115.3(10)	C1-N1-C25	117.1(9)
C44-C45-H45A	108.5	C18-O3-C37	118.6(9)

	$U^{11}$	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	26(6)	34(7)	30(7)	3(6)	-9(5)	-5(5)
C2	40(7)	18(6)	21(6)	-2(5)	4(5)	0(5)
C3	34(7)	25(6)	24(6)	7(5)	0(5)	4(5)
C4	52(8)	29(7)	27(7)	5(6)	10(6)	3(6)
C5	45(7)	26(6)	21(6)	-10(5)	8(5)	-1(5)
C6	27(6)	21(6)	37(7)	6(5)	-5(5)	-4(5)
C7	44(7)	16(6)	22(6)	-4(5)	0(5)	-3(5)
C8	42(7)	23(6)	29(7)	11(5)	-5(5)	8(5)
C9	36(7)	40(7)	35(7)	5(6)	6(6)	-1(6)
C10	37(7)	16(6)	20(6)	6(5)	4(5)	6(5)
C11	33(7)	29(7)	24(7)	-8(6)	-2(5)	-1(5)
C12	32(6)	17(6)	23(6)	12(5)	11(5)	-4(5)
C13	32(7)	24(6)	32(7)	6(5)	8(5)	-8(5)
C14	34(6)	18(6)	28(7)	5(5)	6(5)	0(5)
C15	34(7)	28(6)	29(7)	0(5)	-3(5)	4(5)
C16	31(7)	27(6)	33(7)	0(5)	-3(5)	-4(5)
C17	35(7)	21(6)	29(7)	-10(5)	7(5)	1(5)
C18	35(7)	20(6)	26(7)	4(5)	-7(5)	5(5)
C19	34(7)	20(6)	28(7)	2(5)	5(5)	8(5)
C20	38(7)	29(6)	34(7)	3(6)	-2(6)	2(5)
C21	38(7)	36(7)	32(7)	-5(6)	-4(5)	3(5)
C22	44(7)	37(7)	28(7)	1(6)	7(6)	-3(6)
C23	42(7)	27(6)	30(7)	-1(5)	4(6)	3(5)
C24	27(6)	29(6)	27(7)	1(5)	1(5)	-3(5)
C25	37(7)	13(6)	36(7)	-4(5)	5(5)	7(5)
C26	41(7)	22(6)	37(7)	-3(5)	3(5)	2(5)
C27	50(7)	22(6)	33(7)	3(5)	5(6)	-3(5)
C28	42(7)	31(7)	42(7)	6(6)	7(6)	4(5)
C29	43(7)	28(6)	35(7)	2(5)	-4(5)	2(5)
C30	54(7)	21(6)	28(7)	3(5)	2(6)	-4(5)
C31	53(8)	24(6)	33(7)	4(5)	-1(6)	0(5)

Table **120**.4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **120**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	49(7)	32(7)	35(7)	1(6)	0(6)	4(5)
C33	58(8)	17(6)	34(7)	3(5)	0(6)	3(5)
C34	46(7)	25(6)	34(7)	6(5)	4(6)	2(5)
C35	62(8)	25(7)	46(7)	-2(6)	5(6)	1(6)
C36	65(10)	27(7)	66(9)	4(7)	0(7)	-5(7)
C37	45(7)	31(7)	32(7)	-6(6)	14(6)	2(5)
C38	50(7)	27(6)	40(7)	-5(6)	1(6)	-3(6)
C39	44(7)	23(6)	36(7)	-4(5)	9(5)	12(5)
C40	42(7)	16(6)	40(7)	-6(5)	2(6)	3(5)
C41	47(7)	18(6)	39(7)	-1(5)	1(6)	6(5)
C42	53(7)	19(6)	30(7)	4(5)	7(6)	5(5)
C43	52(7)	21(6)	32(7)	1(5)	-6(5)	3(5)
C44	50(7)	24(6)	34(7)	3(5)	3(6)	3(5)
C45	42(7)	24(6)	34(7)	3(5)	0(5)	5(5)
C46	52(7)	23(6)	31(7)	5(5)	14(6)	9(5)
C47	60(8)	21(6)	40(7)	6(5)	9(6)	4(6)
C48	78(10)	28(8)	47(9)	3(6)	7(7)	5(7)
N1	36(5)	24(5)	18(5)	3(4)	1(4)	9(4)
01	54(5)	31(5)	30(5)	-1(4)	-2(4)	18(4)
02	60(6)	43(5)	35(5)	-4(4)	-6(4)	13(5)
O3	57(5)	25(4)	30(5)	1(4)	8(4)	6(4)
	х	у	Z	U(eq)		
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H3	-3373	5469	2943	33		
H4	-112	5164	2543	43		
H5	2727	4951	3600	36		
H8	4330	4995	6634	38		
H9	1023	5298	7006	44		
H16	8189	4538	3389	37		
H17	11566	4238	2996	34		
H20	15444	3916	5646	41		
H21	15042	3992	7069	43		
H22	11730	4286	7458	43		
H23	9008	4509	6413	40		
H25A	-6858	5857	6174	34		
H25B	-7913	5897	5166	34		
H26A	-3897	6159	5058	40		
H26B	-3032	6128	6080	40		
H27A	-8323	6350	5353	42		
H27B	-7338	6328	6372	42		
H28A	-4265	6607	5206	46		
H28B	-3397	6590	6230	46		
H29A	-8593	6822	5466	43		
H29B	-7602	6812	6488	43		
H30A	-3538	7060	6293	41		
H30B	-4406	7062	5266	41		
H31A	-7706	7293	6501	45		
H31B	-8635	7292	5476	45		
H32A	-3534	7528	6285	47		
H32B	-4416	7524	5259	47		
H33A	-7645	7770	6472	44		
H33B	-8539	7766	5446	44		
H34A	-3377	7993	6247	42		

Table **120**.5. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **120**.

H34B	-4295	7990	5224	42
H35A	-8348	8244	5424	53
H35B	-7410	8247	6448	53
H36A	-3093	8459	6195	80
H36B	-5884	8615	5839	80
H36C	-4144	8463	5177	80
H37A	16083	4038	2927	42
H37B	13217	3872	2820	42
H38A	18620	3687	3595	47
H38B	17609	3651	2583	47
H39A	13522	3425	2958	41
H39B	14723	3449	3960	41
H40A	18709	3200	3748	39
H40B	17775	3191	2724	39
H41A	14508	2973	3998	42
H41B	13537	2966	2977	42
H42A	17660	2721	2777	41
H42B	18524	2722	3804	41
H43A	14270	2501	4007	43
H43B	13366	2503	2982	43
H44A	17354	2248	2775	43
H44B	18277	2247	3798	43
H45A	13044	2037	3007	40
H45B	14054	2031	4025	40
H46A	17961	1769	3766	42
H46B	16934	1775	2748	42
H47A	13660	1560	4024	48
H47B	12584	1569	3009	48
H48A	16355	1302	2718	76
H48B	14450	1176	3398	76
H48C	17499	1297	3729	76

O2-C1-C2-C3 -2.3(17)C7-C6-C12-C10 1.3(15)N1-C1-C2-C3 175.9(9) C14-C15-C16-C17 -179.3(10)O2-C1-C2-C12 C24-C15-C16-C17 179.8(11) -1.3(17)N1-C1-C2-C12 -1.9(16) C15-C16-C17-C18 2.0(16) C12-C2-C3-C4 C16-C17-C18-O3 -2.8(17)176.6(9) C16-C17-C18-C19 C1-C2-C3-C4 179.4(11) -1.6(17)C2-C3-C4-C5 2.2(17)C17-C18-C19-C20 -177.9(11)C3-C4-C5-C6 -2.5(17)O3-C18-C19-C20 3.8(16) C4-C5-C6-C7 179.5(11) C17-C18-C19-C24 0.6(17)C4-C5-C6-C12 3.1(16) O3-C18-C19-C24 -177.8(9)C5-C6-C7-C8 -179.0(11)C18-C19-C20-C21 178.4(12) C12-C6-C7-C8 -2.6(15)C24-C19-C20-C21 -0.1(17)C5-C6-C7-C13 4.1(16) C19-C20-C21-C22 1.3(18) C12-C6-C7-C13 -179.5(10)C20-C21-C22-C23 -1.3(18)C13-C7-C8-C9 179.6(11) C21-C22-C23-C24 0.0(18)C6-C7-C8-C9 C22-C23-C24-C19 2.7(17)1.3(17)C7-C8-C9-C10 -1.5(18)C22-C23-C24-C15 -178.7(11)C8-C9-C10-C12 C20-C19-C24-C23 0.2(17)-1.2(16)C8-C9-C10-C11 -179.3(10)C18-C19-C24-C23 -179.8(10)C9-C10-C11-O1 1.7(17) C20-C19-C24-C15 178.7(10) C12-C10-C11-O1 -177.9(10)C18-C19-C24-C15 0.2(16)C9-C10-C11-N1 -179.7(10)C16-C15-C24-C23 -179.8(11)C12-C10-C11-N1 0.8(15) C14-C15-C24-C23 -1.8(17)C3-C2-C12-C10 -178.0(11)C16-C15-C24-C19 0.2(17)C1-C2-C12-C10 C14-C15-C24-C19 -0.3(16)178.2(10) C3-C2-C12-C6 3.4(16) N1-C25-C26-C27 176.2(9) C1-C2-C12-C6 -178.8(10)C25-C26-C27-C28 -177.4(10)C9-C10-C12-C2 -178.7(12)C26-C27-C28-C29 177.7(9) C11-C10-C12-C2 0.9(15) C27-C28-C29-C30 -177.5(10)C9-C10-C12-C6 -0.2(16) C28-C29-C30-C31 177.5(9) C11-C10-C12-C6 179.4(10) C29-C30-C31-C32 -178.8(9) C5-C6-C12-C2 -3.5(15)C30-C31-C32-C33 179.0(9) C7-C6-C12-C2 179.9(10) C31-C32-C33-C34 -179.8(10)

Table **120**.6. Torsion angles [°] for **120**.

C5-C6-C12-C10

C32-C33-C34-C35

-179.5(10)

177.9(9)

C33-C34-C35-C36	-179.6(10)
O3-C37-C38-C39	71.0(13)
C37-C38-C39-C40	176.1(10)
C38-C39-C40-C41	-174.4(10)
C39-C40-C41-C42	179.2(10)
C40-C41-C42-C43	-177.8(10)
C41-C42-C43-C44	179.1(10)
C42-C43-C44-C45	179.6(10)
C43-C44-C45-C46	178.1(9)
C44-C45-C46-C47	179.7(10)
C45-C46-C47-C48	178.9(10)
01-C11-N1-C1	175.5(11)
C10-C11-N1-C1	-3.1(15)
01-C11-N1-C25	2.5(16)
C10-C11-N1-C25	-176.2(10)
O2-C1-N1-C11	-177.9(10)
C2-C1-N1-C11	3.7(16)
O2-C1-N1-C25	-4.8(16)
C2-C1-N1-C25	176.9(9)
C26-C25-N1-C11	87.8(12)
C26-C25-N1-C1	-85.8(12)
C17-C18-O3-C37	2.6(16)
C19-C18-O3-C37	-179.0(10)
C38-C37-O3-C18	-173.5(9)

End crystallographic info for 120.

## **CRYSTALLOGRAPHIC MATERIAL FOR M6N8**

Crystallographic Material for M6N8.

X-ray Experimental.

Table M6N8.1. Crystallographic Data for M6N8.

Table M6N8.2. Fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for the non-hydrogen atoms of M6N8.

Table M6N8.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of M6N8.

Table M6N8.4. Anisotropic thermal parameters for the non-hydrogen atoms of M6N8.

Table M6N8.5. Fractional coordinates and isotropic thermal parameters ( $Å^2$ ) for the hydrogen atoms of M6N8.

Table M6N8.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of M6N8.

X-ray Experimental for complex  $C_{38}H_{41}NO_3$  (**M6N8**): Crystals grew as long, yellow laths by vapor diffusion (xylenes, ethanol). The data crystal was cut from a larger crystal and had approximate dimensions; 0.36 x 0.14 x 0.04 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda$ = 1.5418Å) with collimating mirror monochromators. A total of 974 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 12.5 seconds per frame with a detector offset of +/- 39.8° and 45 seconds per frame with a detector offset of +/- 112.0°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.39.46.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1211*P)^2]$ and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.333, with R(F) equal to 0.1078 and a goodness of fit, S, = 1.04. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.39.46.
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  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
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Empirical formula	C38 H41 N O3		
Formula weight	559.72		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	triclinic		
Space group	P -1		
Unit cell dimensions	a = 10.7618(17) Å	α= 85.568(9)°.	
	b = 10.7781(11) Å	β= 85.579(12)°.	
	c = 26.506(3)  Å	$\gamma = 87.082(11)^{\circ}.$	
Volume	3053.1(7) Å <sup>3</sup>		
Ζ	4		
Density (calculated)	1.218 Mg/m <sup>3</sup>		
Absorption coefficient	0.593 mm <sup>-1</sup>		
F(000)	1200		
Crystal size	0.360 x 0.140 x 0.044 mm <sup>3</sup>		
Theta range for data collection	3.354 to 68.202°.		
Index ranges	-9<=h<=12, -12<=k<=12, -31<=l<=31		
Reflections collected	15978		
Independent reflections	10441 [R(int) = 0.0729]		
Completeness to theta = $67.684^{\circ}$	93.9 %		
Absorption correction	Semi-empirical from equivalent	its	
Max. and min. transmission	1.00 and 0.360		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	10441 / 0 / 761		
Goodness-of-fit on F <sup>2</sup>	1.042		
Final R indices [I>2sigma(I)]	R1 = 0.1074, wR2 = 0.2601		
R indices (all data)	R1 = 0.1840, wR2 = 0.3333		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.488 and -0.340 e.Å <sup>-3</sup>		

Table M6N8.1. Crystal data and structure refinement for M6N8.

	Х	у	Z	U(eq)
C1	2879(5)	4055(5)	7274(2)	29(1)
C2	2466(4)	3939(4)	6757(2)	23(1)
C3	1895(4)	2851(4)	6664(2)	26(1)
C4	1515(4)	2721(4)	6176(2)	26(1)
C5	1680(4)	3623(4)	5789(2)	26(1)
C6	2260(4)	4761(4)	5873(2)	23(1)
C7	2496(4)	5710(5)	5493(2)	27(1)
C8	3073(4)	6770(4)	5592(2)	26(1)
С9	3408(4)	6909(5)	6090(2)	28(1)
C10	3216(4)	5990(4)	6469(2)	23(1)
C11	3602(4)	6165(5)	6979(2)	28(1)
C12	2646(4)	4884(4)	6371(2)	22(1)
C13	1290(4)	3486(4)	5296(2)	25(1)
C14	994(4)	3486(4)	4860(2)	24(1)
C15	734(4)	3583(4)	4341(2)	25(1)
C16	1032(4)	4664(5)	4040(2)	27(1)
C17	809(4)	4830(4)	3530(2)	26(1)
C18	230(4)	3931(4)	3301(2)	26(1)
C19	-100(4)	2798(4)	3593(2)	24(1)
C20	-693(4)	1854(5)	3368(2)	26(1)
C21	-1006(4)	764(5)	3653(2)	27(1)
C22	-770(4)	598(4)	4169(2)	27(1)
C23	-189(4)	1504(4)	4385(2)	26(1)
C24	153(4)	2628(4)	4115(2)	23(1)
C25	3855(5)	5307(5)	7851(2)	32(1)
C26	5123(5)	4638(5)	7907(2)	37(1)
C27	5573(5)	4731(6)	8440(2)	40(1)
C28	6561(5)	3755(5)	8587(2)	38(1)
C29	6914(5)	3843(5)	9134(2)	41(1)
C30	7889(5)	2837(6)	9308(2)	44(1)
C31	7448(6)	1524(6)	9306(3)	49(2)

Table **M6N8**.2. Atomic coordinates ( $x \ 10^4$ ) and equivalent isotropic displacement parameters ( $\mathring{A}^2x \ 10^3$ ) for **M6N8**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	8336(6)	541(7)	9546(3)	58(2)
C33	359(5)	5098(5)	2494(2)	31(1)
C34	-55(5)	5002(5)	1972(2)	35(1)
C35	617(5)	3988(5)	1677(2)	38(1)
C36	74(5)	3853(6)	1171(2)	42(1)
C37	763(5)	2929(6)	841(2)	42(1)
C38	66(6)	2718(7)	378(3)	52(2)
C39	7863(4)	9018(5)	7291(2)	28(1)
C40	7452(4)	8904(5)	6776(2)	25(1)
C41	6870(4)	7847(4)	6672(2)	28(1)
C42	6496(4)	7726(4)	6183(2)	26(1)
C43	6675(4)	8628(4)	5793(2)	24(1)
C44	7286(4)	9749(4)	5889(2)	21(1)
C45	7517(4)	10720(4)	5509(2)	26(1)
C46	8110(4)	11754(4)	5615(2)	25(1)
C47	8439(4)	11887(5)	6111(2)	27(1)
C48	8229(4)	10959(4)	6488(2)	24(1)
C49	8624(4)	11115(5)	7002(2)	28(1)
C50	7648(4)	9870(4)	6388(2)	24(1)
C51	6292(4)	8503(4)	5301(2)	24(1)
C52	5995(4)	8493(4)	4867(2)	24(1)
C53	5729(4)	8564(4)	4346(2)	25(1)
C54	6027(4)	9630(5)	4039(2)	25(1)
C55	5795(4)	9779(4)	3526(2)	27(1)
C56	5208(4)	8876(4)	3311(2)	25(1)
C57	4885(4)	7745(4)	3608(2)	24(1)
C58	4304(4)	6793(4)	3389(2)	27(1)
C59	3989(4)	5716(5)	3677(2)	27(1)
C60	4252(4)	5569(4)	4193(2)	25(1)
C61	4813(4)	6476(5)	4409(2)	28(1)
C62	5144(4)	7607(4)	4122(2)	24(1)
C63	8938(5)	10227(5)	7864(2)	34(1)
C64	10308(5)	9717(5)	7856(2)	37(1)
C65	10918(5)	9887(6)	8346(2)	39(1)
C66	11089(5)	11222(6)	8457(2)	40(1)
C67	11919(5)	11330(6)	8896(2)	41(1)

C68	12025(5)	12666(6)	9030(2)	43(1)
C69	12940(6)	12794(6)	9433(3)	50(2)
C70	12929(6)	14113(7)	9610(3)	54(2)
C71	5300(4)	9983(5)	2492(2)	30(1)
C72	4843(5)	9855(5)	1976(2)	32(1)
C73	5045(5)	11002(5)	1613(2)	37(1)
C74	4604(6)	10889(7)	1096(2)	50(2)
C75	4751(7)	12035(7)	738(3)	56(2)
C76	6061(8)	12460(8)	628(3)	72(2)
N1	3416(4)	5192(4)	7349(2)	26(1)
N2	8430(4)	10136(4)	7366(2)	28(1)
O1	2761(3)	3257(3)	7616(1)	34(1)
O2	4079(3)	7111(4)	7080(2)	38(1)
O3	-41(3)	4002(3)	2814(1)	29(1)
O4	7723(3)	8218(3)	7628(1)	34(1)
O5	9119(4)	12044(4)	7104(2)	40(1)
O6	4910(3)	8924(3)	2823(1)	29(1)

C1-O1	1.204(7)	C19-C24	1.426(7)
C1-N1	1.415(6)	C20-C21	1.388(7)
C1-C2	1.489(7)	C20-H20	0.95
C2-C12	1.397(7)	C21-C22	1.408(7)
C2-C3	1.399(6)	C21-H21	0.95
C3-C4	1.404(7)	C22-C23	1.369(6)
С3-Н3	0.95	C22-H22	0.95
C4-C5	1.366(8)	C23-C24	1.410(7)
С4-Н4	0.95	С23-Н23	0.95
C5-C13	1.423(7)	C25-N1	1.463(6)
C5-C6	1.445(6)	C25-C26	1.522(8)
C6-C7	1.398(7)	C25-H25A	0.9900
C6-C12	1.429(7)	C25-H25B	0.9900
C7-C8	1.379(6)	C26-C27	1.541(7)
С7-Н7	0.95	C26-H26A	0.9900
C8-C9	1.416(7)	C26-H26B	0.9900
С8-Н8	0.95	C27-C28	1.508(8)
C9-C10	1.367(7)	C27-H27A	0.9900
С9-Н9	0.95	С27-Н27В	0.9900
C10-C12	1.418(6)	C28-C29	1.538(8)
C10-C11	1.472(7)	C28-H28A	0.9900
C11-O2	1.222(6)	C28-H28B	0.9900
C11-N1	1.390(7)	C29-C30	1.539(9)
C13-C14	1.223(7)	С29-Н29А	0.9900
C14-C15	1.419(7)	C29-H29B	0.9900
C15-C16	1.397(7)	C30-C31	1.516(9)
C15-C24	1.424(6)	C30-H30A	0.9900
C16-C17	1.388(7)	C30-H30B	0.9900
C16-H16	0.95	C31-C32	1.524(10)
C17-C18	1.380(6)	C31-H31A	0.9900
C17-H17	0.95	C31-H31B	0.9900
C18-O3	1.342(6)	C32-H32A	0.98
C18-C19	1.439(7)	C32-H32B	0.98
C19-C20	1.419(6)	C32-H32C	0.98

Table M6N8.3. Bond lengths [Å] and angles [°] for M6N8.

