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Investigation of the relationships between component side-chain identity and bulk material properties of donor-acceptor columnar liquid crystals

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Denison University Chemistry and Biochemistry
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Abstract

The combination of two component aromatic molecules, one with electron-donating groups (donor) and the other having electron-withdrawing groups (acceptor) can lead to the self-assembly of donor-acceptor columnar liquid crystals (DACLCs). The peripheral side chains of these component molecules play an essential role in several key properties of DACLC materials, including phase change temperatures, phase structure, solubility, and even charge mobility. However, the extent to which, and exactly how, altering these sidechains affects the DACLC properties is poorly understood. In particular, looking beyond simple alkyl chains to the inclusion of heteroatoms should significantly affect the range of properties in DACLCs, but has yet to be explored. Here we present a modular series of side-chain derivatives, including heteroatom chains, based on the 1,5–diamino naphthalene (1,5-DAN) donor and naphthalene diimide (NDI) acceptor aromatic cores. The design, synthesis, and characterization of these component molecules will be described as well as the characterization of their combination to form new DACLC materials. Analysis of the phase change behavior of the DACLCs from differential scanning calorimetry data will be discussed, including general insights into the effects of side-chain identity on bulk DACLC properties.

Acknowledgments

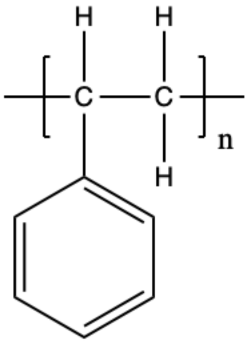
I would like to thank Dr. Joe for being an amazing research advisor. I am grateful that you allowed me to join your research team my junior year. Thank you for teaching me new techniques and skills to better guide me in my future research career. Thank you for being a great mentor as well as a great research advisor.

I would like to thank Dr. Fantini for being my second reader for my senior research. I would like to thank the Reczek research group for being there for me and helping me figure out how to operate different chemical machinery in the lab. Lastly, I would like to tank Dr. Edwards for being a great advisor and encouraging me to pursue research at Denison.

Introduction and Background

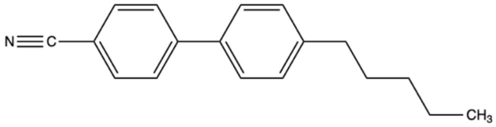
Organic Material

Everything we interact with as we move through the world is made of chemicals. This includes the various “structural” material that makes up things like our living spaces, furniture, clothes, and our electronic devices. These materials can be broken up into multiple categories by chemical types, such as Synthetic vs Natural, and Organic vs Inorganic. In this paper, I will be focusing on a class of synthetic (made in the lab) organic materials. Organic materials are largely compromised of a diversely bonded set of carbon and hydrogen atoms. One appealing feature of organic materials in particular is our ability to control, alter, and tune their molecular structure relatively easily, allowing for well-designed experiments relating the molecular structure of organic materials to the characterization of their physical properties (Figure 1). In addition to many common items, organic materials offer exciting potential for use in advanced technology such as photoreceptors and electrophotography.[7] They can also be used as a key component in semi-conducting materials.[7] This concept was more concretely explored in the 1990's by Adam and others.[5] It was a great component for semiconducting material due to its small nanoparticles that contain π conjugating building blocks. A specific form of organic materials are liquid crystals which play a role in order and dynamic of the molecules.



Polystyrene – Molecular Structure

Packing Foam – Bulk Application



5-CB – Molecular Structure

Flat Screen TV – Bulk Application

Figure 1: Synthetic Organic Material

Liquid Crystals

Liquid crystals are a class of organic materials defined by having a transitional phase between crystalline solids and completely isotropic liquids. As they have a phase that is in the "middle" of these two well-known phases of matter, the liquid crystal state has some physical properties similar with liquids and crystals. It is also characterized as a supramolecular system due to its intermolecular forces, such as hydrogen bonding which helps in the assembly of its self-organization. A supramolecular system is composed of lots of complex molecules that are able to assemble because of non-covalent bonding. Liquid crystals are generally broken up in two categories: lyotropic and thermotropic.[4] Lyotropic purpose is to become a micelle and orient itself on a cylinder or hexagonal orientation. In this research we will be focusing more on thermotropic liquid crystals. The thermotropic system create flexibility once heated allowing molecules to position its orientation as transitional and/or rotational. Thermotropic liquid crystals can be further specified into two categories: calamitic and discotic (Figure 2).[4]

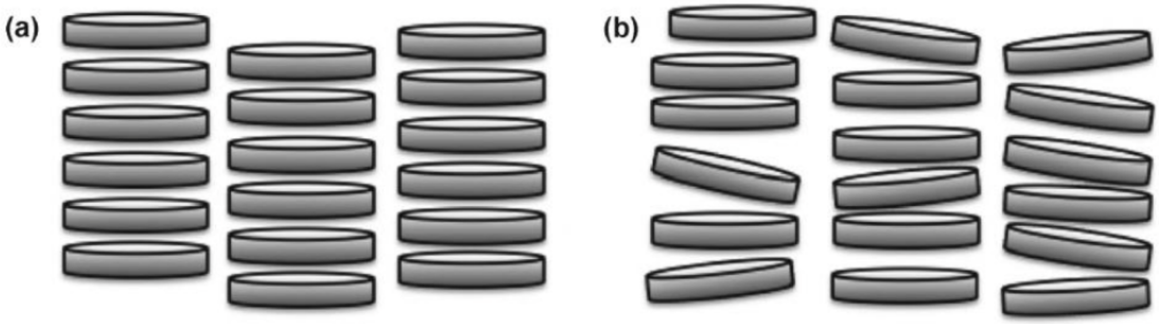
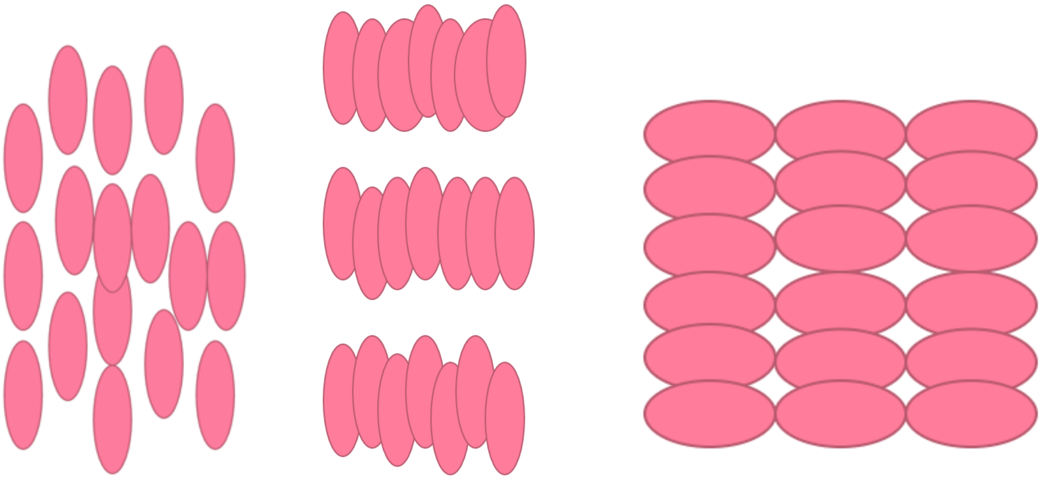


Figure 2: Depiction of (a) evenly stacks DLC's and (b) disarranged stacks of DLC's (Adapted from Reczek, 2017)

Discotic Liquid Crystals/ Columnar Liquid Crystals

This research focuses on discotic liquid crystals which can be tracked back to 1977 by Chandrasekhar.[2] Discotic liquid crystals exemplify 2 dimensional columns that exemplify face stacking column packing. Around the columns are rigid cores that's have the ability to form π- π overlap between neighboring molecules within the columns with a distance of about 3.9 and 4.4 Å.[4] Face centered stacking can alternate from donors and acceptors.

Discotic liquid crystals have similar characteristics to other liquid crystals phases. Discotic liquid crystals are characterized by its orientation and order within a column just like the smectic phases. Also, the discotic liquid crystals and the nematic phase both share a similar orientation. As far as stacking, the discotic liquid crystal prefers hexagonal packing the most but is able to do face-oriented stacking as well. A lot of the phases within discotic liquid crystals are considered columnar plastic due to the molecules having the ability to attain rotational orientations more than the columns.[4]



Nematic phase Smectic Phase Discotic (Columnar) Phase

Figure 3: Different Liquid crystal materials

Donor-Acceptor Columnar Liquid Crystals

Donors acceptor liquid crystals derive from discotic liquid crystals. It describes the face stacking mechanisms of each molecule. The acceptors are electron poor (LUMO), in this research the acceptor is Napthalenediimids (NDI). The donors are electron rich (HOMO), in this research the donor was 1,5 -diaminonaphthalene (DAN). The alternation between donors and acceptors within the π- π face stacking causes and increase in charge mobility. This π- π stacking can stabilize the mesophase behavior unlike regular columnar liquid crystals. These distinctive charge mobility properties on DACLC's can further advance the optoelectronic field.[3] Donor acceptor liquid crystals experience unique properties due to its combination of HOMO and LUMO molecules. One of these unique characteristics is it's charge transfer (CT) absorption frequency, which allows colors to be observed (Figure 4). When the HOMO and LUMO are thoroughly mixed via heat it causes extreme color change. This extreme color change derives from a strong absorption from the donor to acceptor electrons. The intensity of absorption changes based on the distance traveled between the two molecules.[1] Donor acceptor liquid crystals charge mobility, charge transfer absorption, and the intensity of absorption causes it to vary from regular columnar liquid crystals which make it a great candidate for advancing technology.

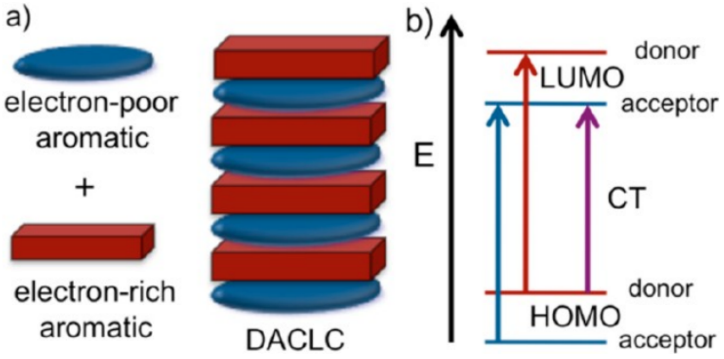


Figure 4: (a) Depiction of a donor acceptor columnar liquid crystal. (b) Diagram of CT, HOMO and LUMO absorbance in donor acceptor columnar liquid crystals. (Adapted from Reczek, 2012).

Project Overview

As mentioned in the introduction, one of the attractive features of synthetic organic materials is the potential to control their molecular structure and therefore tune their various properties. This is especially true of DACLC materials, as there two molecular components that can be altered independently. However, exactly how changes in molecular structure affect property changes in DACLC is largely unknown. We therefore need to devise thoughtful, iterative experiments in changing molecular structure to learn about the related effects and trends in DACLC material properties.

Here, I will discuss my work towards understanding how heteroatoms affect the range of properties in Donor Acceptor Liquid Crystals. Specifically, I would like to analyze how alcohol, ether, and alkene side chain groups on the donor molecules affect the temperature of the phase changes of the 1:1 donor acceptor relationship between 1,5-diamenonaphthalene (DAN) and naphthalenediimide (NDI). Then I delved deeper and investigated the effects of temperature when the acceptor naphthalenediimide (NDI) has two variations; Octyl NDI and GP6 1-82 that possess different side chains groups.

The purpose of the experiment is to understand how sidechains on the donor and acceptor liquid crystals can affect its bulk properties. Each side chain was chosen strategically to further understand how differentiating side chains would have an effect on the molecule. This work was originally done by Niquana Smith who observed how different length of alkane chains affected bulk material. She highlighted that a simple addition of two carbons on an alkane chain can change the molecules color properties from white to black. This change made it possible to understand that heteroatoms effects DACLC's properties. The side chains I will be focusing on are alkenes, alcohols, and ethers. Alkenes possess a different shape than the other side chains, so it'll be interesting to see how that might affect the donor molecule properties. Alcohol is able to form hydrogen bonds, which is a unique characteristic that might affect the donor molecule properties. Ether has greater flexibility than the other side chains due to the oxygen being in the middle of the chain, which can possibly produce interesting results about the donor molecule properties. Not only were the side chains on the donor molecules changed, but the side chains on the acceptor molecule was changed as well. The Octyl NDI acceptor possessed an alkane chain to represent the standard NDI. The GP6 1-82 contained ether groups within its sidechain, and we used this to explore how the flexibility within an acceptor molecule might change the DACLC property. In this experiment we mixed alkene, alcohol, and ether with GP6 1-82 NDI and Octyl NDI to understand how the different combinations of standard and flexible acceptor molecule side chains would interact with the variability of donor molecules and affect the temperature of the phase changes (Figure 5).