C33-O3	1.463(6)	C47-C48	1.371(7)
C33-C34	1.500(7)	C47-H47	0.95
С33-Н33А	0.9900	C48-C50	1.409(6)
С33-Н33В	0.9900	C48-C49	1.484(7)
C34-C35	1.513(7)	C49-O5	1.216(6)
C34-H34A	0.9900	C49-N2	1.387(7)
C34-H34B	0.9900	C51-C52	1.219(7)
C35-C36	1.525(8)	C52-C53	1.428(7)
C35-H35A	0.9900	C53-C54	1.392(7)
С35-Н35В	0.9900	C53-C62	1.423(6)
C36-C37	1.505(8)	C54-C55	1.395(7)
C36-H36A	0.9900	C54-H54	0.95
С36-Н36В	0.9900	C55-C56	1.369(6)
C37-C38	1.524(8)	С55-Н55	0.95
С37-Н37А	0.9900	C56-O6	1.355(6)
С37-Н37В	0.9900	C56-C57	1.442(7)
C38-H38A	0.98	C57-C62	1.408(7)
C38-H38B	0.98	C57-C58	1.412(6)
C38-H38C	0.98	C58-C59	1.382(7)
C39-O4	1.200(7)	C58-H58	0.95
C39-N2	1.413(6)	C59-C60	1.412(7)
C39-C40	1.482(7)	С59-Н59	0.95
C40-C41	1.384(6)	C60-C61	1.359(6)
C40-C50	1.417(7)	С60-Н60	0.95
C41-C42	1.405(7)	C61-C62	1.432(7)
C41-H41	0.95	С61-Н61	0.95
C42-C43	1.372(7)	C63-N2	1.479(6)
C42-H42	0.95	C63-C64	1.545(7)
C43-C51	1.415(7)	C63-H63A	0.9900
C43-C44	1.453(6)	C63-H63B	0.9900
C44-C45	1.414(7)	C64-C65	1.527(7)
C44-C50	1.425(7)	C64-H64A	0.9900
C45-C46	1.369(7)	C64-H64B	0.9900
C45-H45	0.95	C65-C66	1.513(8)
C46-C47	1.409(7)	C65-H65A	0.9900
С46-Н46	0.95	C65-H65B	0.9900

C66-C67	1.537(8)	C71-H71A	0.9900
С66-Н66А	0.9900	C71-H71B	0.9900
С66-Н66В	0.9900	C72-C73	1.520(8)
C67-C68	1.521(8)	С72-Н72А	0.9900
С67-Н67А	0.9900	С72-Н72В	0.9900
С67-Н67В	0.9900	C73-C74	1.500(8)
C68-C69	1.527(8)	С73-Н73А	0.9900
C68-H68A	0.9900	С73-Н73В	0.9900
C68-H68B	0.9900	C74-C75	1.506(10)
C69-C70	1.531(9)	C74-H74A	0.9900
С69-Н69А	0.9900	C74-H74B	0.9900
С69-Н69В	0.9900	C75-C76	1.505(10)
С70-Н70А	0.98	С75-Н75А	0.9900
С70-Н70В	0.98	С75-Н75В	0.9900
С70-Н70С	0.98	С76-Н76А	0.98
C71-O6	1.444(6)	С76-Н76В	0.98
C71-C72	1.506(7)	С76-Н76С	0.98
01-C1-N1	120.7(5)	C8-C7-C6	121.1(5)
O1-C1-C2	123.6(5)	С8-С7-Н7	119.4
N1-C1-C2	115.7(4)	С6-С7-Н7	119.4
C12-C2-C3	120.3(4)	C7-C8-C9	119.3(5)
C12-C2-C1	121.4(4)	С7-С8-Н8	120.3
C3-C2-C1	118.4(4)	С9-С8-Н8	120.3
C2-C3-C4	119.0(4)	C10-C9-C8	121.1(4)
С2-С3-Н3	120.5	С10-С9-Н9	119.4
С4-С3-Н3	120.5	С8-С9-Н9	119.4
C5-C4-C3	122.3(4)	C9-C10-C12	120.1(4)
С5-С4-Н4	118.9	C9-C10-C11	119.2(4)
С3-С4-Н4	118.9	C12-C10-C11	120.6(4)
C4-C5-C13	122.0(4)	O2-C11-N1	120.2(5)
C4-C5-C6	120.1(5)	O2-C11-C10	122.6(5)
C13-C5-C6	117.9(5)	N1-C11-C10	117.2(4)
C7-C6-C12	119.3(4)	C2-C12-C10	120.0(4)
C7-C6-C5	123.5(5)	C2-C12-C6	121.1(4)
C12-C6-C5	117.2(4)	C10-C12-C6	118.9(4)

C14-C13-C5	173.6(5)	C26-C25-H25B	109.3
C13-C14-C15	174.3(4)	H25A-C25-H25B	108.0
C16-C15-C14	119.2(4)	C25-C26-C27	111.6(5)
C16-C15-C24	118.2(5)	C25-C26-H26A	109.3
C14-C15-C24	122.5(4)	C27-C26-H26A	109.3
C17-C16-C15	122.7(4)	C25-C26-H26B	109.3
С17-С16-Н16	118.6	C27-C26-H26B	109.3
С15-С16-Н16	118.6	H26A-C26-H26B	108.0
C18-C17-C16	120.4(4)	C28-C27-C26	114.4(5)
С18-С17-Н17	119.8	С28-С27-Н27А	108.7
С16-С17-Н17	119.8	С26-С27-Н27А	108.7
O3-C18-C17	125.3(4)	С28-С27-Н27В	108.7
O3-C18-C19	115.3(4)	С26-С27-Н27В	108.7
C17-C18-C19	119.3(5)	H27A-C27-H27B	107.6
C20-C19-C24	119.6(4)	C27-C28-C29	112.0(5)
C20-C19-C18	120.7(5)	C27-C28-H28A	109.2
C24-C19-C18	119.8(4)	C29-C28-H28A	109.2
C21-C20-C19	120.2(5)	C27-C28-H28B	109.2
С21-С20-Н20	119.9	C29-C28-H28B	109.2
С19-С20-Н20	119.9	H28A-C28-H28B	107.9
C20-C21-C22	120.4(4)	C28-C29-C30	114.0(5)
С20-С21-Н21	119.8	С28-С29-Н29А	108.8
C22-C21-H21	119.8	С30-С29-Н29А	108.8
C23-C22-C21	119.4(4)	С28-С29-Н29В	108.8
С23-С22-Н22	120.3	С30-С29-Н29В	108.8
С21-С22-Н22	120.3	H29A-C29-H29B	107.7
C22-C23-C24	122.6(5)	C31-C30-C29	113.2(5)
С22-С23-Н23	118.7	С31-С30-Н30А	108.9
С24-С23-Н23	118.7	С29-С30-Н30А	108.9
C23-C24-C15	122.8(5)	С31-С30-Н30В	108.9
C23-C24-C19	117.7(4)	С29-С30-Н30В	108.9
C15-C24-C19	119.5(4)	H30A-C30-H30B	107.8
N1-C25-C26	111.5(4)	C30-C31-C32	113.1(5)
N1-C25-H25A	109.3	C30-C31-H31A	109.0
С26-С25-Н25А	109.3	С32-С31-Н31А	109.0
N1-C25-H25B	109.3	C30-C31-H31B	109.0

С32-С31-Н31В	109.0	С38-С37-Н37В	109.2
H31A-C31-H31B	107.8	H37A-C37-H37B	107.9
C31-C32-H32A	109.5	C37-C38-H38A	109.5
C31-C32-H32B	109.5	C37-C38-H38B	109.5
H32A-C32-H32B	109.5	H38A-C38-H38B	109.5
C31-C32-H32C	109.5	С37-С38-Н38С	109.5
H32A-C32-H32C	109.5	H38A-C38-H38C	109.5
H32B-C32-H32C	109.5	H38B-C38-H38C	109.5
O3-C33-C34	108.4(4)	O4-C39-N2	121.2(5)
O3-C33-H33A	110.0	O4-C39-C40	122.7(4)
С34-С33-Н33А	110.0	N2-C39-C40	116.1(4)
О3-С33-Н33В	110.0	C41-C40-C50	119.6(4)
С34-С33-Н33В	110.0	C41-C40-C39	119.8(5)
H33A-C33-H33B	108.4	C50-C40-C39	120.6(4)
C33-C34-C35	115.2(5)	C40-C41-C42	120.0(5)
С33-С34-Н34А	108.5	C40-C41-H41	120.0
С35-С34-Н34А	108.5	C42-C41-H41	120.0
С33-С34-Н34В	108.5	C43-C42-C41	122.7(4)
С35-С34-Н34В	108.5	C43-C42-H42	118.7
H34A-C34-H34B	107.5	C41-C42-H42	118.7
C34-C35-C36	112.8(5)	C42-C43-C51	122.4(4)
С34-С35-Н35А	109.0	C42-C43-C44	118.7(4)
С36-С35-Н35А	109.0	C51-C43-C44	118.9(4)
С34-С35-Н35В	109.0	C45-C44-C50	119.3(4)
С36-С35-Н35В	109.0	C45-C44-C43	122.5(4)
H35A-C35-H35B	107.8	C50-C44-C43	118.2(4)
C37-C36-C35	115.4(5)	C46-C45-C44	120.5(5)
С37-С36-Н36А	108.4	C46-C45-H45	119.8
С35-С36-Н36А	108.4	С44-С45-Н45	119.8
С37-С36-Н36В	108.4	C45-C46-C47	120.1(4)
С35-С36-Н36В	108.4	С45-С46-Н46	119.9
H36A-C36-H36B	107.5	С47-С46-Н46	119.9
C36-C37-C38	112.1(5)	C48-C47-C46	120.6(4)
С36-С37-Н37А	109.2	С48-С47-Н47	119.7
С38-С37-Н37А	109.2	С46-С47-Н47	119.7
С36-С37-Н37В	109.2	C47-C48-C50	120.6(5)

C47-C48-C49	119.1(4)	С62-С61-Н61	119.5
C50-C48-C49	120.3(5)	C57-C62-C53	120.6(4)
O5-C49-N2	120.6(5)	C57-C62-C61	117.9(4)
O5-C49-C48	122.3(5)	C53-C62-C61	121.5(5)
N2-C49-C48	117.1(4)	N2-C63-C64	110.7(4)
C48-C50-C40	120.4(4)	N2-C63-H63A	109.5
C48-C50-C44	118.8(5)	С64-С63-Н63А	109.5
C40-C50-C44	120.8(4)	N2-C63-H63B	109.5
C52-C51-C43	174.7(5)	С64-С63-Н63В	109.5
C51-C52-C53	174.9(4)	H63A-C63-H63B	108.1
C54-C53-C62	117.7(5)	C65-C64-C63	113.0(4)
C54-C53-C52	118.9(4)	C65-C64-H64A	109.0
C62-C53-C52	123.4(4)	C63-C64-H64A	109.0
C53-C54-C55	122.7(4)	C65-C64-H64B	109.0
С53-С54-Н54	118.7	C63-C64-H64B	109.0
С55-С54-Н54	118.7	H64A-C64-H64B	107.8
C56-C55-C54	120.0(4)	C66-C65-C64	115.6(5)
С56-С55-Н55	120.0	С66-С65-Н65А	108.4
С54-С55-Н55	120.0	С64-С65-Н65А	108.4
O6-C56-C55	125.5(4)	С66-С65-Н65В	108.4
O6-C56-C57	114.5(4)	С64-С65-Н65В	108.4
C55-C56-C57	120.0(5)	H65A-C65-H65B	107.4
C62-C57-C58	120.3(4)	C65-C66-C67	113.0(5)
C62-C57-C56	119.0(4)	С65-С66-Н66А	109.0
C58-C57-C56	120.7(5)	С67-С66-Н66А	109.0
C59-C58-C57	120.3(5)	С65-С66-Н66В	109.0
С59-С58-Н58	119.8	С67-С66-Н66В	109.0
С57-С58-Н58	119.8	H66A-C66-H66B	107.8
C58-C59-C60	119.7(4)	C68-C67-C66	113.1(5)
С58-С59-Н59	120.2	С68-С67-Н67А	109.0
С60-С59-Н59	120.2	С66-С67-Н67А	109.0
C61-C60-C59	120.7(4)	С68-С67-Н67В	109.0
С61-С60-Н60	119.6	С66-С67-Н67В	109.0
С59-С60-Н60	119.6	H67A-C67-H67B	107.8
C60-C61-C62	121.1(5)	C67-C68-C69	113.4(5)
C60-C61-H61	119.5	C67-C68-H68A	108.9

С69-С68-Н68А	108.9	С72-С73-Н73А	108.8
С67-С68-Н68В	108.9	С74-С73-Н73В	108.8
С69-С68-Н68В	108.9	С72-С73-Н73В	108.8
H68A-C68-H68B	107.7	Н73А-С73-Н73В	107.7
C68-C69-C70	113.0(6)	C73-C74-C75	114.7(5)
С68-С69-Н69А	109.0	С73-С74-Н74А	108.6
С70-С69-Н69А	109.0	С75-С74-Н74А	108.6
С68-С69-Н69В	109.0	С73-С74-Н74В	108.6
С70-С69-Н69В	109.0	С75-С74-Н74В	108.6
H69A-C69-H69B	107.8	H74A-C74-H74B	107.6
С69-С70-Н70А	109.5	C76-C75-C74	115.8(7)
С69-С70-Н70В	109.5	С76-С75-Н75А	108.3
H70A-C70-H70B	109.5	С74-С75-Н75А	108.3
С69-С70-Н70С	109.5	С76-С75-Н75В	108.3
H70A-C70-H70C	109.5	С74-С75-Н75В	108.3
Н70В-С70-Н70С	109.5	H75A-C75-H75B	107.4
O6-C71-C72	108.2(4)	С75-С76-Н76А	109.5
O6-C71-H71A	110.1	С75-С76-Н76В	109.5
С72-С71-Н71А	110.1	H76A-C76-H76B	109.5
O6-C71-H71B	110.0	С75-С76-Н76С	109.5
С72-С71-Н71В	110.0	H76A-C76-H76C	109.5
H71A-C71-H71B	108.4	H76B-C76-H76C	109.5
C71-C72-C73	113.1(4)	C11-N1-C1	125.1(4)
С71-С72-Н72А	109.0	C11-N1-C25	118.5(4)
С73-С72-Н72А	109.0	C1-N1-C25	116.3(4)
С71-С72-Н72В	109.0	C49-N2-C39	125.4(4)
С73-С72-Н72В	109.0	C49-N2-C63	117.4(4)
H72A-C72-H72B	107.8	C39-N2-C63	117.0(4)
C74-C73-C72	113.9(5)	C18-O3-C33	117.2(4)
С74-С73-Н73А	108.8	C56-O6-C71	117.5(4)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	31(3)	26(3)	31(3)	-6(2)	-3(2)	3(2)
C2	16(2)	25(2)	30(2)	-8(2)	-4(2)	2(2)
C3	26(2)	13(2)	38(3)	-1(2)	-1(2)	6(2)
C4	21(2)	16(2)	43(3)	-9(2)	-5(2)	0(2)
C5	19(2)	20(2)	40(3)	-10(2)	-5(2)	1(2)
C6	14(2)	13(2)	43(3)	-6(2)	-6(2)	7(2)
C7	22(2)	22(2)	37(3)	-11(2)	-4(2)	3(2)
C8	22(2)	16(2)	38(3)	-1(2)	-2(2)	4(2)
C9	21(2)	19(2)	44(3)	-8(2)	-9(2)	4(2)
C10	16(2)	20(2)	34(2)	-7(2)	-3(2)	7(2)
C11	26(2)	26(3)	33(3)	-6(2)	-5(2)	1(2)
C12	20(2)	13(2)	32(2)	-4(2)	-6(2)	4(2)
C13	24(2)	15(2)	38(3)	-4(2)	-6(2)	2(2)
C14	25(2)	12(2)	35(3)	-5(2)	-3(2)	-2(2)
C15	18(2)	20(2)	38(3)	-9(2)	-3(2)	4(2)
C16	26(2)	20(2)	36(3)	-12(2)	1(2)	-6(2)
C17	26(2)	15(2)	37(3)	-2(2)	-4(2)	-3(2)
C18	20(2)	20(2)	37(3)	-4(2)	-1(2)	0(2)
C19	18(2)	18(2)	35(3)	-7(2)	-2(2)	3(2)
C20	20(2)	19(2)	39(3)	-8(2)	-2(2)	7(2)
C21	20(2)	19(2)	45(3)	-10(2)	-5(2)	0(2)
C22	23(2)	15(2)	42(3)	-2(2)	-4(2)	1(2)
C23	24(2)	20(2)	35(3)	-6(2)	-4(2)	5(2)
C24	12(2)	21(2)	36(3)	-7(2)	-2(2)	5(2)
C25	33(3)	30(3)	33(3)	-7(2)	-8(2)	1(2)
C26	36(3)	34(3)	43(3)	-9(2)	-12(2)	1(2)
C27	44(3)	36(3)	43(3)	-4(2)	-9(2)	-1(2)
C28	37(3)	34(3)	44(3)	1(2)	-8(2)	-6(2)
C29	40(3)	31(3)	55(3)	-6(2)	-14(2)	-2(2)
C30	36(3)	45(4)	51(3)	-7(3)	-6(2)	0(3)
C31	60(4)	33(3)	56(4)	-2(3)	-13(3)	-2(3)