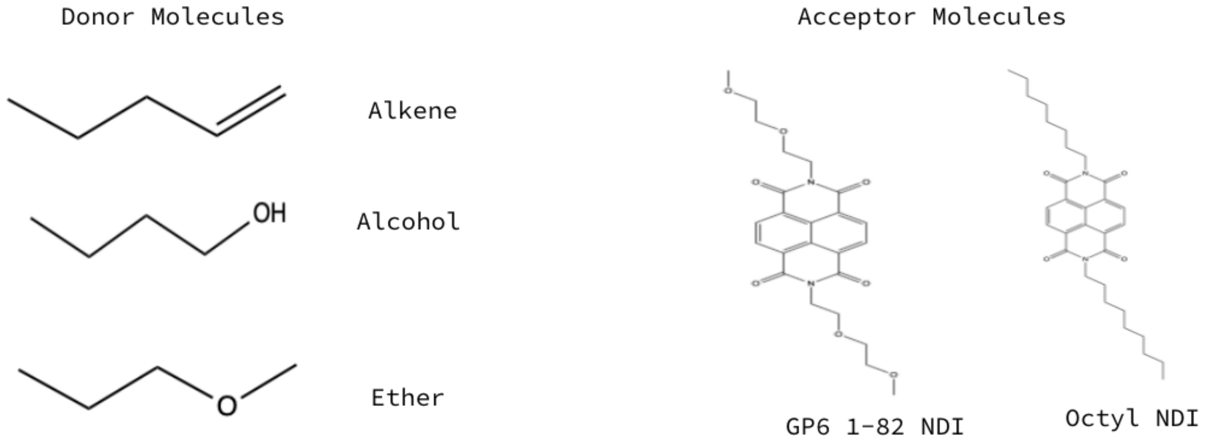


Figure 5: Donor and Acceptor side chain variability

Experimental

Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC) can be used to identify a specific compound or track a reactions progression. To carry out TLC a silica plate is needed which has a powdery consistency on one side. To get started in the process you take the original compound, in this research our original compound is 1,5 -diaminonaphthalene, and dot it on the silica plate using the tip of a small pipette. To compare the reaction progression, we take the reactions compound liquid and spot it on the same side as the original compound. After the solvent and mixture has been spotted it is then concealed in a mason jar where ~1mL of a polar solvent, dichloromethane (DCM) is added. Then the top of the mason jar is closed to allow the DCM to travel to ~90% of the silica plate. Once it has reached that point the silica plate is then brought under a UV light to observe the reactions process. The UV light shows how far the original and reaction compound moved on the silica plate. If the reaction compound is separated into 3 dots, then the reaction is considered complete and can move on to vacuum filtration which will lead to an NMR being taken.

Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) can be used to identify molecular identity and structures. In this research NMR was used as an analysis tool to check if the molecular structure is a consistent product from the reaction. For NMR to work the hydrogen nucleus is put in a magnetic field that explores different aspects of the molecule. It can be used to explore a molecules chemical shift, composition of atomic group, atomic ration, and different compounds in a mixture. We are able to analyze all of these components when looking at the NMR final product sheet. In this research the NMR was to analyze the 1:1 ratio between NDI and DAN, and also to analyze the new products of DAN when the ether, alcohol, and alkene sidechains were added. After NMR is interpreted, we then use DSC.

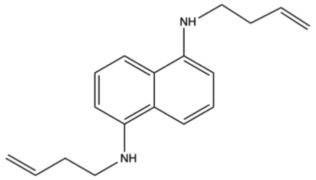
Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) tracks the temperature changes of the experimental sample based on the samples chemical and physical properties. DSC was first introduced in the

1960's to be used for polymer science.[6] In this experiment DSC was used as an analytical technique to observe the heating and cooling rates of the experimental sample. In the DSC machine it has a reference pan and a sample pan. The sample pan contains ~1– 3mg of the experimental sample. The machine is set up to heat at a maximum of 180 °C and to cool down to a maximum of -20 °C. The machine operates on a heat, cool, heat cycle which changes temperatures 10 °C per minute. The system is keeping track of the different phase changes the sample is going through by heating the reference and sample pan equally. Once the sample pan is going through a phase change, we'll see a sharp peak in the results to indicate that the sample is going through a change while the reference pan is not. The amount of heat absorbed from the reference and sample pans are different which is how we get our results.

General Reagents and Instruments

All reagents and solvents used were purchased from Sigma Aldrich. The Rotovape used was. The H' NMR spectra used was 400 MHz JEOL NMR instrument. The DSC information derived from the Q20 series instrument (Figure 6).



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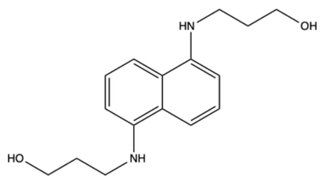

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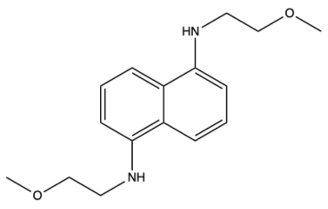

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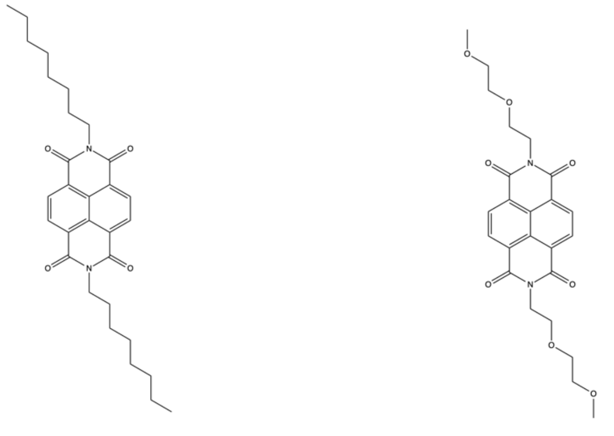

d e

Figure 6: (a) Donor molecule with an alkene side chain. (b) Donor molecule with an alcohol side chain. (c) Donor molecule with an ether side chain. (e) Octyl NDI. (f) GP6 1-82 NDI.

1,5-Diaminonaphthalene Recrystallization Methods

General Synthesis of 1, 5 -diaminonaphthalene derivates: Alkene

In a 250 mL round bottom flask ~1.00g of 1,5-diaminonaphthalene and ~5.27g of $K_2CO_{3,}$ were stirred together in 50 mL of acetone. The mixture refluxed at 65°C for 30 minutes. After 30 minutes 4-Bromo-1-butene was added and refluxed for 72 hours. After 72 hours the reaction was checked by TLC. The reaction was removed from reflux and cooled to room temperature. Then the filtrate was collected after vacuum filtration. The solute is then collected after rotovapping mixture at 55°C for ~15 minutes. 5 mL of isopropanol is added to rotovaped solute and heated slightly until mixture becomes homogeneous. Mixture is then cooled down to room temperature, covered with parafilm and put in the freezer at -20 °C for 24 hours. After 24 hours the product is cooled to room temperature. The crystals are then collected from vacuum filtration.

General Synthesis of 1, 5 -diaminonaphthalene derivates: Alcohol

In a 250 mL round bottom flask ~1.00g of 1,5-diaminonaphthalene and ~5.25g of $K_2CO_{3,}$ were stirred together in 50 mL of acetone. The mixture refluxed at 62°C for 30 minutes. After 30 minutes 3-Bromo-1-Propanol was added and refluxed for 72 hours. After 72 hours the reaction was checked by TLC. The reaction was removed from reflux and cooled to room temperature. Then the filtrate was collected after vacuum filtration. The solute is then collected after rotovapping mixture at 52°C for ~15 minutes. 5 mL of isopropanol is added to rotovaped solute and heated slightly until mixture becomes homogeneous. Mixture is then cooled down to room temperature, covered with parafilm and put in the freezer at -20 °C for 24 hours. After 24 hours the product is cooled to room temperature. The crystals are then collected from vacuum filtration.