Table **M6N8.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M6N8**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	54(4)	50(4)	69(5)	0(3)	-12(3)	4(3)
C33	34(3)	19(2)	40(3)	1(2)	-2(2)	-3(2)
C34	35(3)	31(3)	38(3)	1(2)	-5(2)	1(2)
C35	32(3)	30(3)	50(3)	-3(2)	-5(2)	2(2)
C36	41(3)	39(3)	48(3)	-4(2)	-10(2)	3(2)
C37	46(3)	36(3)	44(3)	-4(2)	-7(2)	-4(2)
C38	58(4)	49(4)	51(4)	-17(3)	-5(3)	-5(3)
C39	28(2)	24(3)	35(3)	-8(2)	-4(2)	0(2)
C40	21(2)	25(2)	30(2)	-5(2)	-4(2)	-2(2)
C41	30(2)	18(2)	35(3)	-1(2)	-3(2)	3(2)
C42	21(2)	16(2)	43(3)	-10(2)	-6(2)	1(2)
C43	21(2)	15(2)	37(3)	-4(2)	-5(2)	3(2)
C44	13(2)	17(2)	34(2)	-6(2)	-10(2)	7(2)
C45	18(2)	20(2)	38(3)	-4(2)	-6(2)	8(2)
C46	21(2)	16(2)	37(3)	0(2)	-4(2)	7(2)
C47	25(2)	19(2)	38(3)	-10(2)	-4(2)	1(2)
C48	15(2)	18(2)	38(3)	-7(2)	-6(2)	4(2)
C49	27(2)	20(2)	38(3)	-7(2)	-6(2)	2(2)
C50	21(2)	18(2)	34(3)	-7(2)	-2(2)	5(2)
C51	21(2)	10(2)	43(3)	-11(2)	-7(2)	6(2)
C52	21(2)	13(2)	40(3)	-5(2)	-4(2)	-1(2)
C53	19(2)	16(2)	40(3)	-4(2)	-7(2)	6(2)
C54	17(2)	20(2)	40(3)	-11(2)	-4(2)	2(2)
C55	21(2)	17(2)	43(3)	-4(2)	-4(2)	0(2)
C56	22(2)	20(2)	33(3)	-7(2)	1(2)	3(2)
C57	19(2)	15(2)	39(3)	-5(2)	-3(2)	3(2)
C58	16(2)	18(2)	46(3)	-2(2)	-9(2)	4(2)
C59	24(2)	22(2)	36(3)	-14(2)	-4(2)	-1(2)
C60	19(2)	17(2)	40(3)	-4(2)	-2(2)	0(2)
C61	26(2)	24(2)	32(2)	-2(2)	-1(2)	0(2)
C62	18(2)	15(2)	38(3)	-6(2)	-3(2)	3(2)
C63	38(3)	34(3)	33(3)	-6(2)	-12(2)	-3(2)
C64	34(3)	35(3)	45(3)	-13(2)	-12(2)	5(2)
C65	34(3)	37(3)	49(3)	-11(2)	-13(2)	1(2)
C66	36(3)	42(3)	45(3)	-6(2)	-8(2)	-9(2)
C67	31(3)	39(3)	56(4)	-8(3)	-12(2)	-4(2)

C68	42(3)	36(3)	52(3)	-3(2)	-9(2)	-5(2)
C69	43(3)	47(4)	60(4)	-10(3)	-9(3)	-10(3)
C70	60(4)	49(4)	55(4)	-10(3)	-6(3)	-13(3)
C71	29(2)	23(2)	39(3)	-1(2)	-4(2)	-2(2)
C72	35(3)	28(3)	34(3)	-5(2)	-7(2)	4(2)
C73	28(3)	32(3)	51(3)	-3(2)	-5(2)	-4(2)
C74	57(4)	45(4)	52(4)	-7(3)	-10(3)	-11(3)
C75	69(4)	47(4)	55(4)	-11(3)	-16(3)	0(3)
C76	99(6)	60(5)	59(4)	3(4)	-12(4)	-23(4)
N1	26(2)	22(2)	33(2)	-6(2)	-2(2)	-3(2)
N2	28(2)	24(2)	34(2)	-8(2)	-5(2)	-3(2)
01	40(2)	24(2)	39(2)	0(2)	-7(2)	-2(2)
02	40(2)	29(2)	47(2)	-6(2)	-13(2)	-13(2)
03	32(2)	20(2)	37(2)	-5(1)	-5(1)	-1(1)
04	37(2)	26(2)	39(2)	1(2)	-7(2)	-5(2)
O5	46(2)	32(2)	45(2)	-8(2)	-14(2)	-15(2)
O6	31(2)	23(2)	36(2)	-3(1)	-7(1)	-2(1)

	Х	у	Z	U(eq)
Н3	1767	2209	6926	31
H4	1129	1979	6114	32
H7	2254	5624	5161	32
H8	3245	7399	5328	31
Н9	3772	7654	6162	33
H16	1404	5311	4191	32
H17	1056	5568	3337	31
H20	-877	1969	3023	31
H21	-1382	126	3498	33
H22	-1011	-136	4366	32
H23	-8	1369	4731	31
H25A	3243	4950	8114	38
H25B	3917	6199	7906	38
H26A	5739	5009	7650	45
H26B	5066	3750	7844	45
H27A	5907	5564	8456	49
H27B	4847	4659	8692	49
H28A	7314	3858	8351	45
H28B	6251	2918	8554	45
H29A	6151	3774	9366	49
H29B	7244	4673	9162	49
H30A	8661	2917	9081	53
H30B	8096	2984	9655	53
H31A	7355	1337	8952	59
H31B	6617	1477	9493	59
H32A	9153	562	9356	87
H32B	8000	-284	9537	87
H32C	8425	714	9898	87
H33A	1278	5137	2480	38
H33B	-16	5865	2637	38

Table **M6N8.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M6N8**.

H34A	63	5811	1775	42
H34B	-959	4854	2001	42
H35A	569	3186	1885	45
H35B	1509	4178	1615	45
H36A	-799	3604	1239	51
H36B	55	4679	979	51
H37A	883	2126	1043	50
H37B	1598	3236	728	50
H38A	-763	2420	489	78
H38B	533	2095	180	78
H38C	-20	3503	169	78
H41	6723	7202	6932	33
H42	6103	6990	6119	32
H45	7259	10656	5177	31
H46	8300	12382	5353	30
H47	8809	12627	6186	32
H54	6405	10282	4184	30
H55	6043	10508	3327	32
H58	4129	6893	3042	32
Н59	3597	5077	3530	32
H60	4034	4829	4391	30
H61	4988	6357	4756	33
H63A	8429	9746	8130	41
H63B	8894	11108	7948	41
H64A	10336	8819	7798	45
H64B	10794	10148	7568	45
H65A	10404	9486	8633	47
H65B	11746	9442	8331	47
H66A	10261	11629	8540	48
H66B	11466	11674	8147	48
H67A	11572	10832	9199	50
H67B	12764	10973	8803	50
H68A	11191	12997	9153	51
H68B	12296	13180	8719	51
H69A	13792	12558	9295	59
H69B	12728	12206	9730	59

H70A	13055	14711	9314	80
H70B	13601	14168	9836	80
H70C	12124	14307	9792	80
H71A	6221	10010	2466	36
H71B	4946	10764	2629	36
H72A	3942	9696	2015	39
H72B	5283	9125	1827	39
H73A	4601	11729	1763	44
H73B	5946	11163	1578	44
H74A	3712	10691	1134	61
H74B	5073	10181	943	61
H75A	4418	11873	413	67
H75B	4230	12726	881	67
H76A	6364	12738	938	108
H76B	6069	13151	365	108
H76C	6604	11768	510	108

O1-C1-C2-C12	-178.8(5)	C5-C6-C12-C10	-179.8(4)
N1-C1-C2-C12	2.2(7)	C14-C15-C16-C17	180.0(4)
01-C1-C2-C3	0.8(8)	C24-C15-C16-C17	-1.3(7)
N1-C1-C2-C3	-178.2(4)	C15-C16-C17-C18	2.4(8)
C12-C2-C3-C4	0.4(7)	C16-C17-C18-O3	179.4(5)
C1-C2-C3-C4	-179.2(4)	C16-C17-C18-C19	-2.2(7)
C2-C3-C4-C5	-0.2(7)	O3-C18-C19-C20	-1.3(7)
C3-C4-C5-C13	-179.9(4)	C17-C18-C19-C20	-179.8(4)
C3-C4-C5-C6	-0.2(7)	O3-C18-C19-C24	179.8(4)
C4-C5-C6-C7	178.0(4)	C17-C18-C19-C24	1.2(7)
C13-C5-C6-C7	-2.2(7)	C24-C19-C20-C21	-1.1(7)
C4-C5-C6-C12	0.2(7)	C18-C19-C20-C21	180.0(4)
C13-C5-C6-C12	180.0(4)	C19-C20-C21-C22	1.7(7)
C12-C6-C7-C8	-1.1(7)	C20-C21-C22-C23	-2.2(7)
C5-C6-C7-C8	-178.8(4)	C21-C22-C23-C24	2.1(7)
C6-C7-C8-C9	-1.4(7)	C22-C23-C24-C15	178.7(4)
C7-C8-C9-C10	2.8(7)	C22-C23-C24-C19	-1.4(7)
C8-C9-C10-C12	-1.5(7)	C16-C15-C24-C23	-179.8(5)
C8-C9-C10-C11	178.7(4)	C14-C15-C24-C23	-1.2(7)
C9-C10-C11-O2	0.8(7)	C16-C15-C24-C19	0.3(6)
C12-C10-C11-O2	-178.9(5)	C14-C15-C24-C19	178.9(4)
C9-C10-C11-N1	-178.4(4)	C20-C19-C24-C23	0.9(6)
C12-C10-C11-N1	1.8(7)	C18-C19-C24-C23	179.9(4)
C3-C2-C12-C10	179.5(4)	C20-C19-C24-C15	-179.2(4)
C1-C2-C12-C10	-1.0(7)	C18-C19-C24-C15	-0.2(6)
C3-C2-C12-C6	-0.3(7)	N1-C25-C26-C27	-178.6(4)
C1-C2-C12-C6	179.2(4)	C25-C26-C27-C28	159.8(5)
C9-C10-C12-C2	179.1(4)	C26-C27-C28-C29	-176.5(4)
C11-C10-C12-C2	-1.1(7)	C27-C28-C29-C30	178.1(5)
C9-C10-C12-C6	-1.1(7)	C28-C29-C30-C31	-61.5(7)
C11-C10-C12-C6	178.7(4)	C29-C30-C31-C32	-172.1(6)
C7-C6-C12-C2	-177.9(4)	O3-C33-C34-C35	-69.4(5)
C5-C6-C12-C2	0.0(6)	C33-C34-C35-C36	174.5(4)
C7-C6-C12-C10	2.3(7)	C34-C35-C36-C37	175.4(5)

Table M6N8.6. Torsion angles [°] for M6N8.

C35-C36-C37-C38	172.1(5)	C62-C53-C54-C55	-1.1(7)
O4-C39-C40-C41	0.6(8)	C52-C53-C54-C55	-179.7(4)
N2-C39-C40-C41	-179.0(4)	C53-C54-C55-C56	2.5(7)
O4-C39-C40-C50	-179.5(5)	C54-C55-C56-O6	178.6(4)
N2-C39-C40-C50	0.9(7)	C54-C55-C56-C57	-2.9(7)
C50-C40-C41-C42	1.1(7)	O6-C56-C57-C62	-179.3(4)
C39-C40-C41-C42	-179.0(4)	C55-C56-C57-C62	2.0(7)
C40-C41-C42-C43	-0.4(8)	O6-C56-C57-C58	0.0(7)
C41-C42-C43-C51	-179.8(4)	C55-C56-C57-C58	-178.6(4)
C41-C42-C43-C44	0.6(7)	C62-C57-C58-C59	-0.2(7)
C42-C43-C44-C45	179.5(4)	C56-C57-C58-C59	-179.5(4)
C51-C43-C44-C45	-0.2(7)	C57-C58-C59-C60	-0.1(7)
C42-C43-C44-C50	-1.3(6)	C58-C59-C60-C61	-0.1(7)
C51-C43-C44-C50	179.0(4)	C59-C60-C61-C62	0.5(7)
C50-C44-C45-C46	1.6(7)	C58-C57-C62-C53	-180.0(4)
C43-C44-C45-C46	-179.2(4)	C56-C57-C62-C53	-0.7(7)
C44-C45-C46-C47	-3.3(7)	C58-C57-C62-C61	0.7(7)
C45-C46-C47-C48	3.4(7)	C56-C57-C62-C61	180.0(4)
C46-C47-C48-C50	-1.9(7)	C54-C53-C62-C57	0.2(7)
C46-C47-C48-C49	178.1(4)	C52-C53-C62-C57	178.8(4)
C47-C48-C49-O5	0.6(8)	C54-C53-C62-C61	179.5(4)
C50-C48-C49-O5	-179.4(5)	C52-C53-C62-C61	-1.9(7)
C47-C48-C49-N2	-178.0(4)	C60-C61-C62-C57	-0.8(7)
C50-C48-C49-N2	2.0(7)	C60-C61-C62-C53	179.8(4)
C47-C48-C50-C40	179.0(4)	N2-C63-C64-C65	175.1(5)
C49-C48-C50-C40	-1.0(7)	C63-C64-C65-C66	-65.7(7)
C47-C48-C50-C44	0.2(7)	C64-C65-C66-C67	-169.2(5)
C49-C48-C50-C44	-179.7(4)	C65-C66-C67-C68	-176.3(5)
C41-C40-C50-C48	179.5(4)	C66-C67-C68-C69	-174.8(5)
C39-C40-C50-C48	-0.5(7)	C67-C68-C69-C70	-173.3(5)
C41-C40-C50-C44	-1.9(7)	O6-C71-C72-C73	172.2(4)
C39-C40-C50-C44	178.2(4)	C71-C72-C73-C74	179.6(5)
C45-C44-C50-C48	-0.1(6)	C72-C73-C74-C75	177.7(6)
C43-C44-C50-C48	-179.3(4)	C73-C74-C75-C76	59.4(9)
C45-C44-C50-C40	-178.8(4)	O2-C11-N1-C1	-179.7(5)
C43-C44-C50-C40	2.0(7)	C10-C11-N1-C1	-0.5(7)

O2-C11-N1-C25	-2.7(7)	O4-C39-N2-C49	-179.5(5)
C10-C11-N1-C25	176.5(4)	C40-C39-N2-C49	0.1(7)
O1-C1-N1-C11	179.5(5)	O4-C39-N2-C63	5.2(7)
C2-C1-N1-C11	-1.5(7)	C40-C39-N2-C63	-175.2(4)
01-C1-N1-C25	2.4(7)	C64-C63-N2-C49	-86.8(6)
C2-C1-N1-C25	-178.5(4)	C64-C63-N2-C39	88.9(5)
C26-C25-N1-C11	-97.6(5)	C17-C18-O3-C33	2.8(7)
C26-C25-N1-C1	79.7(5)	C19-C18-O3-C33	-175.7(4)
O5-C49-N2-C39	179.9(5)	C34-C33-O3-C18	-178.9(4)
C48-C49-N2-C39	-1.6(7)	C55-C56-O6-C71	3.6(7)
O5-C49-N2-C63	-4.8(7)	C57-C56-O6-C71	-175.0(4)
C48-C49-N2-C63	173.7(4)	C72-C71-O6-C56	-178.6(4)

End crystallographic info for M6N8.

## **CRYSTALLOGRAPHIC MATERIAL FOR M8N6**

Crystallographic Material for M8N6.

X-ray Experimental.

Table M8N6.1. Crystallographic Data for M8N6.

Table **M8N6**.2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of **M8N6**.

Table M8N6.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of M8N6.

Table M8N6.4. Anisotropic thermal parameters for the non-hydrogen atoms of M8N6.

Table M8N6.5. Fractional coordinates and isotropic thermal parameters (Å<sup>2</sup>) for the hydrogen atoms of M8N6.

Table M8N6.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of M8N6.

X-ray Experimental for complex  $C_{38}H_{41}NO_3$  (**M8N6**): Crystals grew as long, thin needles by slow evaporation from 1:1:1 dichloromethane:acetonitrile:chloroform. The data crystal was cut from a longer crystal and had approximate dimensions; 0.61 x 0.04 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 790 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 15 seconds per frame with a detector offset of +/- 42.2° and 50 seconds per frame with a detector offset of +/- 110.4°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs  $PLATON^4$  and  $WinGX.^5$  The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.12*P)^2]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.413, with R(F) equal to 0.155 and a goodness of fit, S, = 1.35. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.39.46.
- 2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
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- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$

- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Empirical formula	C38 H41 N O3		
Formula weight	559.72		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	C 2/c		
Unit cell dimensions	a = 24.732(4) Å	α= 90°.	
	b = 4.9439(9) Å	β= 101.290(14)°.	
	c = 50.615(10)  Å	$\gamma = 90^{\circ}$ .	
Volume	6068.9(19) Å <sup>3</sup>		
Z	8		
Density (calculated)	1.225 Mg/m <sup>3</sup>		
Absorption coefficient	0.597 mm <sup>-1</sup>		
F(000)	2400		
Crystal size	0.610 x 0.040 x 0.030 mm <sup>3</sup>		
Theta range for data collection	3.562 to 50.574°.		
Index ranges	-24<=h<=22, -4<=k<=4, -50<=	=1<=43	
Reflections collected	7837		
Independent reflections	3133 [R(int) = 0.1759]		
Completeness to theta = $50.574^{\circ}$	98.5 %		
Absorption correction	Semi-empirical from equivalen	ts	
Max. and min. transmission	1.00 and 0.114		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	3133 / 252 / 381		
Goodness-of-fit on F <sup>2</sup>	1.347		
Final R indices [I>2sigma(I)]	R1 = 0.1549, $wR2 = 0.3362$		
R indices (all data)	R1 = 0.2369, WR2 = 0.4127		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.531 and -0.493 e.Å <sup>-3</sup>		

Table M8N6.1. Crystal data and structure refinement for M8N6.