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General Synthesis of 1, 5 -diaminonaphthalene derivates: Ether

In a 250 mL round bottom flask ~1.05g of 1,5-diaminonaphthalene and ~5.49g of $K_2CO_{3,}$ were stirred together in 50 mL of acetone. The mixture refluxed at 40°C for 30 minutes. After 30 minutes 1-Bromo-2-Methoxyethane was added and refluxed for 72 hours. After 72 hours the reaction was checked by TLC. The reaction was removed from reflux and cooled to room temperature. Then the filtrate was collected after vacuum filtration. The solute is then collected after rotovapping mixture at 30°C for ~15 minutes. 5 mL of isopropanol is added to rotovaped solute and heated slightly until mixture becomes homogeneous. Mixture is then cooled down to room temperature, covered with parafilm and put in the freezer at -20 °C for 24 hours. After 24 hours the product is cooled to room temperature. The crystals are then collected from vacuum filtration.

1,5-Diaminonaphthalene Recrystallization Results and Discussion

An H' NMR was taken for 1,5 diamenonaphthalene with an alkene, alcohol, and ether side chains. All of the H' NMR represented the component of each individual molecule. When comparing the three molecules they all share the same triple, single, double peak pairing at ~ 7.3. The alkene and alcohol NMR both share double peaks at ~6.6, while ether has a triple bond at ~6.7. Alkene is the only molecule that has peaks at ~5 and 6 due to its alkene bonding. Ether and alcohol both have peaks at ~4 due to the oxygen that is present within the molecule. Alkene and alcohol both share peaks at ~2. In these H' NMR results there are no particular trends between the molecules to connect one molecule more than the other. The biggest similarities are between ether and alcohol which contains an oxygen within the molecule.

Naphthalenediimide Variations Methods

General Synthesis of Octyl Naphthalenediimide

In a 250 mL round bottom flask ~2.00g of 1,4,5,8-Naphthalenetetracarboxylic Dianhydride in 50 mL of isopropanol. Then ~3.71g of Octylamine was added and refluxed for 24 hours. After 24 hours the reaction was checked by TLC. Reaction was removed from reflux and cooled to room temperature. Then the filtrate was collected after vacuum filtration. After the vacuum filtration an H’ NMR was taken to further analyze the components of the Octyl Naphthalenediimide product.

General Synthesis of GP6 1-82 NDI

Previously, a now graduate, from the Reczek laboratory created the GP6 1-82 molecule for a previous experiment that focus was on the alignment of Naphthalenediimide and 1,5-Diaminonaphthalene as they created donor acceptor columnar liquid crystals.

1:1 NDI and DAN Methods

General Synthesis of DAN with an Alkene side chain and Octyl NDI

In a small disposable vial ~0.049g of DAN with an alkene side chain and ~0.073g of Octyl NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis. After NMR analysis 1.67g of the 1:1 mixture was used for DSC analysis.

General Synthesis of DAN with an Alkene side chain and GP6 1-82 NDI

In a small disposable vial ~0.044g of DAN with an alkene side chain and ~0.057g of GP6 1-82 NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis. After NMR analysis 47g of the 1:1 mixture was used for DSC analysis.

General Synthesis of DAN with an Alcohol side chain and Octyl NDI

In a small disposable vial ~0.093g of DAN with an alcohol side chain and ~0.050g of Octyl NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis. After NMR analysis 1.64g of the 1:1 mixture was used for DSC analysis.

General Synthesis of DAN with an Alcohol side chain and GP6 1-82 NDI

In a small disposable vial ~0.066g of DAN with an alcohol side chain and ~0.048g of GP6 1-82 NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis. After NMR analysis 2.38g of the 1:1 mixture was used for DSC analysis.

General Synthesis of DAN with an Ether side chain and Octyl NDI

In a small disposable vial ~0.029g of DAN with an ether side chain and ~0.060g of Octyl NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis (Figure 8). After NMR analysis 1.07g of the 1:1 mixture was used for DSC analysis (Figure 9).

General Synthesis of DAN with an Ether side chain and GP6 1-82 NDI

In a small disposable vial ~0.044g of DAN with an ether side chain and ~0.114g of GP6 1-82 NDI was mixed together. A heating gun was used to heat mixture until it was a black, homogeneous, liquid mixture. The reaction was then cooled to room temperature and taken for NMR analysis. After NMR analysis 2.1g of the 1:1 mixture was used for DSC analysis.

1:1 NDI and DAN Results

Each 1:1 molar ratio of NDI and DAN results were analyzed via NMR to prove that it was a 1:1 ratio. To prove that the NDI and DAN has a 1:1 molar ratio, the NMR would display a 2:1 NMR integral ratio. As seen in the figures below each NDI variant and DAN variant followed this 1:1 ratio. After the 1:1 molar ratio was double checked the reaction was now able to be analyzed by DSC.

Conclusion

Multiple molecular analysis techniques were conducted to determine if the side chain identities of the donor acceptor columnar liquid crystals will affect its bulk material property, specifically it's phase change temperatures. As of right now the results are inconclusive. Further test with analytical tools such as the polarized optical microscope to see physical properties of the DACLC during the isotropic liquid phase are needed. DSC results are in, but further analysis of the results need to occur to determine if the side chains have a significant difference on the

DACLC phase change temperatures (Figure 7). The current DSC data shows that the DAN alkene and alcohol side chain with Octyl NDI both had to be ran at a temperature below 0°C to see all the mesophases within the heating, cooling, heating process. Ethers lowest temperature was set at 0°C for both NDI variants. Further analysis would have to be executed to acknowledge if this is a significant difference. Overall, this data shows promising results that with further analyzation of the DSC data and utilization of the polarized optical microscope will lead to the discovery of, does changing the side chains on DACLC molecules have a significant effect on its bulk properties.

NDI	DAN	MASS (mg)	Mesophase 1	Mesophase 2	Mesophase 3	Mesophase 4	Mesophase 5
Octyl	Alkene	1.67	13°C	121°C	131°C	120°C	-1°C
GP6 1-82	Alkene	47*	106°C	84°C	67°C		
Octyl	Alcohol	1.64	8°C	138°C	158°C	148°C	
GP6 1-82	Alcohol	2.38	18°C	60°C	67°C	119°C	83°C
Octyl	Ether	1.07	138°C	143°C	129°C	103°C	
GP6 1-82	Ether	2.1	108°C	119°C	123°C	177°C	78°C