	X	у	Z	U(eq)
C1	6490(4)	7700(20)	1740(2)	44(3)
C2	6208(4)	7280(20)	1970(2)	36(3)
C3	5768(4)	8800(20)	2001(2)	43(3)
C4	5508(4)	8470(20)	2223(2)	43(3)
C5	5711(4)	6580(20)	2415(2)	46(3)
C6	6152(4)	4856(19)	2389(2)	35(3)
C7	6382(4)	2840(20)	2584(2)	39(3)
C8	6793(4)	1250(20)	2541(2)	43(3)
C9	7049(4)	1680(20)	2316(2)	41(3)
C10	6865(4)	3680(20)	2133(2)	37(3)
C11	7144(4)	4090(20)	1901(2)	36(2)
C12	6411(4)	5220(20)	2160(2)	34(2)
C13	6141(4)	2470(20)	2814(2)	41(3)
C14	5923(4)	2210(20)	3008(2)	43(3)
C15	5679(4)	2000(20)	3242(2)	43(3)
C16	5258(4)	3730(20)	3266(2)	47(3)
C17	5001(4)	3610(20)	3493(2)	46(3)
C18	5194(4)	1830(20)	3695(2)	44(3)
C19	5642(4)	60(20)	3683(2)	34(2)
C20	5845(5)	-1710(20)	3892(2)	52(3)
C21	6271(4)	-3380(20)	3880(2)	52(3)
C22	6498(4)	-3320(30)	3643(2)	53(3)
C23	6323(4)	-1710(20)	3440(2)	45(3)
C24	5883(4)	160(20)	3452(2)	37(3)
C25	7263(4)	6910(20)	1520(2)	51(3)
C26	7084(5)	5440(30)	1261(2)	60(3)
C27	7419(5)	6350(30)	1046(2)	56(3)
C28	7290(6)	4810(30)	784(2)	73(4)
C29	7619(6)	5800(30)	583(3)	75(4)
C30	7507(6)	4230(30)	318(3)	80(4)
C31	4504(5)	3220(30)	3938(2)	61(3)

Table **M8N6**.2. Atomic coordinates (x  $10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x  $10^3$ ) for **M8N6**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	4358(8)	3010(40)	4204(4)	115(6)
C33	4307(8)	480(40)	4307(4)	124(7)
C34	4117(9)	180(40)	4589(4)	127(7)
C35	4238(8)	-1640(40)	4754(4)	119(6)
C36	4026(7)	-1830(40)	5008(3)	103(5)
C37	4189(9)	-3700(50)	5192(4)	143(8)
C38	3956(7)	-4210(40)	5435(3)	104(6)
N1	6948(3)	6233(17)	1728(2)	37(2)
O1	6322(3)	9499(18)	1569(2)	60(2)
O2	7536(3)	2772(16)	1868(1)	49(2)
O3	4979(3)	1643(18)	3925(2)	64(2)

C1-O1	1.256(13)	C19-C24	1.414(14)
C1-N1	1.357(14)	C20-C21	1.349(16)
C1-C2	1.483(14)	С20-Н20	0.95
C2-C3	1.357(14)	C21-C22	1.421(15)
C2-C12	1.421(14)	С21-Н21	0.95
C3-C4	1.414(14)	C22-C23	1.304(15)
С3-Н3	0.95	С22-Н22	0.95
C4-C5	1.369(15)	C23-C24	1.438(15)
С4-Н4	0.95	С23-Н23	0.95
C5-C6	1.409(15)	C25-N1	1.470(13)
С5-Н5	0.95	C25-C26	1.486(15)
C6-C7	1.439(14)	C25-H25A	0.99
C6-C12	1.443(13)	C25-H25B	0.99
C7-C8	1.335(15)	C26-C27	1.557(15)
C7-C13	1.419(15)	C26-H26A	0.99
C8-C9	1.424(14)	С26-Н26В	0.99
С8-Н8	0.95	C27-C28	1.507(16)
C9-C10	1.371(15)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.388(14)	C28-C29	1.506(17)
C10-C11	1.486(14)	C28-H28A	0.99
C11-O2	1.204(12)	C28-H28B	0.99
C11-N1	1.400(14)	C29-C30	1.524(17)
C13-C14	1.218(14)	С29-Н29А	0.99
C14-C15	1.436(15)	С29-Н29В	0.99
C15-C16	1.371(15)	С30-Н30А	0.98
C15-C24	1.413(15)	С30-Н30В	0.98
C16-C17	1.417(14)	С30-Н30С	0.98
С16-Н16	0.95	C31-O3	1.421(14)
C17-C18	1.363(15)	C31-C32	1.465(18)
C17-H17	0.95	C31-H31A	0.99
C18-O3	1.378(12)	C31-H31B	0.99
C18-C19	1.420(14)	C32-C33	1.37(2)
C19-C20	1.390(15)	C32-H32A	0.99

Table M8N6.3. Bond lengths [Å] and angles [°] for M8N6.

С32-Н32В	0.99	C36-C37	1.32(3)
C33-C34	1.59(2)	С36-Н36А	0.99
С33-Н33А	0.99	C36-H36B	0.99
С33-Н33В	0.99	C37-C38	1.48(2)
C34-C35	1.23(2)	С37-Н37А	0.99
C34-H34A	0.99	С37-Н37В	0.99
C34-H34B	0.99	C38-H38A	0.98
C35-C36	1.49(2)	C38-H38B	0.98
С35-Н35А	0.99	C38-H38C	0.98
С35-Н35В	0.99		
01-C1-N1	120.9(9)	С10-С9-Н9	119.7
O1-C1-C2	120.0(10)	С8-С9-Н9	119.7
N1-C1-C2	119.0(10)	C9-C10-C12	119.8(9)
C3-C2-C12	120.3(9)	C9-C10-C11	119.3(9)
C3-C2-C1	121.4(10)	C12-C10-C11	120.9(9)
C12-C2-C1	118.2(9)	O2-C11-N1	120.9(9)
C2-C3-C4	121.7(10)	O2-C11-C10	123.0(9)
С2-С3-Н3	119.1	N1-C11-C10	116.0(9)
С4-С3-Н3	119.1	C10-C12-C2	120.8(9)
C5-C4-C3	119.0(10)	C10-C12-C6	120.4(9)
С5-С4-Н4	120.5	C2-C12-C6	118.7(9)
С3-С4-Н4	120.5	C14-C13-C7	178.1(11)
C4-C5-C6	122.0(9)	C13-C14-C15	177.4(11)
С4-С5-Н5	119.0	C16-C15-C24	120.0(9)
С6-С5-Н5	119.0	C16-C15-C14	118.4(10)
C5-C6-C7	124.5(9)	C24-C15-C14	121.5(10)
C5-C6-C12	118.2(9)	C15-C16-C17	120.9(10)
C7-C6-C12	117.3(9)	С15-С16-Н16	119.5
C8-C7-C13	120.8(10)	С17-С16-Н16	119.5
C8-C7-C6	120.7(9)	C18-C17-C16	119.1(10)
C13-C7-C6	118.4(9)	C18-C17-H17	120.5
C7-C8-C9	120.9(10)	С16-С17-Н17	120.5
С7-С8-Н8	119.6	C17-C18-O3	122.8(10)
С9-С8-Н8	119.6	C17-C18-C19	121.9(9)
C10-C9-C8	120.6(10)	O3-C18-C19	115.3(9)

C20-C19-C24	120.2(10)	C29-C28-C27	112.5(11)
C20-C19-C18	121.7(9)	С29-С28-Н28А	109.1
C24-C19-C18	118.1(9)	C27-C28-H28A	109.1
C21-C20-C19	121.3(10)	C29-C28-H28B	109.1
С21-С20-Н20	119.4	C27-C28-H28B	109.1
С19-С20-Н20	119.4	H28A-C28-H28B	107.8
C20-C21-C22	118.0(11)	C28-C29-C30	113.6(12)
С20-С21-Н21	121.0	С28-С29-Н29А	108.8
С22-С21-Н21	121.0	С30-С29-Н29А	108.8
C23-C22-C21	123.4(11)	С28-С29-Н29В	108.8
С23-С22-Н22	118.3	С30-С29-Н29В	108.8
С21-С22-Н22	118.3	H29A-C29-H29B	107.7
C22-C23-C24	119.9(10)	С29-С30-Н30А	109.5
С22-С23-Н23	120.1	С29-С30-Н30В	109.5
С24-С23-Н23	120.1	H30A-C30-H30B	109.5
C15-C24-C19	119.8(9)	С29-С30-Н30С	109.5
C15-C24-C23	122.9(9)	H30A-C30-H30C	109.5
C19-C24-C23	117.2(9)	H30B-C30-H30C	109.5
N1-C25-C26	114.5(9)	O3-C31-C32	110.9(12)
N1-C25-H25A	108.6	O3-C31-H31A	109.5
С26-С25-Н25А	108.6	С32-С31-Н31А	109.5
N1-C25-H25B	108.6	O3-C31-H31B	109.5
С26-С25-Н25В	108.6	С32-С31-Н31В	109.5
H25A-C25-H25B	107.6	H31A-C31-H31B	108.1
C25-C26-C27	111.5(10)	C33-C32-C31	118.3(18)
С25-С26-Н26А	109.3	С33-С32-Н32А	107.7
С27-С26-Н26А	109.3	С31-С32-Н32А	107.7
С25-С26-Н26В	109.3	С33-С32-Н32В	107.7
С27-С26-Н26В	109.3	С31-С32-Н32В	107.7
H26A-C26-H26B	108.0	H32A-C32-H32B	107.1
C28-C27-C26	114.7(10)	C32-C33-C34	119.5(18)
С28-С27-Н27А	108.6	С32-С33-Н33А	107.4
С26-С27-Н27А	108.6	С34-С33-Н33А	107.4
С28-С27-Н27В	108.6	С32-С33-Н33В	107.4
С26-С27-Н27В	108.6	С34-С33-Н33В	107.4
H27A-C27-H27B	107.6	H33A-C33-H33B	107.0

C35-C34-C33	127(2)	H36A-C36-H36B	106.6			
C35-C34-H34A	105.5	C36-C37-C38	126(2)			
C33-C34-H34A	105.5	С36-С37-Н37А	105.8			
С35-С34-Н34В	105.5	С38-С37-Н37А	105.8			
С33-С34-Н34В	105.5	С36-С37-Н37В	105.8			
H34A-C34-H34B	106.1	С38-С37-Н37В	105.8			
C34-C35-C36	123.7(19)	Н37А-С37-Н37В	106.2			
С34-С35-Н35А	106.4	С37-С38-Н38А	109.5			
С36-С35-Н35А	106.4	С37-С38-Н38В	109.5			
С34-С35-Н35В	106.4	H38A-C38-H38B	109.5			
С36-С35-Н35В	106.4	С37-С38-Н38С	109.5			
H35A-C35-H35B	106.5	H38A-C38-H38C	109.5			
C37-C36-C35	122.8(18)	H38B-C38-H38C	109.5			
С37-С36-Н36А	106.6	C1-N1-C11	124.6(8)			
С35-С36-Н36А	106.6	C1-N1-C25	118.4(9)			
С37-С36-Н36В	106.6	C11-N1-C25	117.0(9)			
С35-С36-Н36В	106.6	C18-O3-C31	117.4(9)			
	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
-----	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------
C1	48(6)	34(5)	50(6)	-8(5)	12(5)	-5(5)
C2	27(5)	33(5)	47(5)	2(4)	5(4)	-1(4)
C3	45(6)	34(5)	49(5)	3(5)	5(5)	-2(5)
C4	33(5)	40(6)	54(6)	1(5)	4(5)	0(4)
C5	44(6)	54(6)	43(5)	-8(5)	13(5)	-13(5)
C6	39(5)	24(5)	41(5)	-1(4)	8(4)	-12(4)
C7	33(5)	43(6)	43(5)	-7(4)	14(4)	-2(5)
C8	41(5)	37(6)	49(6)	6(5)	5(5)	-7(5)
С9	27(5)	41(6)	54(6)	-2(5)	2(5)	-9(4)
C10	39(5)	30(5)	41(5)	7(4)	4(4)	-6(4)
C11	26(5)	32(5)	49(6)	5(5)	4(4)	0(4)
C12	32(5)	27(5)	43(5)	-4(4)	9(4)	-7(4)
C13	34(5)	35(5)	53(6)	8(4)	4(5)	1(4)
C14	30(5)	36(5)	61(6)	-4(5)	3(5)	-7(4)
C15	39(5)	48(6)	43(5)	-2(5)	12(5)	-6(5)
C16	49(6)	38(6)	56(6)	6(5)	13(5)	-5(5)
C17	33(5)	53(6)	50(6)	-4(5)	2(5)	9(5)
C18	31(5)	48(6)	52(6)	0(5)	7(5)	0(5)
C19	32(5)	32(5)	38(5)	1(4)	5(4)	-4(4)
C20	47(6)	64(7)	46(6)	2(5)	11(5)	7(5)
C21	40(6)	59(6)	55(6)	-3(5)	3(5)	-4(5)
C22	37(5)	56(6)	65(7)	0(6)	7(5)	6(5)
C23	42(6)	50(6)	44(5)	-2(5)	13(5)	-10(5)
C24	30(5)	36(5)	46(6)	-1(4)	8(4)	1(4)
C25	43(6)	47(6)	62(6)	2(5)	8(5)	-3(5)
C26	57(6)	64(7)	56(6)	13(5)	7(5)	-13(5)
C27	47(6)	64(6)	54(6)	5(5)	4(5)	-3(5)
C28	81(7)	77(7)	67(7)	-2(6)	33(6)	-16(6)
C29	72(7)	82(8)	72(7)	0(6)	20(6)	4(6)
C30	90(10)	82(9)	71(8)	-16(7)	25(7)	-16(8)
C31	58(7)	79(8)	51(6)	14(5)	21(5)	10(6)

Table **M8N6**.4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M8N6**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	113(9)	121(10)	119(9)	25(8)	42(8)	24(8)
C33	119(10)	126(11)	146(10)	21(8)	68(8)	26(8)
C34	133(10)	137(11)	123(10)	24(8)	55(8)	17(8)
C35	123(10)	123(10)	117(10)	16(8)	39(8)	16(8)
C36	104(9)	101(9)	114(9)	23(8)	47(7)	14(7)
C37	136(11)	165(12)	137(11)	19(9)	47(9)	22(9)
C38	99(11)	130(13)	87(10)	21(9)	31(9)	13(10)
N1	37(5)	38(5)	37(4)	1(4)	12(4)	-7(4)
01	57(5)	67(6)	55(5)	22(4)	14(4)	15(4)
02	51(5)	50(5)	48(4)	-4(4)	18(4)	0(4)
O3	64(5)	78(6)	54(4)	5(4)	23(4)	22(4)

	х	У	Z	U(eq)
H3	5632	10133	1869	52
H4	5197	9533	2240	52
Н5	5549	6421	2570	55
H8	6917	-185	2663	51
Н9	7349	567	2292	49
H16	5138	5027	3129	57
H17	4698	4755	3504	55
H20	5680	-1752	4047	63
H21	6415	-4558	4025	62
H22	6793	-4520	3631	64
H23	6486	-1766	3285	53
H25A	7657	6500	1590	61
H25B	7232	8876	1484	61
H26A	6687	5786	1192	72
H26B	7133	3474	1292	72
H27A	7347	8296	1007	67
H27B	7816	6151	1123	67
H28A	7369	2869	821	87
H28B	6892	4993	706	87
H29A	8017	5661	663	89
H29B	7534	7731	544	89
H30A	7681	2445	346	120
H30B	7660	5225	182	120
H30C	7108	4014	257	120
H31A	4191	2586	3798	74
H31B	4576	5135	3899	74
H32A	4641	4002	4333	138
H32B	4004	3971	4196	138
H33A	4668	-435	4324	149
H33B	4041	-542	4172	149

Table **M8N6.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M8N6**.

H34A	4234	1876	4688	152
H34B	3709	226	4546	152
H35A	4646	-1643	4806	143
H35B	4135	-3357	4656	143
H36A	4101	-60	5100	123
H36B	3620	-1992	4956	123
H37A	4588	-3375	5258	172
H37B	4160	-5437	5093	172
H38A	4254	-4228	5594	156
H38B	3767	-5960	5418	156
H38C	3693	-2775	5454	156

01-C1-C2-C3	-0.1(16)	C7-C6-C12-C2	-177.5(9)
N1-C1-C2-C3	176.0(9)	C24-C15-C16-C17	-3.7(16)
O1-C1-C2-C12	180.0(10)	C14-C15-C16-C17	179.8(10)
N1-C1-C2-C12	-3.9(14)	C15-C16-C17-C18	3.1(17)
C12-C2-C3-C4	1.8(16)	C16-C17-C18-O3	177.9(10)
C1-C2-C3-C4	-178.1(10)	C16-C17-C18-C19	-0.8(17)
C2-C3-C4-C5	1.0(16)	C17-C18-C19-C20	178.7(11)
C3-C4-C5-C6	-3.6(16)	O3-C18-C19-C20	-0.1(15)
C4-C5-C6-C7	-179.9(10)	C17-C18-C19-C24	-1.0(16)
C4-C5-C6-C12	3.4(15)	O3-C18-C19-C24	-179.7(9)
C5-C6-C7-C8	178.7(10)	C24-C19-C20-C21	-0.3(17)
C12-C6-C7-C8	-4.6(14)	C18-C19-C20-C21	-180.0(11)
C5-C6-C7-C13	2.0(15)	C19-C20-C21-C22	-1.6(18)
C12-C6-C7-C13	178.7(9)	C20-C21-C22-C23	1.4(19)
C13-C7-C8-C9	-177.6(10)	C21-C22-C23-C24	0.9(18)
C6-C7-C8-C9	5.8(15)	C16-C15-C24-C19	1.8(16)
C7-C8-C9-C10	-2.1(16)	C14-C15-C24-C19	178.3(9)
C8-C9-C10-C12	-2.9(15)	C16-C15-C24-C23	-180.0(10)
C8-C9-C10-C11	179.5(9)	C14-C15-C24-C23	-3.5(16)
C9-C10-C11-O2	-1.7(16)	C20-C19-C24-C15	-179.2(10)
C12-C10-C11-O2	-179.3(10)	C18-C19-C24-C15	0.5(15)
C9-C10-C11-N1	-177.6(9)	C20-C19-C24-C23	2.5(15)
C12-C10-C11-N1	4.8(14)	C18-C19-C24-C23	-177.8(9)
C9-C10-C12-C2	-179.0(9)	C22-C23-C24-C15	179.0(11)
C11-C10-C12-C2	-1.4(15)	C22-C23-C24-C19	-2.8(16)
C9-C10-C12-C6	3.9(15)	N1-C25-C26-C27	177.5(10)
C11-C10-C12-C6	-178.5(9)	C25-C26-C27-C28	175.7(11)
C3-C2-C12-C10	-179.1(10)	C26-C27-C28-C29	179.2(12)
C1-C2-C12-C10	0.8(14)	C27-C28-C29-C30	178.7(12)
C3-C2-C12-C6	-2.0(14)	O3-C31-C32-C33	-51(2)
C1-C2-C12-C6	177.9(9)	C31-C32-C33-C34	-176.7(15)
C5-C6-C12-C10	176.6(9)	C32-C33-C34-C35	-151(3)
C7-C6-C12-C10	-0.3(14)	C33-C34-C35-C36	-177.5(19)
C5-C6-C12-C2	-0.5(13)	C34-C35-C36-C37	-175(3)

Table **M8N6**.6. Torsion angles [°] for **M8N6**..

C35-C36-C37-C38	-173(2)
01-C1-N1-C11	-175.8(10)
C2-C1-N1-C11	8.1(15)
01-C1-N1-C25	3.7(15)
C2-C1-N1-C25	-172.3(9)
O2-C11-N1-C1	175.6(10)
C10-C11-N1-C1	-8.4(14)
O2-C11-N1-C25	-4.0(14)
C10-C11-N1-C25	172.0(9)
C26-C25-N1-C1	-89.6(13)
C26-C25-N1-C11	90.0(12)
C17-C18-O3-C31	5.9(17)
C19-C18-O3-C31	-175.4(10)
C32-C31-O3-C18	-174.4(13)

End crystallographic info for M8N6.

#### **CRYSTALLOGRAPHIC MATERIAL FOR M10N8**

Crystallographic Material for M10N8.

X-ray Experimental.

Table M10N8.1. Crystallographic Data for M10N8.

Table M10N8.2. Fractional coordinates and equivalent isotropic thermal parameters ( $Å^2$ ) for the non-hydrogen atoms of M10N8.

Table M10N8.3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of M10N8.

Table M10N8.4. Anisotropic thermal parameters for the non-hydrogen atoms of M10N8.

Table M10N8.5. Fractional coordinates and isotropic thermal parameters ( $Å^2$ ) for the hydrogen atoms of M10N8.

Table M10N8.6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of M10N8.

X-ray Experimental for complex  $C_{42}H_{49}NO_3$  (**M10N8**): Crystals grew as long, yellow-orange needles by vapor diffusion (benzene, cyclohexane). The data crystal was cut from a larger crystal and had approximate dimensions; 0.37 x 0.05 x 0.02 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 917 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 23 seconds per frame with a detector offset of +/- 36.2° and 75 seconds per frame with a detector offset of +/-83.0°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.<sup>3</sup> Structure analysis was aided by use of the programs PLATON98<sup>4</sup> and WinGX.<sup>5</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1179^*P)^2 + (7.3878^*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.444, with R(F) equal to 0.166 and a goodness of fit, S, = 1.17. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

# **References**

- CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
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- 5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Empirical formula	C42 H49 N O3		
Formula weight	615.82		
Temperature	100(2) K		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	C 2/c		
Unit cell dimensions	a = 24.607(11) Å	α= 90°.	
	b = 5.034(3)  Å	β= 99.55(4)°.	
	c = 56.37(2)  Å	$\gamma = 90^{\circ}$ .	
Volume	6885(6) Å <sup>3</sup>		
Ζ	8		
Density (calculated)	1.188 Mg/m <sup>3</sup>		
Absorption coefficient	0.569 mm <sup>-1</sup>		
F(000)	2656		
Crystal size	0.37 x 0.05 x 0.02 mm <sup>3</sup>		
Theta range for data collection	4.211 to 58.932°.		
Index ranges	-15<=h<=26, -5<=k<=5, -62<=	=l<=62	
Reflections collected	eflections collected 14214		
Independent reflections	tions $4874 [R(int) = 0.2411]$		
Completeness to theta = $58.932^{\circ}$	98.4 %		
Absorption correction	Semi-empirical from equivalent	its	
Max. and min. transmission	1.00 and 0.576		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	4874 / 276 / 417		
Goodness-of-fit on F <sup>2</sup>	1.170		
Final R indices [I>2sigma(I)]	R1 = 0.1655, wR2 = 0.3600		
R indices (all data)	R1 = 0.2967, wR2 = 0.4440		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.633 and -0.394 e.Å <sup>-3</sup>		

Table M10N8.1. Crystal data and structure refinement for M10N8.

	X	у	Z	U(eq)
		0(0/20)	1924(2)	(2)(2)
Cl	6545(4)	-860(20)	1824(2)	43(3)
C2	6237(4)	-300(20)	2032(2)	40(3)
C3	5794(5)	-1970(20)	2056(2)	53(3)
C4	5522(5)	-1550(20)	2260(2)	51(3)
C5	5699(4)	300(19)	2425(2)	42(3)
C6	6148(4)	1990(20)	2406(2)	42(3)
C7	6354(4)	3968(19)	2572(2)	40(3)
C8	6787(4)	5590(20)	2540(2)	44(3)
C9	7052(4)	5210(20)	2339(2)	42(3)
C10	6885(4)	3285(17)	2178(2)	33(2)
C11	7196(4)	2790(20)	1970(2)	42(3)
C12	6433(4)	1636(19)	2198(2)	39(3)
C13	6093(5)	4360(20)	2783(2)	55(3)
C14	5871(5)	4600(20)	2961(2)	53(3)
C15	5601(4)	4850(20)	3168(2)	41(3)
C16	5167(4)	3190(20)	3195(2)	48(3)
C17	4903(4)	3360(20)	3394(2)	44(3)
C18	5063(5)	5200(20)	3569(2)	53(3)
C19	5522(4)	6930(20)	3558(2)	43(3)
C20	5734(4)	8700(20)	3736(2)	49(3)
C21	6158(4)	10420(20)	3717(2)	51(3)
C22	6409(4)	10260(20)	3510(2)	47(3)
C23	6237(5)	8520(20)	3331(2)	50(3)
C24	5791(4)	6700(20)	3347(2)	43(3)
C25	7356(4)	10(20)	1633(2)	48(3)
C26	7202(5)	1540(30)	1401(2)	62(3)
C27	7531(5)	490(20)	1210(2)	57(3)
C28	7502(5)	2120(20)	987(2)	62(3)
C29	7847(6)	1050(30)	805(2)	68(3)
C30	7893(6)	2790(30)	593(2)	84(4)
C31	7360(7)	3250(30)	422(3)	91(5)

Table **M10N8**.2. Atomic coordinates (x  $10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x  $10^3$ ) for **M10N8**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C32	7437(7)	5110(40)	214(3)	104(5)
C33	4344(5)	4050(30)	3789(2)	64(3)
C34	4187(7)	4600(40)	4025(3)	104(5)
C35	4089(7)	7260(30)	4067(3)	106(5)
C36	3880(7)	8120(40)	4309(3)	103(5)
C37	4216(7)	7180(40)	4540(3)	109(5)
C38	4022(7)	8320(30)	4762(3)	98(5)
C39	4316(9)	7420(50)	4989(4)	144(7)
C40	4151(7)	8190(40)	5213(3)	107(5)
C41	4432(9)	7300(50)	5447(4)	151(8)
C42	4276(8)	7760(40)	5665(3)	135(7)
N1	7008(4)	692(17)	1820(2)	47(2)
O1	6391(3)	-2528(16)	1675(1)	58(2)
O2	7590(3)	4148(15)	1942(1)	55(2)
O3	4848(3)	5498(17)	3775(1)	65(2)

C1-O1	1.203(12)	C19-C24	1.459(13)
C1-N1	1.386(13)	C20-C21	1.373(15)
C1-C2	1.526(14)	С20-Н20	0.95
C2-C3	1.401(14)	C21-C22	1.410(14)
C2-C12	1.381(14)	C21-H21	0.95
C3-C4	1.436(14)	C22-C23	1.347(15)
С3-Н3	0.95	C22-H22	0.95
C4-C5	1.339(14)	C23-C24	1.440(15)
С4-Н4	0.95	С23-Н23	0.95
C5-C6	1.415(13)	C25-N1	1.504(11)
С5-Н5	0.95	C25-C26	1.512(15)
C6-C7	1.401(14)	C25-H25A	0.99
C6-C12	1.471(13)	С25-Н25В	0.99
C7-C8	1.377(14)	C26-C27	1.543(14)
C7-C13	1.455(14)	C26-H26A	0.99
C8-C9	1.410(13)	C26-H26B	0.99
С8-Н8	0.95	C27-C28	1.494(16)
C9-C10	1.348(13)	С27-Н27А	0.99
С9-Н9	0.95	С27-Н27В	0.99
C10-C12	1.408(13)	C28-C29	1.532(15)
C10-C11	1.522(13)	C28-H28A	0.99
C11-O2	1.219(11)	C28-H28B	0.99
C11-N1	1.383(13)	C29-C30	1.501(17)
C13-C14	1.226(13)	С29-Н29А	0.99
C14-C15	1.439(13)	С29-Н29В	0.99
C15-C16	1.383(14)	C30-C31	1.51(2)
C15-C24	1.400(14)	С30-Н30А	0.99
C16-C17	1.394(13)	С30-Н30В	0.99
С16-Н16	0.95	C31-C32	1.534(19)
C17-C18	1.359(15)	C31-H31A	0.99
C17-H17	0.95	C31-H31B	0.99
C18-O3	1.360(12)	C32-H32A	0.98
C18-C19	1.439(15)	C32-H32B	0.98
C19-C20	1.378(15)	C32-H32C	0.98

Table M10N8.3.~ Bond lengths [Å] and angles [°] for ~M10N8.

C33-O3	1.452(13)	C38-C39	1.44(2)
C33-C34	1.475(17)	C38-H38A	0.99
С33-Н33А	0.99	C38-H38B	0.99
С33-Н33В	0.99	C39-C40	1.44(2)
C34-C35	1.39(2)	С39-Н39А	0.99
C34-H34A	0.99	С39-Н39В	0.99
C34-H34B	0.99	C40-C41	1.46(3)
C35-C36	1.60(2)	C40-H40A	0.99
С35-Н35А	0.99	C40-H40B	0.99
С35-Н35В	0.99	C41-C42	1.37(2)
C36-C37	1.50(2)	C41-H41A	0.99
С36-Н36А	0.99	C41-H41B	0.99
С36-Н36В	0.99	C42-H42A	0.98
C37-C38	1.52(2)	C42-H42B	0.98
С37-Н37А	0.99	C42-H42C	0.98
С37-Н37В	0.99		
01-C1-N1	123.3(9)	C8-C7-C13	118.8(9)
O1-C1-C2	121.8(9)	C6-C7-C13	118.9(9)
N1-C1-C2	115.0(9)	C7-C8-C9	119.8(9)
C3-C2-C12	123.2(8)	С7-С8-Н8	120.1
C3-C2-C1	117.2(9)	С9-С8-Н8	120.1
C12-C2-C1	119.3(9)	C10-C9-C8	120.5(9)
C2-C3-C4	117.5(10)	С10-С9-Н9	119.8
С2-С3-Н3	121.2	С8-С9-Н9	119.8
С4-С3-Н3	121.2	C9-C10-C12	121.9(8)
C5-C4-C3	121.2(10)	C9-C10-C11	120.1(8)
С5-С4-Н4	119.4	C12-C10-C11	118.1(9)
С3-С4-Н4	119.4	O2-C11-N1	122.7(9)
C4-C5-C6	122.3(9)	O2-C11-C10	121.5(9)
С4-С5-Н5	118.9	N1-C11-C10	115.9(9)
С6-С5-Н5	118.9	C2-C12-C10	123.6(8)
C5-C6-C7	125.1(9)	C2-C12-C6	117.8(8)
C5-C6-C12	117.9(9)	C10-C12-C6	118.6(9)
C7-C6-C12	116.9(8)	C14-C13-C7	177.8(12)
C8-C7-C6	122.2(8)	C13-C14-C15	178.9(13)

C16-C15-C24	119.6(8)	C25-C26-C27	110.2(10)
C16-C15-C14	120.3(10)	C25-C26-H26A	109.6
C24-C15-C14	120.1(9)	C27-C26-H26A	109.6
C15-C16-C17	121.6(10)	C25-C26-H26B	109.6
С15-С16-Н16	119.2	C27-C26-H26B	109.6
С17-С16-Н16	119.2	H26A-C26-H26B	108.1
C18-C17-C16	120.6(10)	C28-C27-C26	116.2(10)
С18-С17-Н17	119.7	C28-C27-H27A	108.2
С16-С17-Н17	119.7	С26-С27-Н27А	108.2
O3-C18-C17	125.9(10)	С28-С27-Н27В	108.2
O3-C18-C19	112.8(10)	С26-С27-Н27В	108.2
C17-C18-C19	121.1(9)	H27A-C27-H27B	107.4
C20-C19-C18	124.5(9)	C27-C28-C29	114.4(10)
C20-C19-C24	118.5(10)	C27-C28-H28A	108.7
C18-C19-C24	116.9(10)	C29-C28-H28A	108.7
C21-C20-C19	123.2(9)	C27-C28-H28B	108.7
С21-С20-Н20	118.4	C29-C28-H28B	108.7
С19-С20-Н20	118.4	H28A-C28-H28B	107.6
C20-C21-C22	118.3(10)	C30-C29-C28	116.7(11)
С20-С21-Н21	120.9	С30-С29-Н29А	108.1
С22-С21-Н21	120.9	С28-С29-Н29А	108.1
C23-C22-C21	121.9(10)	С30-С29-Н29В	108.1
С23-С22-Н22	119.1	С28-С29-Н29В	108.1
С21-С22-Н22	119.1	H29A-C29-H29B	107.3
C22-C23-C24	121.0(9)	C29-C30-C31	115.2(12)
С22-С23-Н23	119.5	С29-С30-Н30А	108.5
С24-С23-Н23	119.5	С31-С30-Н30А	108.5
C23-C24-C15	123.0(9)	С29-С30-Н30В	108.5
C23-C24-C19	117.0(10)	С31-С30-Н30В	108.5
C15-C24-C19	120.0(9)	H30A-C30-H30B	107.5
N1-C25-C26	113.7(9)	C30-C31-C32	112.1(13)
N1-C25-H25A	108.8	С30-С31-Н31А	109.2
С26-С25-Н25А	108.8	С32-С31-Н31А	109.2
N1-C25-H25B	108.8	С30-С31-Н31В	109.2
С26-С25-Н25В	108.8	С32-С31-Н31В	109.2
H25A-C25-H25B	107.7	H31A-C31-H31B	107.9

С31-С32-Н32А	109.5	H37A-C37-H37B	107.8
С31-С32-Н32В	109.5	C39-C38-C37	115.6(15)
H32A-C32-H32B	109.5	С39-С38-Н38А	108.4
С31-С32-Н32С	109.5	С37-С38-Н38А	108.4
H32A-C32-H32C	109.5	С39-С38-Н38В	108.4
H32B-C32-H32C	109.5	С37-С38-Н38В	108.4
O3-C33-C34	107.9(11)	H38A-C38-H38B	107.4
O3-C33-H33A	110.1	C38-C39-C40	121.4(18)
С34-С33-Н33А	110.1	С38-С39-Н39А	107.0
О3-С33-Н33В	110.1	С40-С39-Н39А	107.0
С34-С33-Н33В	110.1	С38-С39-Н39В	107.0
H33A-C33-H33B	108.4	С40-С39-Н39В	107.0
C35-C34-C33	114.4(15)	H39A-C39-H39B	106.7
С35-С34-Н34А	108.7	C39-C40-C41	123.5(18)
С33-С34-Н34А	108.7	С39-С40-Н40А	106.4
С35-С34-Н34В	108.7	C41-C40-H40A	106.4
С33-С34-Н34В	108.7	С39-С40-Н40В	106.5
H34A-C34-H34B	107.6	C41-C40-H40B	106.4
C34-C35-C36	119.9(14)	H40A-C40-H40B	106.5
С34-С35-Н35А	107.3	C42-C41-C40	127(2)
С36-С35-Н35А	107.3	C42-C41-H41A	105.6
С34-С35-Н35В	107.3	C40-C41-H41A	105.6
С36-С35-Н35В	107.3	C42-C41-H41B	105.6
H35A-C35-H35B	106.9	C40-C41-H41B	105.6
C37-C36-C35	116.5(14)	H41A-C41-H41B	106.1
С37-С36-Н36А	108.2	C41-C42-H42A	109.5
С35-С36-Н36А	108.2	C41-C42-H42B	109.5
С37-С36-Н36В	108.2	H42A-C42-H42B	109.5
С35-С36-Н36В	108.2	C41-C42-H42C	109.5
H36A-C36-H36B	107.3	H42A-C42-H42C	109.5
C36-C37-C38	113.0(14)	H42B-C42-H42C	109.5
С36-С37-Н37А	109.0	C11-N1-C1	127.9(8)
С38-С37-Н37А	109.0	C11-N1-C25	115.6(8)
С36-С37-Н37В	109.0	C1-N1-C25	116.5(8)
С38-С37-Н37В	109.0	C18-O3-C33	116.4(9)