Figure 7: DSC results for 1:1 Donor Acceptor Columnar liquid crystals

*Mass needs to be reconfirmed

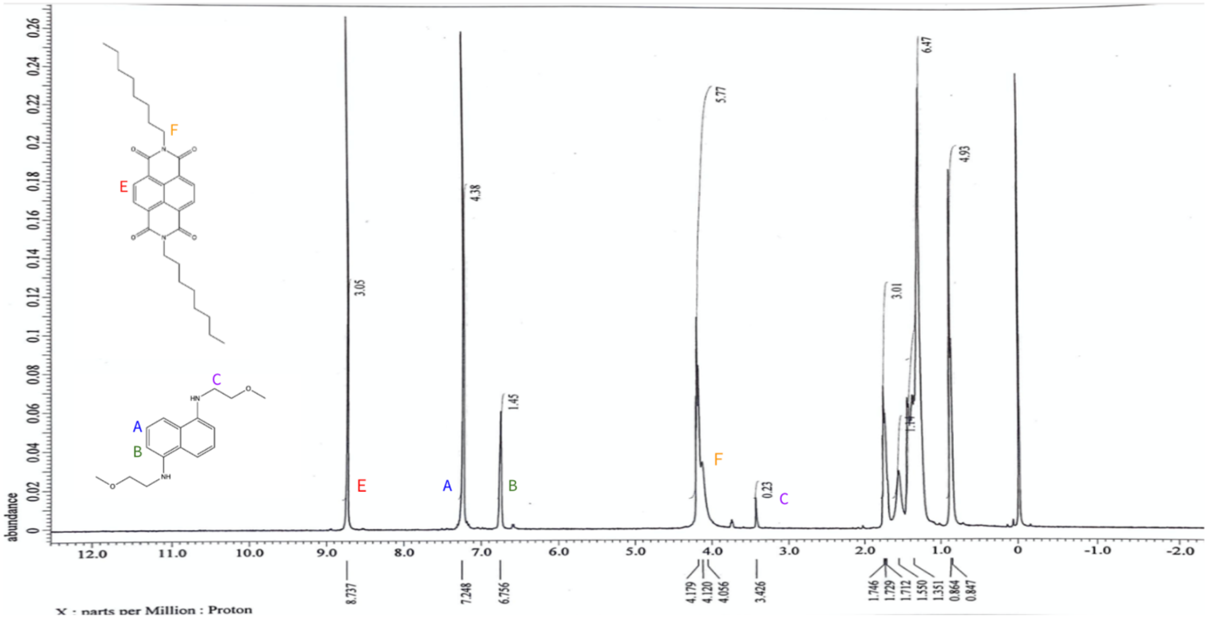

Figure 8: H’ NMR of a donor molecule containing a DAN ether side chain and acceptor molecule containing Octyl NDI.

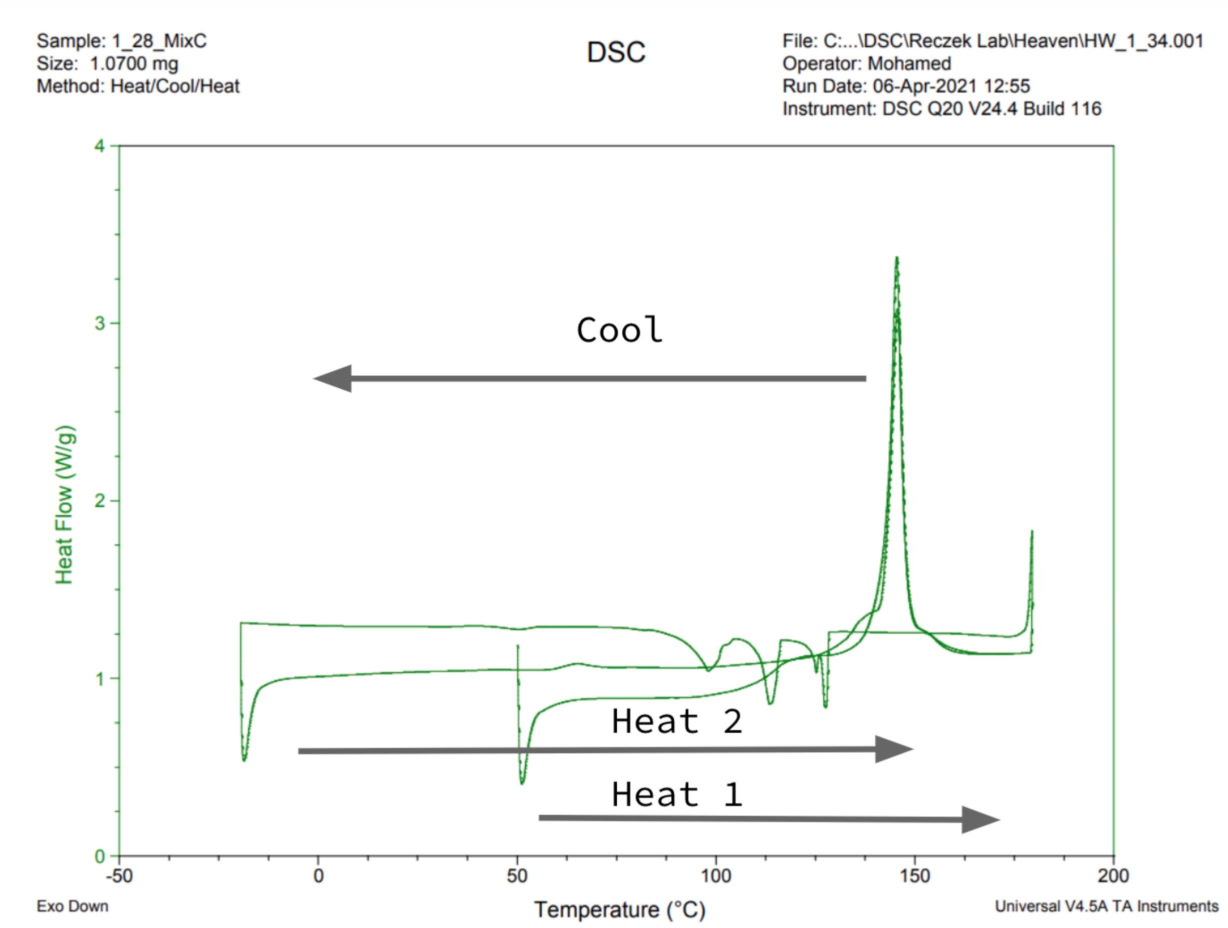

Figure 9: DSC of a donor molecule containing a DAN ether side chain and acceptor molecule containing Octyl NDI.