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	46(6)	35(5)	47(6)	4(5)	6(5)	-11(5)
C2	40(5)	49(5)	35(5)	-3(5)	14(4)	-4(5)
C3	57(6)	54(6)	52(6)	-6(5)	22(5)	-4(5)
C4	52(6)	56(6)	46(6)	6(5)	15(5)	-9(5)
C5	44(5)	37(5)	46(5)	-7(5)	14(5)	6(5)
C6	42(6)	43(5)	43(5)	0(4)	12(5)	-11(5)
C7	51(6)	41(5)	32(5)	-3(4)	14(5)	7(5)
C8	48(6)	42(5)	46(6)	0(4)	17(5)	-3(5)
С9	41(5)	43(5)	46(5)	-1(5)	20(5)	-7(5)
C10	39(5)	29(4)	35(5)	1(4)	21(4)	-5(4)
C11	48(6)	40(5)	43(6)	14(5)	19(5)	1(5)
C12	39(6)	40(5)	41(5)	0(4)	21(5)	7(4)
C13	56(6)	55(6)	55(6)	-2(5)	14(5)	11(5)
C14	54(6)	61(6)	49(6)	3(5)	23(5)	3(5)
C15	41(5)	48(5)	35(5)	-3(4)	13(5)	-8(5)
C16	56(6)	49(6)	45(6)	-8(5)	22(5)	6(5)
C17	44(6)	50(5)	41(5)	-4(5)	16(5)	-7(5)
C18	58(6)	60(6)	45(6)	7(5)	17(5)	4(5)
C19	48(6)	49(5)	37(5)	-1(4)	15(5)	2(5)
C20	50(6)	53(6)	48(6)	-6(5)	21(5)	9(5)
C21	45(6)	57(6)	53(6)	-4(5)	16(5)	-3(5)
C22	40(6)	52(6)	52(6)	8(5)	13(5)	11(5)
C23	57(6)	49(5)	51(6)	10(5)	25(5)	7(5)
C24	49(6)	40(5)	42(5)	3(4)	13(5)	8(5)
C25	55(6)	48(5)	48(5)	-6(5)	33(5)	4(5)
C26	68(7)	74(7)	50(6)	6(5)	24(5)	-7(5)
C27	66(6)	65(6)	44(6)	-11(5)	17(5)	-3(5)
C28	87(7)	56(6)	48(6)	-3(5)	26(6)	-4(6)
C29	84(7)	67(7)	58(6)	-1(5)	29(6)	3(6)
C30	105(8)	85(8)	68(7)	9(6)	33(7)	-2(7)
C31	113(9)	91(8)	75(7)	11(6)	32(7)	14(7)

Table **M10N8.4**. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M10N8**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

C32	128(12)	107(11)	85(10)	19(8)	38(9)	40(9)
C33	71(7)	74(7)	58(6)	2(5)	42(6)	-14(6)
C34	108(8)	114(9)	100(8)	-5(7)	51(7)	-13(7)
C35	105(8)	100(9)	124(9)	7(7)	53(7)	5(7)
C36	110(9)	110(9)	102(9)	-4(7)	53(7)	1(7)
C37	107(9)	117(9)	116(9)	-2(7)	56(8)	4(7)
C38	106(9)	106(8)	88(8)	25(7)	30(7)	10(7)
C39	134(10)	169(11)	137(10)	10(9)	47(9)	8(9)
C40	115(9)	117(9)	87(8)	0(7)	11(7)	-3(8)
C41	146(11)	173(12)	135(11)	16(9)	28(9)	0(9)
C42	138(13)	197(16)	81(10)	-17(11)	52(10)	18(12)
N1	57(5)	43(4)	44(5)	-2(4)	22(4)	0(4)
01	70(5)	61(5)	48(5)	-13(4)	27(4)	-19(4)
O2	60(5)	61(5)	53(4)	4(4)	34(4)	0(4)
O3	69(5)	86(5)	48(4)	-2(4)	32(4)	-22(4)

	Х	У	Z	U(eq)
H3	5677	-3328	1942	64
H4	5211	-2605	2277	61
Н5	5517	483	2560	50
H8	6906	6955	2653	53
Н9	7352	6329	2318	50
H16	5047	1904	3074	58
H17	4608	2189	3409	53
H20	5579	8739	3880	58
H21	6279	11681	3839	61
H22	6709	11404	3496	56
H23	6411	8488	3193	61
H25A	7319	-1915	1598	57
H25B	7747	367	1700	57
H26A	7283	3449	1430	75
H26B	6803	1347	1341	75
H27A	7923	335	1285	69
H27B	7398	-1320	1163	69
H28A	7627	3948	1033	74
H28B	7112	2232	907	74
H29A	8224	695	892	81
H29B	7688	-673	744	81
H30A	8162	1980	502	101
H30B	8043	4534	654	101
H31A	7086	4040	512	109
H31B	7213	1527	356	109
H32A	7643	6686	278	157
H32B	7076	5640	127	157
H32C	7642	4173	104	157
H33A	4403	2122	3770	77
H33B	4047	4633	3658	77

Table **M10N8.5**. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **M10N8**.

H34A	3850	3574	4039	124
H34B	4484	3958	4152	124
H35A	3815	7898	3931	127
H35B	4436	8231	4060	127
H36A	3866	10089	4313	124
H36B	3498	7467	4302	124
H37A	4606	7687	4543	131
H37B	4198	5218	4546	131
H38A	4051	10280	4757	118
H38B	3627	7875	4754	118
H39A	4704	7977	4998	172
H39B	4313	5451	4984	172
H40A	3761	7654	5202	129
H40B	4158	10153	5217	129
H41A	4461	5345	5435	181
H41B	4812	7991	5462	181
H42A	4196	9655	5680	203
H42B	4574	7234	5794	203
H42C	3944	6722	5677	203

01-C1-C2-C3	5.6(16)	C7-C6-C12-C10	-0.4(14)
N1-C1-C2-C3	-174.8(9)	C24-C15-C16-C17	1.7(16)
01-C1-C2-C12	-179.8(10)	C14-C15-C16-C17	179.2(10)
N1-C1-C2-C12	-0.2(14)	C15-C16-C17-C18	0.5(17)
C12-C2-C3-C4	2.2(16)	C16-C17-C18-O3	-177.8(10)
C1-C2-C3-C4	176.6(9)	C16-C17-C18-C19	-2.7(17)
C2-C3-C4-C5	-2.4(17)	O3-C18-C19-C20	0.7(16)
C3-C4-C5-C6	2.1(17)	C17-C18-C19-C20	-175.1(11)
C4-C5-C6-C7	179.9(11)	O3-C18-C19-C24	178.3(9)
C4-C5-C6-C12	-1.4(15)	C17-C18-C19-C24	2.6(16)
C5-C6-C7-C8	-178.7(10)	C18-C19-C20-C21	-177.0(10)
C12-C6-C7-C8	2.6(15)	C24-C19-C20-C21	5.4(16)
C5-C6-C7-C13	-0.1(16)	C19-C20-C21-C22	-3.6(17)
C12-C6-C7-C13	-178.8(9)	C20-C21-C22-C23	1.4(16)
C6-C7-C8-C9	-2.6(16)	C21-C22-C23-C24	-1.2(16)
C13-C7-C8-C9	178.8(9)	C22-C23-C24-C15	-179.4(10)
C7-C8-C9-C10	0.2(16)	C22-C23-C24-C19	2.9(15)
C8-C9-C10-C12	2.0(15)	C16-C15-C24-C23	-179.3(10)
C8-C9-C10-C11	-176.3(9)	C14-C15-C24-C23	3.2(16)
C9-C10-C11-O2	-1.9(15)	C16-C15-C24-C19	-1.7(16)
C12-C10-C11-O2	179.7(9)	C14-C15-C24-C19	-179.1(10)
C9-C10-C11-N1	177.2(9)	C20-C19-C24-C23	-4.8(15)
C12-C10-C11-N1	-1.1(13)	C18-C19-C24-C23	177.4(9)
C3-C2-C12-C10	178.7(10)	C20-C19-C24-C15	177.4(10)
C1-C2-C12-C10	4.5(15)	C18-C19-C24-C15	-0.4(15)
C3-C2-C12-C6	-1.6(15)	N1-C25-C26-C27	-173.5(9)
C1-C2-C12-C6	-175.8(9)	C25-C26-C27-C28	-169.1(11)
C9-C10-C12-C2	177.9(10)	C26-C27-C28-C29	178.4(11)
C11-C10-C12-C2	-3.8(14)	C27-C28-C29-C30	-172.2(12)
C9-C10-C12-C6	-1.8(14)	C28-C29-C30-C31	-65.3(17)
C11-C10-C12-C6	176.5(9)	C29-C30-C31-C32	178.5(12)
C5-C6-C12-C2	1.1(14)	O3-C33-C34-C35	60.3(19)
C7-C6-C12-C2	179.9(9)	C33-C34-C35-C36	176.2(14)
C5-C6-C12-C10	-179.2(9)	C34-C35-C36-C37	53(2)

Table M10N8.6. Torsion angles [°] for M10N8.

C35-C36-C37-C38	174.3(14)
C36-C37-C38-C39	177.9(18)
C37-C38-C39-C40	-175.6(19)
C38-C39-C40-C41	179(2)
C39-C40-C41-C42	-174(2)
O2-C11-N1-C1	-175.0(10)
C10-C11-N1-C1	5.9(15)
O2-C11-N1-C25	6.0(14)
C10-C11-N1-C25	-173.2(8)
01-C1-N1-C11	174.4(10)
C2-C1-N1-C11	-5.2(15)
O1-C1-N1-C25	-6.6(15)
C2-C1-N1-C25	173.8(9)
C26-C25-N1-C11	-88.4(12)
C26-C25-N1-C1	92.4(11)
C17-C18-O3-C33	-11.5(17)
C19-C18-O3-C33	173.1(10)
C34-C33-O3-C18	179.0(12)

End crystallographic info for M10N8.

### **CRYSTALLOGRAPHIC MATERIAL FOR 2,6-DIFLUORO-PDI**

Crystallographic Material for 2,6-difluoro-PDI.

X-ray Experimental.

Table 1. Crystallographic Data for **2,6-difluoro-PDI**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters  $(Å^2)$  for the non-hydrogen atoms of **2,6-difluoro-PDI**.

Table 3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of **2,6-difluoro-PDI**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of 2,6-difluoro-PDI.

Table 5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **2,6-difluoro-PDI**.

Table 6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **2,6-difluoro-PDI**.

X-ray Experimental for C<sub>38</sub>H<sub>18</sub>N<sub>2</sub>F<sub>4</sub>O<sub>4</sub> (**2,6-difluoro-PDI**) Crystals grew as very long, thin red laths by sublimation. The data crystal was cut from a longer crystal and had approximate dimensions; 0.38 x 0.030 x 0.019 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1069 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 12.5 seconds per frame for frames collected with a detector offset of +/- 41.3° and 50 seconds per frame with frames collected with a detector offset of 112°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.70a.<sup>1</sup> The structure was solved by direct methods using

SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and OLEX2.<sup>5</sup> The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1579^*P)^2 + (0.1349^*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.220, with R(F) equal to 0.0753 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## **References**

- 1) CrysAlisPro. Rigaku Oxford Diffraction (2019). CrysAlicPro Software System, 1.171.41.70a.
- 2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
- 3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 3-8.
- 4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
- 5) OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.
- 6)  $\begin{aligned} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each} \\ \text{reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the} \\ \text{number of refined parameters.} \end{aligned}$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Formula weight	642.54	
Temperature	100.04(18) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 4.8899(3) Å	α= 90°.
	b = 29.9472(14) Å	β= 105.044(6)°.
	c = 9.2362(6)  Å	$\gamma = 90^{\circ}$ .
Volume	1306.18(14) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.634 Mg/m <sup>3</sup>	
Absorption coefficient	1.069 mm <sup>-1</sup>	
F(000)	656	
Crystal size	0.38 x 0.03 x 0.019 mm <sup>3</sup>	
Theta range for data collection	2.951 to 68.245°.	
Index ranges	-5<=h<=5, -33<=k<=36, -9<=l	<=11
Reflections collected	6974	
Independent reflections	2352 [R(int) = 0.0729]	
Completeness to theta = $67.684^{\circ}$	98.6 %	
Absorption correction	Gaussian and multi-scan	
Max. and min. transmission	1.000 and 0.607	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2352 / 0 / 217	
Goodness-of-fit on F <sup>2</sup>	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0753, wR2 = 0.2031	
R indices (all data)	R1 = 0.0858, wR2 = 0.2205	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.423 and -0.363 e.Å <sup>-3</sup>	

	Х	у	Z	U(eq)
F1	4587(3)	7085(1)	6825(2)	33(1)
F2	10772(3)	6361(1)	4462(2)	32(1)
01	7379(4)	6627(1)	9676(2)	30(1)
02	6669(4)	5705(1)	5691(2)	29(1)
N1	6959(5)	6170(1)	7659(3)	24(1)
C1	6387(6)	6289(1)	9009(3)	24(1)
C2	4531(5)	5983(1)	9598(3)	24(1)
C3	3855(6)	6089(1)	10913(3)	26(1)
C4	2147(6)	5803(1)	11508(3)	26(1)
C5	1095(5)	5408(1)	10780(3)	22(1)
C6	1730(5)	5295(1)	9406(3)	22(1)
C7	698(5)	4897(1)	8601(3)	22(1)
C8	1388(5)	4809(1)	7266(3)	24(1)
C9	3079(6)	5098(1)	6688(3)	25(1)
C10	4134(5)	5482(1)	7451(3)	22(1)
C11	5977(5)	5783(1)	6835(3)	23(1)
C12	3484(5)	5588(1)	8817(3)	23(1)
C13	8998(6)	6447(1)	7115(3)	26(1)
C14	7734(5)	6710(1)	5716(3)	24(1)
C15	5658(6)	7035(1)	5616(3)	27(1)
C16	4681(6)	7311(1)	4404(4)	31(1)
C17	5784(6)	7258(1)	3170(4)	33(1)
C18	7866(6)	6937(1)	3192(3)	31(1)
C19	8734(6)	6673(1)	4446(3)	27(1)

Table 2. Atomic coordinates (x 10<sup>4</sup>) and equivalent isotropic displacement parameters ( $Å^2x$  10<sup>3</sup>) for **2,6-difluoro-PDI**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

F1-C15	1.359(3)	C8-H8	0.95
F2-C19	1.364(3)	C8-C9	1.397(4)
O1-C1	1.219(4)	С9-Н9	0.95
O2-C11	1.213(3)	C9-C10	1.376(4)
N1-C1	1.394(4)	C10-C11	1.488(3)
N1-C11	1.401(4)	C10-C12	1.415(4)
N1-C13	1.482(3)	C13-H13A	0.99
C1-C2	1.488(4)	C13-H13B	0.99
C2-C3	1.376(4)	C13-C14	1.503(4)
C2-C12	1.410(4)	C14-C15	1.392(4)
С3-Н3	0.95	C14-C19	1.388(4)
C3-C4	1.404(4)	C15-C16	1.372(4)
C4-H4	0.95	C16-H16	0.95
C4-C5	1.391(4)	C16-C17	1.391(4)
C5-C6	1.424(4)	C17-H17	0.95
C5-C7#1	1.480(4)	C17-C18	1.396(5)
C6-C7	1.424(4)	C18-H18	0.95
C6-C12	1.431(4)	C18-C19	1.376(4)
C7-C8	1.386(4)		
C1-N1-C11	125.3(2)	С5-С4-Н4	119.6
C1-N1-C13	118.0(2)	C4-C5-C6	119.6(2)
C11-N1-C13	116.4(2)	C4-C5-C7#1	121.4(2)
01-C1-N1	121.3(2)	C6-C5-C7#1	119.0(3)
O1-C1-C2	121.9(2)	C5-C6-C7	122.3(2)
N1-C1-C2	116.9(2)	C5-C6-C12	118.9(3)
C3-C2-C1	119.4(3)	C7-C6-C12	118.8(2)
C3-C2-C12	120.3(2)	C6-C7-C5#1	118.7(2)
C12-C2-C1	120.3(2)	C8-C7-C5#1	122.0(2)
С2-С3-Н3	119.7	C8-C7-C6	119.3(2)
C2-C3-C4	120.6(3)	С7-С8-Н8	119.1
С4-С3-Н3	119.7	C7-C8-C9	121.7(2)
С3-С4-Н4	119.6	С9-С8-Н8	119.1
C5-C4-C3	120.8(3)	С8-С9-Н9	119.9

Table 3. Bond lengths [Å] and angles  $[\circ]$  for **2,6-difluoro-PDI**.

C10-C9-C8	120.2(2)	C19-C14-C13	121.8(2)
С10-С9-Н9	119.9	C19-C14-C15	114.3(3)
C9-C10-C11	119.6(2)	F1-C15-C14	116.8(2)
C9-C10-C12	120.2(2)	F1-C15-C16	118.5(2)
C12-C10-C11	120.2(2)	C16-C15-C14	124.6(3)
O2-C11-N1	120.0(2)	С15-С16-Н16	120.9
O2-C11-C10	123.3(2)	C15-C16-C17	118.2(3)
N1-C11-C10	116.7(2)	С17-С16-Н16	120.9
C2-C12-C6	119.7(2)	С16-С17-Н17	119.9
C2-C12-C10	120.6(2)	C16-C17-C18	120.2(3)
C10-C12-C6	119.7(2)	С18-С17-Н17	119.9
N1-C13-H13A	108.5	С17-С18-Н18	120.9
N1-C13-H13B	108.5	C19-C18-C17	118.2(3)
N1-C13-C14	115.0(2)	С19-С18-Н18	120.9
H13A-C13-H13B	107.5	F2-C19-C14	117.6(2)
C14-C13-H13A	108.5	F2-C19-C18	117.9(2)
C14-C13-H13B	108.5	C18-C19-C14	124.5(3)
C15-C14-C13	123.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
 F1	35(1)	34(1)	35(1)	1(1)	17(1)	7(1)
F2	32(1)	32(1)	38(1)	-2(1)	19(1)	2(1)
01	35(1)	28(1)	29(1)	-1(1)	13(1)	-8(1)
02	33(1)	26(1)	32(1)	-2(1)	18(1)	-2(1)
N1	24(1)	22(1)	26(1)	2(1)	9(1)	0(1)
C1	23(1)	27(1)	24(1)	3(1)	7(1)	2(1)
C2	22(1)	24(1)	26(1)	2(1)	9(1)	1(1)
C3	27(1)	24(1)	26(1)	-3(1)	7(1)	-2(1)
C4	28(1)	26(1)	26(1)	-2(1)	12(1)	-2(1)
C5	20(1)	23(1)	24(1)	1(1)	6(1)	2(1)
C6	20(1)	22(1)	24(1)	3(1)	7(1)	4(1)
C7	19(1)	24(1)	26(1)	2(1)	7(1)	3(1)
C8	24(1)	23(1)	24(1)	-2(1)	7(1)	1(1)
C9	28(1)	27(1)	24(1)	0(1)	12(1)	4(1)
C10	21(1)	24(1)	24(1)	3(1)	8(1)	3(1)
C11	23(1)	23(1)	25(1)	2(1)	10(1)	5(1)
C12	19(1)	24(1)	25(1)	2(1)	6(1)	4(1)
C13	24(1)	26(1)	29(2)	1(1)	11(1)	-1(1)
C14	22(1)	22(1)	27(1)	0(1)	6(1)	-4(1)
C15	24(1)	26(1)	31(2)	-3(1)	8(1)	-3(1)
C16	25(1)	25(1)	43(2)	2(1)	6(1)	-2(1)
C17	30(2)	33(2)	34(2)	10(1)	4(1)	-8(1)
C18	30(2)	36(2)	28(2)	0(1)	10(1)	-10(1)
C19	24(1)	27(1)	30(1)	-3(1)	9(1)	-5(1)

Table 4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **2,6-difluoro-PDI**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

	Х	у	Z	U(eq)
Н3	4551	6357	11423	31
H4	1705	5880	12419	31
H8	693	4544	6730	29
Н9	3501	5031	5765	30
H13A	10489	6249	6922	31
H13B	9924	6657	7920	31
H16	3289	7532	4408	38
H17	5119	7440	2310	39
H18	8661	6902	2363	37

Table 5. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **2,6-difluoro-PDI**.

F1-C15-C16-C17	-179.9(2)	C8-C9-C10-C12	-0.8(4)
01-C1-C2-C3	1.6(4)	C9-C10-C11-O2	-1.6(4)
O1-C1-C2-C12	-178.2(2)	C9-C10-C11-N1	179.4(2)
N1-C1-C2-C3	-178.8(2)	C9-C10-C12-C2	-179.3(2)
N1-C1-C2-C12	1.4(4)	C9-C10-C12-C6	0.2(4)
N1-C13-C14-C15	61.2(4)	C11-N1-C1-O1	178.2(2)
N1-C13-C14-C19	-124.3(3)	C11-N1-C1-C2	-1.4(4)
C1-N1-C11-O2	-177.9(2)	C11-N1-C13-C14	73.8(3)
C1-N1-C11-C10	1.1(4)	C11-C10-C12-C2	1.0(4)
C1-N1-C13-C14	-112.2(3)	C11-C10-C12-C6	-179.4(2)
C1-C2-C3-C4	-178.9(2)	C12-C2-C3-C4	0.8(4)
C1-C2-C12-C6	179.2(2)	C12-C6-C7-C5#1	179.5(2)
C1-C2-C12-C10	-1.3(4)	C12-C6-C7-C8	-0.7(4)
C2-C3-C4-C5	-0.2(4)	C12-C10-C11-O2	178.1(2)
C3-C2-C12-C6	-0.6(4)	C12-C10-C11-N1	-0.9(4)
C3-C2-C12-C10	178.9(2)	C13-N1-C1-O1	4.8(4)
C3-C4-C5-C6	-0.7(4)	C13-N1-C1-C2	-174.8(2)
C3-C4-C5-C7#1	179.7(2)	C13-N1-C11-O2	-4.4(4)
C4-C5-C6-C7	-179.5(2)	C13-N1-C11-C10	174.7(2)
C4-C5-C6-C12	1.0(4)	C13-C14-C15-F1	-5.6(4)
C5-C6-C7-C5#1	-0.1(4)	C13-C14-C15-C16	173.1(3)
C5-C6-C7-C8	179.7(2)	C13-C14-C19-F2	5.1(4)
C5-C6-C12-C2	-0.3(4)	C13-C14-C19-C18	-173.0(3)
C5-C6-C12-C10	-179.9(2)	C14-C15-C16-C17	1.5(4)
C5#1-C7-C8-C9	179.9(2)	C15-C14-C19-F2	-179.9(2)
C6-C7-C8-C9	0.1(4)	C15-C14-C19-C18	1.9(4)
C7#1-C5-C6-C7	0.1(4)	C15-C16-C17-C18	-1.2(4)
C7#1-C5-C6-C12	-179.5(2)	C16-C17-C18-C19	1.3(4)
C7-C6-C12-C2	-179.9(2)	C17-C18-C19-F2	-179.9(2)
C7-C6-C12-C10	0.6(4)	C17-C18-C19-C14	-1.7(4)
C7-C8-C9-C10	0.6(4)	C19-C14-C15-F1	179.6(2)
C8-C9-C10-C11	178.8(2)	C19-C14-C15-C16	-1.8(4)

Table 6. Torsion angles [°] for  $\pmb{2,6-difluoro-PDI}$  .

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2

End crystallographic info for **2,6-difluoro-PDI**.

### **CRYSTALLOGRAPHIC MATERIAL FOR 3,4-DIFLUORO-PDI**

Crystallographic Material for 3,4-difluoro-PDI.

X-ray Experimental.

Table 1. **3,4-difluoro-PDI** Crystallographic Data for **3,4-difluoro-PDI**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters  $(Å^2)$  for the non-hydrogen atoms of **3,4-difluoro-PDI**.

Table 3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of **3,4-difluoro-PDI**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of 3,4-difluoro-PDI.

Table 5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **3,4-difluoro-PDI**.

Table 6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **3,4-difluoro-PDI**.

X-ray Experimental for C<sub>38</sub>H<sub>18</sub>N<sub>2</sub>F<sub>4</sub>O<sub>4</sub> **3,4-difluoro-PDI:** Crystals grew as very long, thin red laths by sublimation. The data crystal was cut from a longer crystal and had approximate dimensions;  $0.34 \times 0.051 \times 0.027$  mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a µ-focus Cu K $\alpha$  radiation source ( $\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 835 frames of data were collected using  $\omega$ -scans with a scan range of 1° and a counting time of 13.5 seconds per frame for frames collected with a detector offset of +/- 42.4° and 49.5 seconds per frame with frames collected with a detector offset of 92.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.70a.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement

parameters for the non-H atoms using SHELXL-2018/3.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and OLEX2.<sup>5</sup> Most hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on the methylene carbon atom bound to the disordered 3,4-difluorophenyl ring were observed in a  $\Delta$ F map and refined with isotropic displacement parameters.

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1118*P)^2 + (0.3107*P)]$  and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.222, with R(F) equal to 0.0882 and a goodness of fit, S, = 1.13. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

### **References**

- 1) CrysAlisPro. Rigaku Oxford Diffraction (2019). CrysAlicPro Software System, 1.171.41.70a.
- 2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
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- 6) 
  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
- 7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
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Empirical formula	C38 H18 F4 N2 O4		
Formula weight	642.54		
Temperature	99.9(5) K		
Wavelength	1.54184 Å		
Crystal system	triclinic		
Space group	P -1		
Unit cell dimensions	a = 6.7264(12) Å	α= 80.061(15)°.	
	b = 7.6893(12) Å	β= 85.935(16)°.	
	c = 13.506(3)  Å	γ = 73.353(15)°.	
Volume	659.0(2) Å <sup>3</sup>		
Z	1		
Density (calculated)	1.619 Mg/m <sup>3</sup>		
Absorption coefficient	1.059 mm <sup>-1</sup>		
F(000)	328		
Crystal size	0.34 x 0.051 x 0.027 mm <sup>3</sup>		
Theta range for data collection	3.323 to 66.417°.		
Index ranges	-7<=h<=7, -9<=k<=6, -15<=l<=15		
Reflections collected	3383		
Independent reflections	2170 [R(int) = 0.0432]		
Completeness to theta = $66.417^{\circ}$	94.1 %		
Absorption correction	Semi-empirical from equivaler	nts	
Max. and min. transmission	1.00000 and 0.23939		
Refinement method	Full-matrix least-squares on F <sup>2</sup>	2	
Data / restraints / parameters	2170 / 399 / 298		
Goodness-of-fit on F <sup>2</sup>	1.206		
Final R indices [I>2sigma(I)]	R1 = 0.0882, $wR2 = 0.2218$		
R indices (all data)	R1 = 0.1146, $wR2 = 0.2423$		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.419 and -0.474 e.Å <sup>-3</sup>		

## **3,4-difluoro-PDI** Table 1. Crystal data and structure refinement for **3,4-difluoro-PDI**.

	X	у	Z	U(eq)
F1	2311(7)	1607(8)	6401(3)	68(2)
F2	3105(7)	-2030(9)	6390(4)	60(2)
01	3396(5)	961(4)	1384(2)	31(1)
02	2692(5)	5788(4)	3028(2)	38(1)
N1	3059(5)	3364(4)	2219(2)	21(1)
C1	4046(6)	2239(5)	1514(3)	23(1)
C2	5834(5)	2687(5)	935(3)	18(1)
C3	6781(6)	1688(5)	192(3)	23(1)
C4	8451(6)	2107(5)	-368(3)	22(1)
C5	9246(6)	3507(5)	-195(3)	18(1)
C6	8268(5)	4580(4)	564(3)	18(1)
C7	8956(5)	6070(5)	770(3)	18(1)
C8	7907(6)	7088(5)	1498(3)	23(1)
C9	6209(6)	6678(5)	2032(3)	26(1)
C10	5511(5)	5235(5)	1857(3)	21(1)
C11	3683(6)	4851(5)	2420(3)	26(1)
C12	6538(6)	4162(4)	1125(3)	18(1)
C13	1248(6)	2942(5)	2796(3)	24(1)
C14	1850(30)	1627(15)	3758(6)	24(2)
C15	1927(12)	2260(11)	4650(6)	28(2)
C16	2342(11)	1030(13)	5539(5)	33(2)
C17	2743(11)	-822(10)	5503(5)	31(2)
C18	2738(9)	-1498(9)	4618(5)	29(1)
C19	2290(12)	-261(9)	3744(5)	24(1)
C14A	1830(80)	1860(30)	3846(13)	26(3)
C15A	2430(30)	-50(20)	4074(11)	27(2)
C16A	2740(20)	-985(17)	5061(12)	25(2)
C17A	2560(20)	110(20)	5789(9)	27(3)
C18A	1950(20)	2020(20)	5599(10)	28(3)
C19A	1560(30)	2880(20)	4632(12)	27(3)
F1A	3308(15)	-2739(11)	5323(8)	59(3)

**3,4-difluoro-PDI** Table 2. Atomic coordinates (x  $10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>x  $10^3$ ) for **3,4-difluoro-PDI**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

F2A

F1-C16	1.312(8)	C13-C14	1.504(8)
F2-C17	1.373(8)	C13-C14A	1.530(13)
O1-C1	1.226(5)	C13-H13A	0.97(5)
O2-C11	1.220(5)	C13-H13B	1.02(5)
N1-C1	1.401(5)	C14-C15	1.384(12)
N1-C11	1.399(5)	C14-C19	1.400(13)
N1-C13	1.483(5)	C15-H15	0.95
C1-C2	1.479(5)	C15-C16	1.386(12)
C2-C3	1.377(5)	C16-C17	1.380(11)
C2-C12	1.415(5)	C17-C18	1.384(9)
С3-Н3	0.95	C18-H18	0.95
C3-C4	1.393(6)	C18-C19	1.374(9)
С4-Н4	0.95	C19-H19	0.95
C4-C5	1.391(5)	C14A-C15A	1.40(2)
C5-C6	1.431(5)	C14A-C19A	1.39(2)
C5-C7#1	1.475(5)	C15A-H15A	0.95
C6-C7	1.427(5)	C15A-C16A	1.400(17)
C6-C12	1.427(5)	C16A-C17A	1.375(17)
C7-C8	1.389(5)	C16A-F1A	1.285(14)
С8-Н8	0.95	C17A-C18A	1.391(15)
C8-C9	1.392(6)	C17A-F2A	1.398(14)
С9-Н9	0.95	C18A-H18A	0.95
C9-C10	1.383(5)	C18A-C19A	1.366(16)
C10-C11	1.474(6)	C19A-H19A	0.95
C10-C12	1.412(5)		
C1-N1-C13	117.9(3)	C12-C2-C1	120.3(3)
C11-N1-C1	124.1(3)	С2-С3-Н3	119.8
C11-N1-C13	117.9(3)	C2-C3-C4	120.3(3)
01-C1-N1	119.9(4)	С4-С3-Н3	119.8
O1-C1-C2	122.6(4)	С3-С4-Н4	119.0
N1-C1-C2	117.4(3)	C5-C4-C3	122.1(4)
C3-C2-C1	119.6(3)	С5-С4-Н4	119.0
C3-C2-C12	120.1(3)	C4-C5-C6	118.5(4)

 $\textbf{3,4-difluoro-PDI} \text{ Table 3. Bond lengths [Å] and angles [°] for \textbf{3,4-difluoro-PDI}.$ 

C4-C5-C7#1	122.3(3)	C19-C14-C13	118.8(8)
C6-C5-C7#1	119.1(3)	C14-C15-H15	120.0
C7-C6-C5	122.0(4)	C14-C15-C16	120.0(7)
C7-C6-C12	118.9(3)	С16-С15-Н15	120.0
C12-C6-C5	119.1(3)	F1-C16-C15	121.0(8)
C6-C7-C5#1	118.9(3)	F1-C16-C17	120.5(7)
C8-C7-C5#1	121.9(3)	C17-C16-C15	118.5(7)
C8-C7-C6	119.2(3)	F2-C17-C16	118.2(7)
С7-С8-Н8	119.3	F2-C17-C18	119.0(6)
C7-C8-C9	121.4(3)	C16-C17-C18	122.8(6)
С9-С8-Н8	119.3	C17-C18-H18	120.9
С8-С9-Н9	119.5	C19-C18-C17	118.2(6)
C10-C9-C8	121.0(4)	C19-C18-H18	120.9
С10-С9-Н9	119.5	С14-С19-Н19	119.8
C9-C10-C11	119.9(3)	C18-C19-C14	120.4(7)
C9-C10-C12	119.5(4)	С18-С19-Н19	119.8
C12-C10-C11	120.6(3)	C15A-C14A-C13	124.2(18)
O2-C11-N1	119.6(4)	C19A-C14A-C13	117.0(16)
O2-C11-C10	123.0(4)	C19A-C14A-C15A	118.6(12)
N1-C11-C10	117.4(3)	C14A-C15A-H15A	118.8
C2-C12-C6	119.9(3)	C14A-C15A-C16A	122.3(13)
C10-C12-C2	120.0(3)	C16A-C15A-H15A	118.8
C10-C12-C6	120.1(3)	C17A-C16A-C15A	115.7(12)
N1-C13-C14	112.7(9)	F1A-C16A-C15A	125.6(14)
N1-C13-C14A	112(2)	F1A-C16A-C17A	118.6(13)
N1-C13-H13A	103(3)	C16A-C17A-C18A	123.9(11)
N1-C13-H13B	106(3)	C16A-C17A-F2A	117.5(12)
С14-С13-Н13А	113(3)	C18A-C17A-F2A	118.4(12)
С14-С13-Н13В	113(3)	C17A-C18A-H18A	120.7
С14А-С13-Н13А	121(3)	C19A-C18A-C17A	118.6(13)
C14A-C13-H13B	106(3)	C19A-C18A-H18A	120.7
H13A-C13-H13B	108(4)	C14A-C19A-H19A	119.6
C15-C14-C13	121.0(9)	C18A-C19A-C14A	120.7(13)
C15-C14-C19	120.2(6)	C18A-C19A-H19A	119.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
 F1	53(3)	140(5)	30(2)	-33(3)	-1(2)	-45(3)
F2	32(2)	93(4)	42(3)	29(3)	-7(2)	-20(2)
01	34(2)	34(2)	33(2)	-11(1)	2(1)	-21(1)
O2	36(2)	27(2)	53(2)	-18(1)	21(2)	-12(1)
N1	13(2)	19(2)	29(2)	-2(1)	-2(1)	-3(1)
C1	16(2)	22(2)	27(2)	-2(2)	-5(2)	-3(2)
C2	13(2)	18(2)	25(2)	-1(1)	-7(1)	-4(1)
C3	24(2)	20(2)	27(2)	-4(2)	-4(2)	-7(2)
C4	21(2)	18(2)	25(2)	-6(1)	-5(2)	-2(2)
C5	15(2)	16(2)	22(2)	-2(1)	-7(1)	-2(1)
C6	12(2)	14(2)	26(2)	-3(1)	-5(1)	1(1)
C7	13(2)	17(2)	23(2)	-2(1)	-6(1)	-1(1)
C8	21(2)	17(2)	31(2)	-8(2)	-1(2)	-4(2)
С9	26(2)	17(2)	32(2)	-8(2)	1(2)	-2(2)
C10	11(2)	17(2)	30(2)	-2(2)	-2(2)	3(1)
C11	19(2)	18(2)	35(2)	-4(2)	3(2)	0(2)
C12	16(2)	13(2)	24(2)	-2(1)	-6(1)	0(1)
C13	14(2)	28(2)	30(2)	-2(2)	0(2)	-6(2)
C14	11(3)	26(3)	33(3)	-3(2)	-1(3)	-4(3)
C15	16(3)	33(3)	36(3)	-10(3)	1(2)	-4(3)
C16	21(3)	41(4)	38(3)	-11(3)	-1(2)	-8(3)
C17	17(3)	42(3)	32(3)	-1(3)	-5(3)	-5(2)
C18	17(3)	32(3)	35(3)	-1(3)	-1(2)	-5(2)
C19	15(3)	25(3)	33(3)	-6(2)	2(3)	-8(2)
C14A	15(4)	27(5)	34(4)	-1(4)	0(4)	-5(4)
C15A	16(4)	29(4)	34(4)	-5(4)	0(4)	-5(3)
C16A	16(4)	29(4)	33(4)	-10(4)	-3(4)	-8(3)
C17A	16(4)	30(5)	33(5)	-3(4)	-6(4)	-5(4)
C18A	13(4)	34(5)	34(4)	-2(4)	-6(4)	-3(4)
C19A	17(4)	29(5)	33(4)	-1(4)	-2(4)	-5(4)
F1A	42(6)	40(5)	81(7)	22(5)	-7(5)	-4(4)

**3,4-difluoro-PDI** Table 4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **3,4-difluoro-PDI**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

F2A 40(5) 77(7) 38(5) 23(5) -	-10(4) -1	7(5)
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	Х	У	Z	U(eq)
Н3	6293	708	61	28
H4	9067	1414	-884	26
H8	8359	8084	1634	27
Н9	5518	7401	2525	31
H15	1692	3538	4652	34
H18	3037	-2781	4615	35
H19	2276	-690	3126	29
H15A	2636	-748	3540	32
H18A	1814	2709	6131	34
H19A	1091	4182	4493	32
H13A	640(70)	2440(60)	2320(30)	29(11
H13B	250(70)	4180(60)	2900(30)	31(11

**3,4-difluoro-PDI** Table 5. Hydrogen coordinates (  $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **3,4-difluoro-PDI**.