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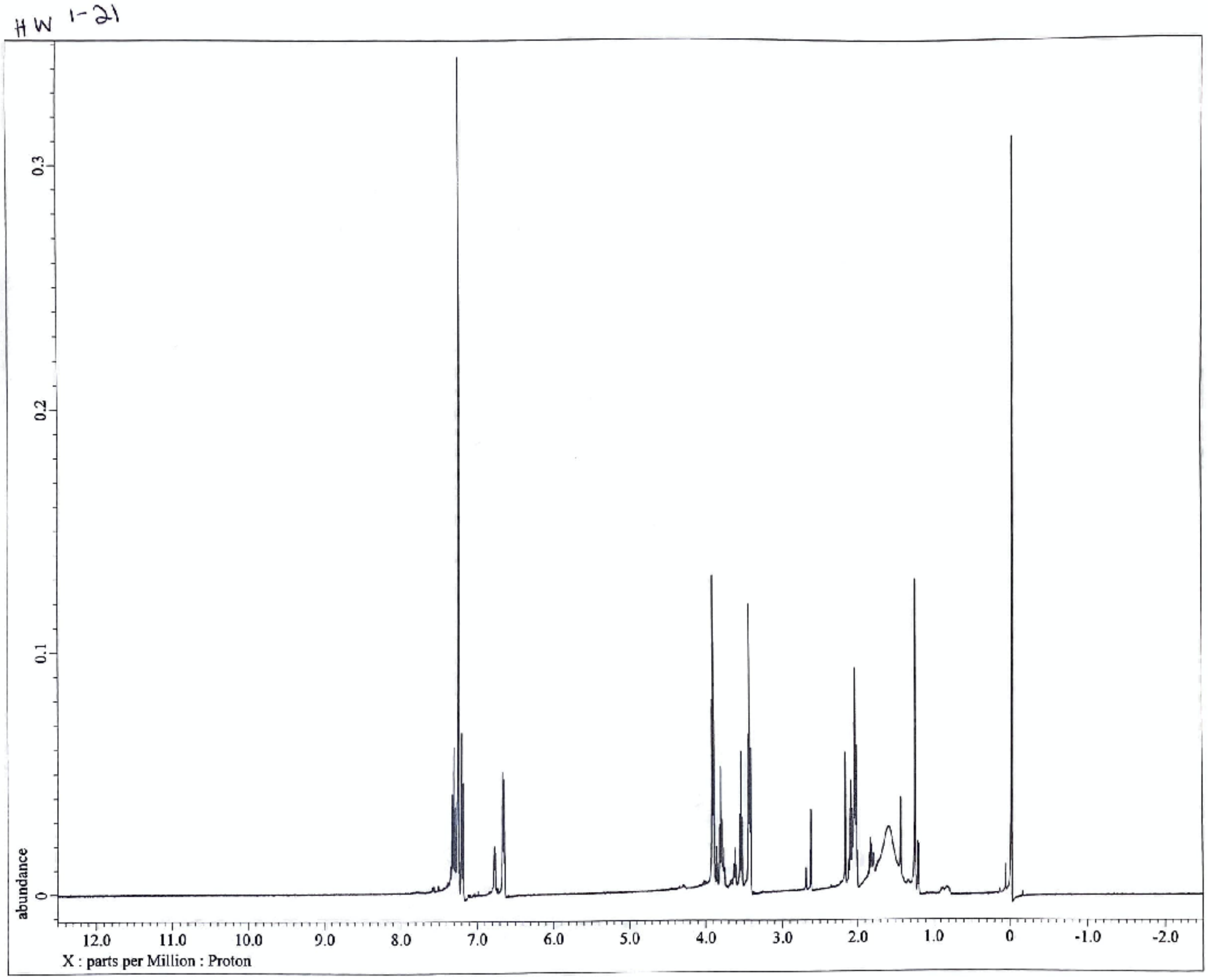
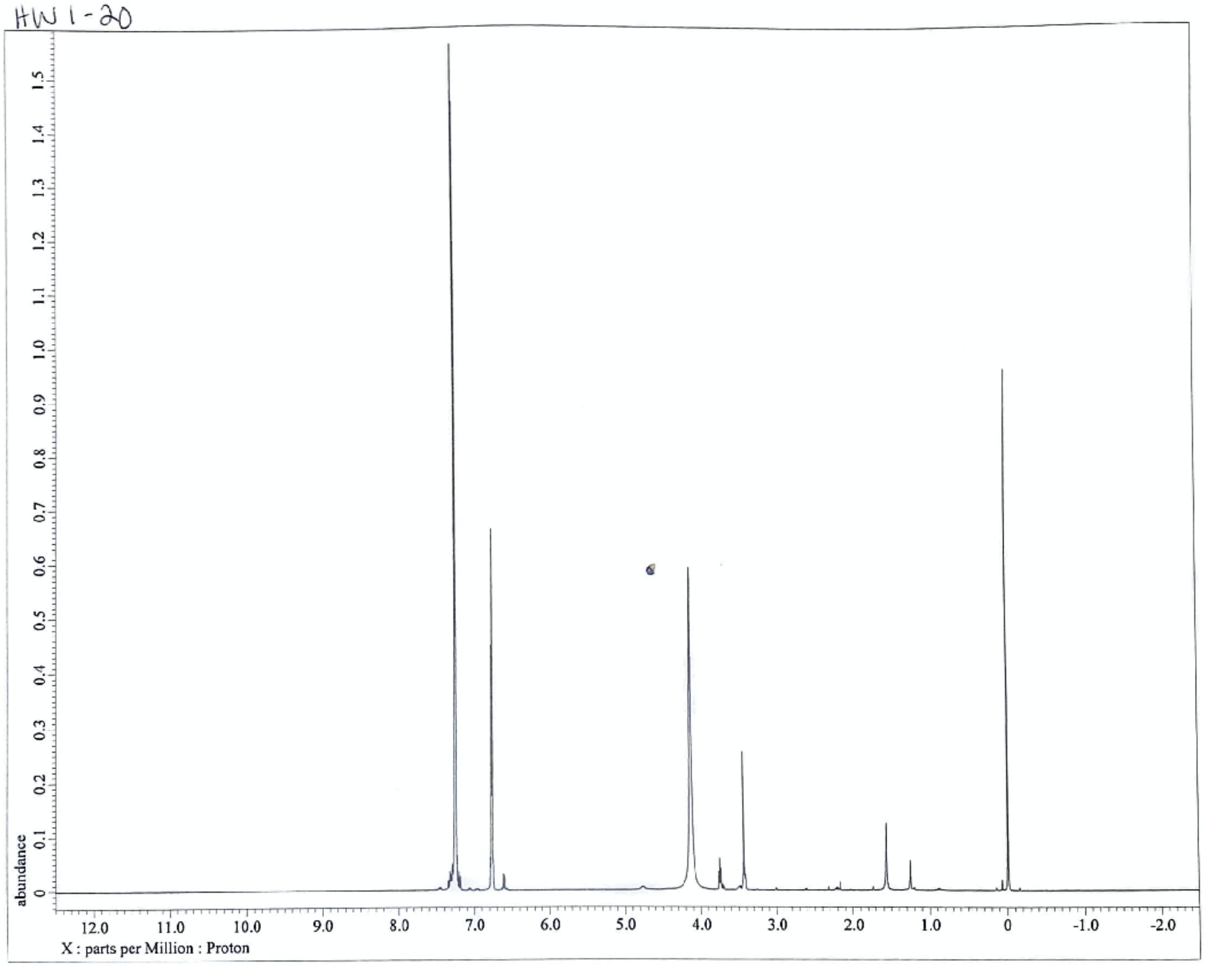
Appendix I: NMR