F1-C16-C17-F2	0.1(10)	C7-C6-C12-C10	1.2(5)
F1-C16-C17-C18	178.2(6)	C7-C8-C9-C10	0.2(6)
F2-C17-C18-C19	177.4(6)	C8-C9-C10-C11	-178.8(3)
01-C1-C2-C3	2.4(6)	C8-C9-C10-C12	0.0(6)
01-C1-C2-C12	-179.2(3)	C9-C10-C11-O2	2.0(6)
N1-C1-C2-C3	-176.3(3)	C9-C10-C11-N1	-179.4(3)
N1-C1-C2-C12	2.1(5)	C9-C10-C12-C2	-179.7(3)
N1-C13-C14-C15	91.2(16)	C9-C10-C12-C6	-0.7(5)
N1-C13-C14-C19	-90.6(16)	C11-N1-C1-O1	-179.9(3)
N1-C13-C14A-C15A	-92(4)	C11-N1-C1-C2	-1.2(5)
N1-C13-C14A-C19A	94(4)	C11-N1-C13-C14	-89.6(6)
C1-N1-C11-O2	177.9(3)	C11-N1-C13-C14A	-80.2(11)
C1-N1-C11-C10	-0.7(5)	C11-C10-C12-C2	-0.9(5)
C1-N1-C13-C14	90.0(6)	C11-C10-C12-C6	178.1(3)
C1-N1-C13-C14A	99.3(11)	C12-C2-C3-C4	0.8(5)
C1-C2-C3-C4	179.2(3)	C12-C6-C7-C5#1	179.5(3)
C1-C2-C12-C6	179.9(3)	C12-C6-C7-C8	-0.9(5)
C1-C2-C12-C10	-1.1(5)	C12-C10-C11-O2	-176.8(4)
C2-C3-C4-C5	1.0(6)	C12-C10-C11-N1	1.8(5)
C3-C2-C12-C6	-1.7(5)	C13-N1-C1-O1	0.5(5)
C3-C2-C12-C10	177.3(3)	C13-N1-C1-C2	179.3(3)
C3-C4-C5-C6	-1.9(5)	C13-N1-C11-O2	-2.5(5)
C3-C4-C5-C7#1	178.6(3)	C13-N1-C11-C10	178.8(3)
C4-C5-C6-C7	-178.4(3)	C13-C14-C15-C16	175.3(12)
C4-C5-C6-C12	0.9(5)	C13-C14-C19-C18	-176.4(11)
C5-C6-C7-C5#1	-1.1(5)	C13-C14A-C15A-C16A	-173(3)
C5-C6-C7-C8	178.4(3)	C13-C14A-C19A-C18A	177(3)
C5-C6-C12-C2	0.9(5)	C14-C15-C16-F1	-176.4(12)
C5-C6-C12-C10	-178.2(3)	C14-C15-C16-C17	2.1(15)
C5#1-C7-C8-C9	179.8(3)	C15-C14-C19-C18	2(2)
C6-C7-C8-C9	0.3(5)	C15-C16-C17-F2	-178.5(6)
C7#1-C5-C6-C7	1.2(6)	C15-C16-C17-C18	-0.3(11)
C7#1-C5-C6-C12	-179.5(3)	C16-C17-C18-C19	-0.8(10)
C7-C6-C12-C2	-179.8(3)	C17-C18-C19-C14	0.0(14)

## **3,4-difluoro-PDI** Table 6. Torsion angles [°] for **3,4-difluoro-PDI**.

C19-C14-C15-C16	-3(2)	C16A-C17A-C18A-C19A	-2(2)
C14A-C15A-C16A-C17A	-5(4)	C17A-C18A-C19A-C14A	-2(3)
C14A-C15A-C16A-F1A	-179(3)	C19A-C14A-C15A-C16A	1(5)
C15A-C14A-C19A-C18A	3(5)	F1A-C16A-C17A-C18A	-179.7(13)
C15A-C16A-C17A-C18A	5(2)	F1A-C16A-C17A-F2A	-5(2)
C15A-C16A-C17A-F2A	179.3(14)	F2A-C17A-C18A-C19A	-176.0(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z

End crystallographic info for **3,4-difluoro-PDI**.

#### **CRYSTALLOGRAPHIC MATERIAL FOR 3,5-DIFLUORO-PDI**

Crystallographic Material for**3,5-difluoro-PDI**.

X-ray Experimental.

Table 1. Crystallographic Data for **3,5-difluoro-PDI**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters  $(Å^2)$  for the non-hydrogen atoms of **3,5-difluoro-PDI**.

Table 3. Bond Lengths (Å) and Angles (<sup>0</sup>) for the non-hydrogen atoms of **3,5-difluoro-PDI**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **3,5-difluoro-PDI**.

Table 5. Fractional coordinates and isotropic thermal parameters  $(Å^2)$  for the hydrogen atoms of **3,5-difluoro-PDI**.

Table 6. Torsion Angles (<sup>0</sup>) for the non-hydrogen atoms of **3,5-difluoro-PDI**.

X-ray Experimental for C<sub>38</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>F<sub>4</sub> (**3,5-difluoro-PDI**): Crystals grew as long, thin red needles by sublimation. The data crystal was cut from a larger crystal and had approximate dimensions of 0.3 x 0.02 x 0.02 mm. The data were collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength = 0.97741Å. A total of 180 frames of data were collected using  $\phi$ -scans with a scan range of 1° and a counting time of 1 seconds per frame for frames collected with a detector offset of 0.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection was performed using the Beamline Operating Software, BOS/B3. The unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.37a.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>2</sup> and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic displacement

parameters for the non-H atoms using SHELXL-2018/3.<sup>3</sup> Structure analysis was aided by use of the programs PLATON<sup>4</sup> and OLEX2<sup>5</sup>. The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The molecule resides around a crystallographic inversion center at  $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ .

The function,  $\Sigma w(|F_0|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_0))^2 + (0.1547*P)^2]$ and  $P = (|F_0|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.152, with R(F) equal to 0.0571 and a goodness of fit, S, = 0.866. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit, S, are given below.<sup>6</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>7</sup> All figures were generated using SHELXTL/PC.<sup>8</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

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  $$\begin{split} R_W(F^2) &= \{ \Sigma w (|F_0|^2 |F_c|^2)^2 / \Sigma w (|F_0|)^4 \}^{1/2} \text{ where } w \text{ is the weight given each reflection.} \\ R(F) &= \Sigma (|F_0| |F_c|) / \Sigma |F_0| \} \text{ for reflections with } F_0 > 4(\sigma(F_0)). \\ S &= [\Sigma w (|F_0|^2 |F_c|^2)^2 / (n p)]^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections and } p \text{ is the number of reflections}. \end{split}$$
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Empirical formula	C38 H18 F4 N2 O4		
Formula weight	642.54		
Temperature	100.15 K		
Wavelength	0.97741 Å		
Crystal system	monoclinic		
Space group	C 1 2/c 1		
Unit cell dimensions	a = 28.576(2) Å	α= 90°.	
	b = 4.3750(2) Å	β= 103.684(8)°.	
	c = 22.0997(14) Å	$\gamma = 90^{\circ}$ .	
Volume	2684.5(3) Å <sup>3</sup>		
Ζ	4		
Density (calculated)	1.590 Mg/m <sup>3</sup>		
Absorption coefficient	0.270 mm <sup>-1</sup>		
F(000)	1312		
Crystal size	0.3 x 0.02 x 0.02 mm <sup>3</sup>		
Theta range for data collection	2.609 to 26.291°.		
Index ranges	-24<=h<=22, -3<=k<=3, -15<=l<=19		
Reflections collected	1545		
Independent reflections	704 [R(int) = 0.0154]		
Completeness to theta = $26.291^{\circ}$	68.5 %		
Absorption correction	Semi-empirical from equivaler	nts	
Max. and min. transmission	1.00000 and 0.64368		
Refinement method	Full-matrix least-squares on F <sup>2</sup>	!	
Data / restraints / parameters	704 / 345 / 217		
Goodness-of-fit on F <sup>2</sup>	1.068		
Final R indices [I>2sigma(I)]	R1 = 0.0571, $wR2 = 0.1493$		
R indices (all data)	R1 = 0.0586, $wR2 = 0.1522$		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.194 and -0.209 e.Å <sup>-3</sup>		

# **3,5-difluoro-PDI** Table 1. Crystal data and structure refinement for **3,5-difluoro-PDI**.

	X	У	Z	U(eq)
C1	6510(2)	6961(11)	6788(2)	47(2)
C2	6153(2)	5967(10)	6230(2)	44(2)
C3	6289(2)	3957(10)	5823(2)	52(2)
C4	5968(2)	2937(9)	5285(2)	55(2)
C5	5495(2)	3919(10)	5142(2)	46(2)
C6	5332(2)	6001(10)	5543(2)	44(2)
C7	4845(2)	7040(10)	5426(3)	48(2)
C8	4721(2)	8965(10)	5861(2)	52(2)
C9	5051(2)	9948(9)	6398(2)	52(2)
C10	5524(2)	9004(10)	6514(2)	46(2)
C11	5869(2)	10119(12)	7075(3)	52(2)
C12	5669(2)	6960(10)	6093(2)	45(2)
C13	6704(2)	10218(9)	7710(2)	53(2)
C14	6789(2)	8061(9)	8253(2)	51(2)
C15	7252(2)	7224(9)	8543(2)	60(2)
C16	7320(2)	5313(11)	9054(2)	66(2)
C17	6952(2)	4121(10)	9277(2)	62(2)
C18	6504(2)	4951(11)	8975(2)	56(2)
C19	6404(2)	6910(10)	8472(2)	56(2)
F1	7779(1)	4465(6)	9334(1)	87(1)
F2	6124(1)	3754(5)	9162(1)	72(1)
N1	6346(1)	9095(8)	7165(2)	52(1)
01	6923(1)	6117(6)	6922(1)	57(1)
02	5761(1)	11921(7)	7439(2)	66(1)

**3,5-difluoro-PDI** Table 2. Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters  $(Å^2x \ 10^3)$  for **3,5-difluoro-PDI**. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

C1-C2	1.468(7)	C10-C12	1.422(7)
C1-N1	1.405(6)	C11-N1	1.402(6)
C1-O1	1.203(5)	C11-O2	1.218(5)
C2-C3	1.377(6)	C13-H13A	0.99
C2-C12	1.414(6)	C13-H13B	0.99
С3-Н3	0.95	C13-C14	1.500(6)
C3-C4	1.392(6)	C13-N1	1.468(5)
С4-Н4	0.95	C14-C15	1.377(6)
C4-C5	1.382(6)	C14-C19	1.396(6)
C5-C6	1.423(8)	C15-H15	0.95
C5-C7#1	1.454(7)	C15-C16	1.381(6)
C6-C7	1.429(6)	C16-C17	1.365(6)
C6-C12	1.422(6)	C16-F1	1.364(6)
C7-C8	1.387(6)	C17-H17	0.95
С8-Н8	0.95	C17-C18	1.345(7)
C8-C9	1.397(6)	C18-C19	1.379(6)
С9-Н9	0.95	C18-F2	1.356(5)
C9-C10	1.378(7)	С19-Н19	0.95
C10-C11	1.472(7)		
N1 C1 C2	115 ((5)	CC 05 C7#1	110 2(5)
NI-CI-C2	115.6(5)	C6-C5-C7#1	118.2(5)
01-01-02	124.2(6)	C5-C6-C7	122.5(5)
OI-CI-NI	120.2(5)	C5-C6-C12	117.8(5)
C3-C2-C1	119.4(5)	C12-C6-C7	119.6(6)
C3-C2-C12	117.9(5)	C6-C7-C5#1	119.2(6)
C12-C2-C1	122.7(6)	C8-C7-C5#1	123.1(5)
С2-С3-Н3	118.9	C8-C7-C6	117.7(6)
C2-C3-C4	122.2(4)	С7-С8-Н8	118.5
С4-С3-Н3	118.9	C7-C8-C9	122.9(4)
С3-С4-Н4	119.8	С9-С8-Н8	118.5
C5-C4-C3	120.5(5)	С8-С9-Н9	119.9
С5-С4-Н4	119.8	C10-C9-C8	120.2(5)
C4-C5-C6	120.1(6)	С10-С9-Н9	119.9
C4-C5-C7#1	121.7(6)	C9-C10-C11	119.4(6)

 $\textbf{3,5-difluoro-PDI} \quad \text{Table 3.} \quad \text{Bond lengths [Å] and angles [°] for } \textbf{3,5-difluoro-PDI}$ 

C9-C10-C12	119.4(5)	C14-C15-C16	118.4(5)
C12-C10-C11	121.2(4)	С16-С15-Н15	120.8
N1-C11-C10	116.7(6)	C17-C16-C15	123.7(5)
O2-C11-C10	123.1(5)	F1-C16-C15	118.1(5)
O2-C11-N1	120.2(5)	F1-C16-C17	118.2(5)
C2-C12-C6	121.5(6)	С16-С17-Н17	121.9
C2-C12-C10	118.3(5)	C18-C17-C16	116.2(5)
C10-C12-C6	120.2(5)	С18-С17-Н17	121.9
H13A-C13-H13B	107.7	C17-C18-C19	124.1(5)
С14-С13-Н13А	108.9	C17-C18-F2	118.7(4)
C14-C13-H13B	108.9	F2-C18-C19	117.2(5)
N1-C13-H13A	108.9	С14-С19-Н19	120.9
N1-C13-H13B	108.9	C18-C19-C14	118.2(5)
N1-C13-C14	113.3(3)	С18-С19-Н19	120.9
C15-C14-C13	119.7(4)	C1-N1-C13	116.3(4)
C15-C14-C19	119.5(4)	C11-N1-C1	125.3(5)
C19-C14-C13	120.8(4)	C11-N1-C13	118.4(5)
С14-С15-Н15	120.8		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C1	45(4)	51(3)	45(3)	6(2)	13(4)	-9(3)
C2	33(4)	52(3)	45(3)	9(2)	9(3)	-1(2)
C3	50(4)	56(3)	53(3)	-1(2)	18(3)	2(2)
C4	52(4)	58(3)	59(3)	1(3)	22(3)	6(2)
C5	51(4)	45(3)	46(4)	-4(2)	19(4)	-2(3)
C6	37(4)	48(3)	47(3)	1(2)	10(4)	-2(2)
C7	44(5)	47(3)	58(4)	2(3)	22(4)	1(2)
C8	40(4)	55(3)	61(3)	-1(2)	13(3)	3(2)
C9	47(4)	54(3)	56(3)	-3(2)	16(3)	3(2)
C10	36(4)	50(3)	51(3)	3(2)	8(3)	0(2)
C11	51(4)	50(3)	58(3)	2(3)	18(4)	2(2)
C12	36(4)	48(3)	48(3)	5(2)	7(3)	3(2)
C13	54(4)	54(3)	52(3)	-5(2)	14(3)	-3(2)
C14	55(4)	51(3)	50(3)	-6(2)	21(3)	3(2)
C15	60(4)	64(3)	59(3)	6(2)	21(3)	-3(2)
C16	52(4)	75(3)	71(4)	7(3)	13(3)	-4(3)
C17	64(4)	65(3)	63(4)	5(2)	25(3)	-10(3)
C18	58(4)	61(3)	59(3)	-7(3)	35(3)	-9(3)
C19	57(4)	59(3)	60(3)	-7(2)	27(3)	2(2)
F1	62(2)	107(2)	91(2)	36(2)	17(2)	-3(2)
F2	70(2)	79(2)	80(2)	-1(1)	46(2)	-11(1)
N1	52(3)	52(3)	56(3)	-2(2)	21(3)	-1(2)
01	42(3)	66(2)	65(2)	-1(2)	14(2)	4(2)
02	67(3)	64(2)	68(2)	-15(2)	18(2)	4(2)

**3,5-difluoro-PDI** Table 4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **3,5-difluoro-PDI**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2$ [ h<sup>2</sup> a<sup>\*2</sup>U<sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

	х	У	Z	U(eq)
H3	6612	3243	5913	63
H4	6075	1555	5015	66
H8	4397	9644	5792	62
Н9	4949	11270	6683	62
H13A	6594	12206	7840	64
H13B	7012	10566	7591	64
H15	7518	7942	8395	72
H17	7009	2782	9625	75
H19	6081	7461	8279	67

**3,5-difluoro-PDI** Table 5. Hydrogen coordinates ( $x \ 10^4$ ) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for **3,5-difluoro-PDI**.

C1-C2-C3-C4	-179.8(3)	C11-C10-C12-C2	1.2(6)
C1-C2-C12-C6	178.9(3)	C11-C10-C12-C6	-177.8(3)
C1-C2-C12-C10	0.0(6)	C12-C2-C3-C4	1.0(6)
C2-C1-N1-C11	5.3(5)	C12-C6-C7-C5#1	179.1(3)
C2-C1-N1-C13	-177.4(3)	C12-C6-C7-C8	-0.1(6)
C2-C3-C4-C5	-0.2(6)	C12-C10-C11-N1	0.8(6)
C3-C2-C12-C6	-1.9(6)	C12-C10-C11-O2	178.3(3)
C3-C2-C12-C10	179.2(3)	C13-C14-C15-C16	177.9(3)
C3-C4-C5-C6	0.3(6)	C13-C14-C19-C18	-179.6(4)
C3-C4-C5-C7#1	178.2(3)	C14-C13-N1-C1	-80.8(4)
C4-C5-C6-C7	-178.5(4)	C14-C13-N1-C11	96.8(4)
C4-C5-C6-C12	-1.2(6)	C14-C15-C16-C17	2.2(6)
C5-C6-C7-C5#1	-3.5(6)	C14-C15-C16-F1	179.3(3)
C5-C6-C7-C8	177.2(3)	C15-C14-C19-C18	-0.2(6)
C5-C6-C12-C2	2.0(6)	C15-C16-C17-C18	-1.1(7)
C5-C6-C12-C10	-179.1(3)	C16-C17-C18-C19	-0.7(7)
C5#1-C7-C8-C9	-178.2(3)	C16-C17-C18-F2	177.8(3)
C6-C7-C8-C9	1.0(6)	C17-C18-C19-C14	1.3(6)
C7#1-C5-C6-C7	3.5(6)	C19-C14-C15-C16	-1.5(6)
C7#1-C5-C6-C12	-179.1(3)	F1-C16-C17-C18	-178.2(4)
C7-C6-C12-C2	179.4(3)	F2-C18-C19-C14	-177.2(3)
C7-C6-C12-C10	-1.6(6)	N1-C1-C2-C3	177.8(3)
C7-C8-C9-C10	-0.1(6)	N1-C1-C2-C12	-3.0(5)
C8-C9-C10-C11	178.6(3)	N1-C13-C14-C15	129.1(4)
C8-C9-C10-C12	-1.7(6)	N1-C13-C14-C19	-51.4(5)
C9-C10-C11-N1	-179.6(3)	01-C1-C2-C3	-0.4(6)
C9-C10-C11-O2	-2.0(6)	01-C1-C2-C12	178.7(3)
C9-C10-C12-C2	-178.5(3)	O1-C1-N1-C11	-176.4(4)
C9-C10-C12-C6	2.5(6)	O1-C1-N1-C13	1.0(5)
C10-C11-N1-C1	-4.2(6)	O2-C11-N1-C1	178.1(3)
C10-C11-N1-C13	178.4(3)	O2-C11-N1-C13	0.8(6)

# **3,5-difluoro-PDI** Table 6. Torsion angles [°] for **3,5-difluoro-PDI**.

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

End 3,5-difluoro-PDI crystal information

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