NMR: DAN alkene

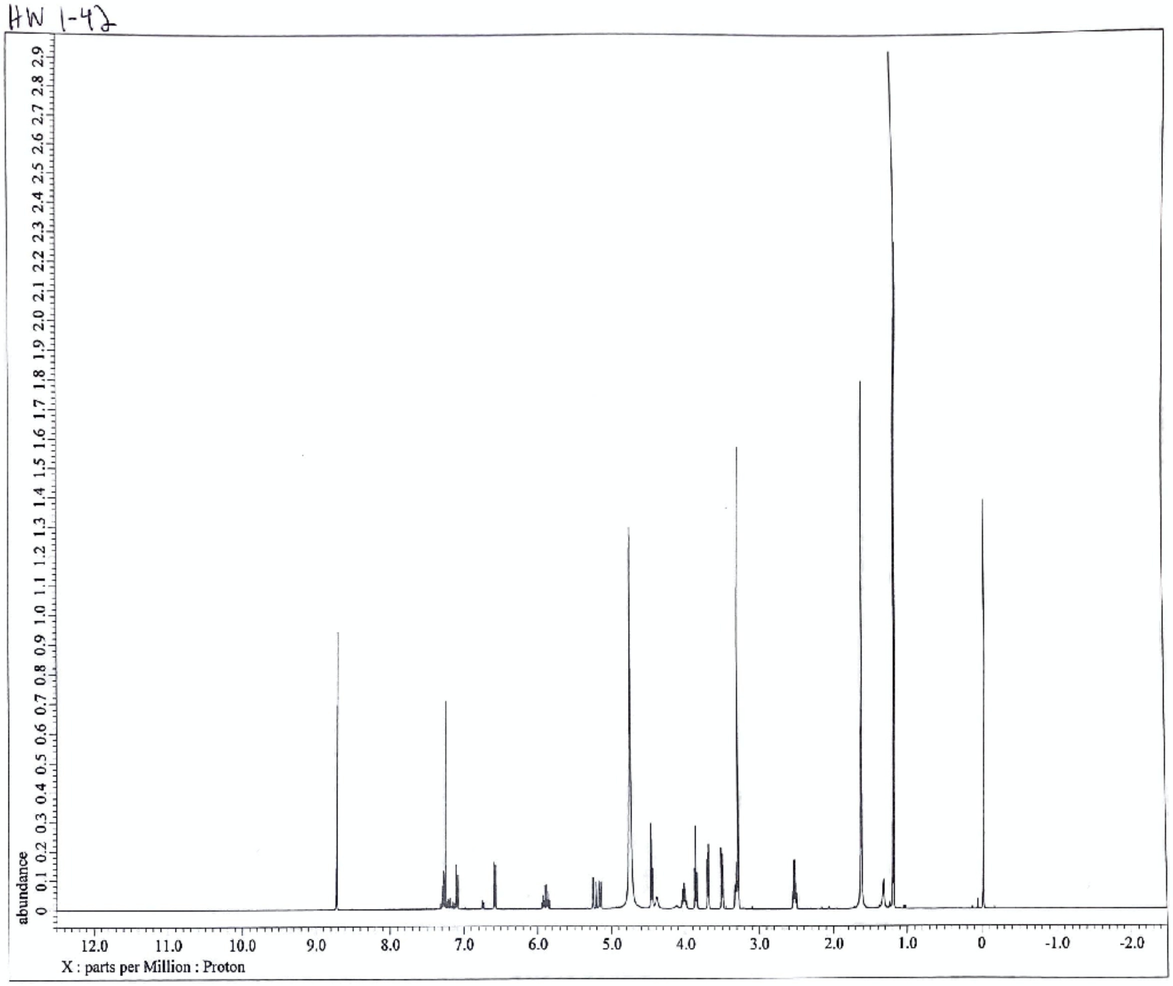


NMR: DAN alcohol

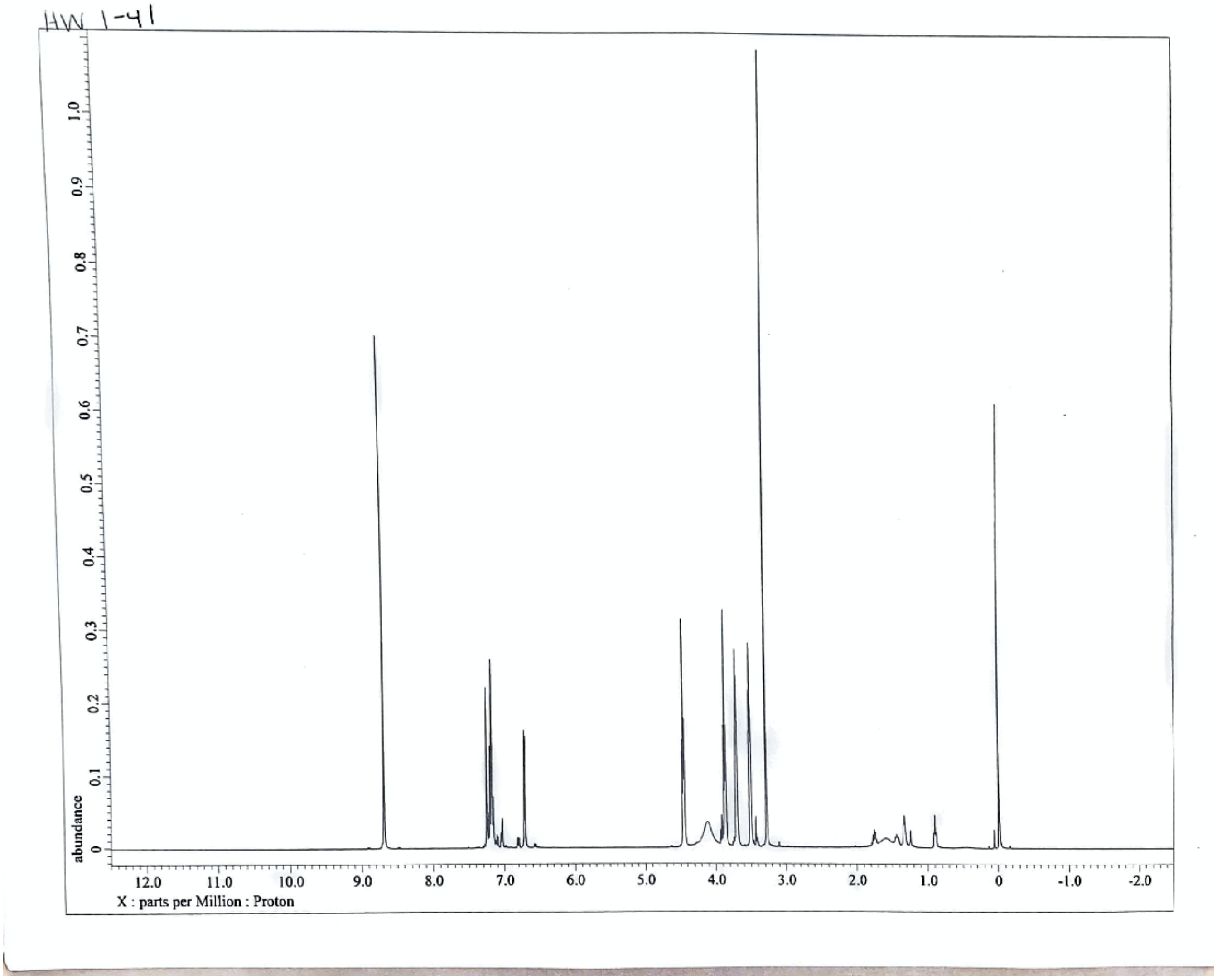


NMR: DAN ether

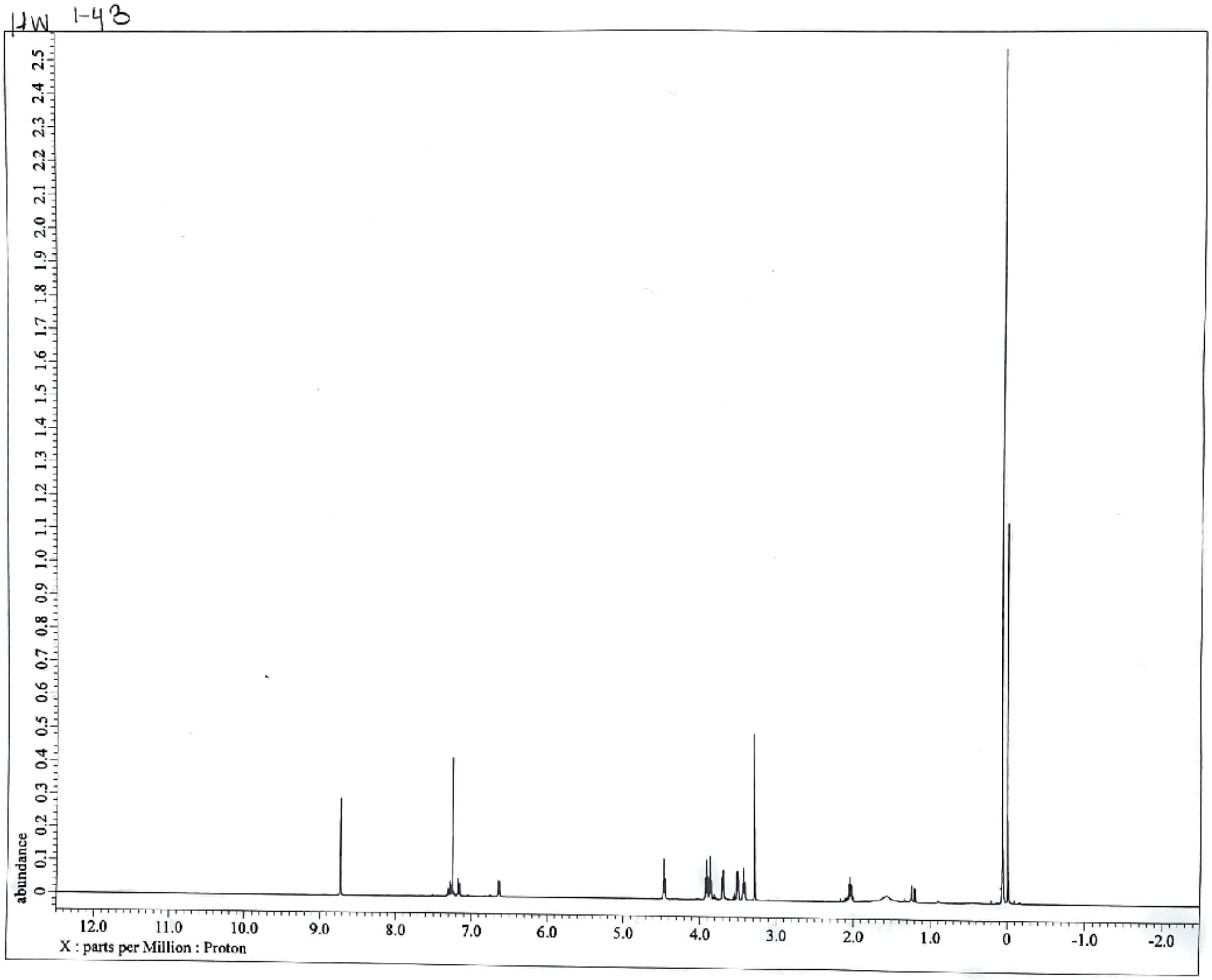
NMR: Octyl NDI + DAN alkene



NMR: GP6 1-82 NDI + DAN alkene

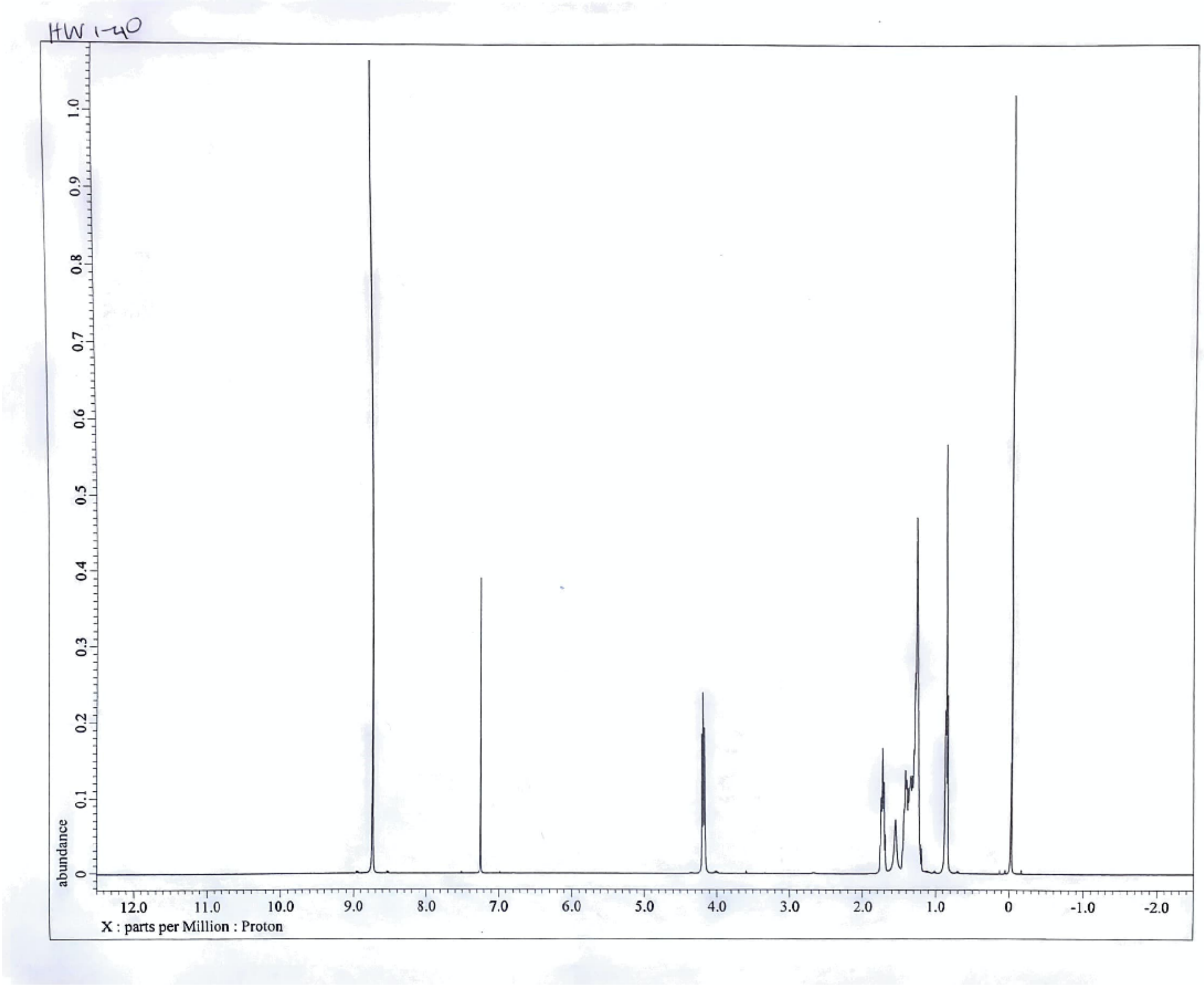


NMR: Octyl NDI + DAN alcohol



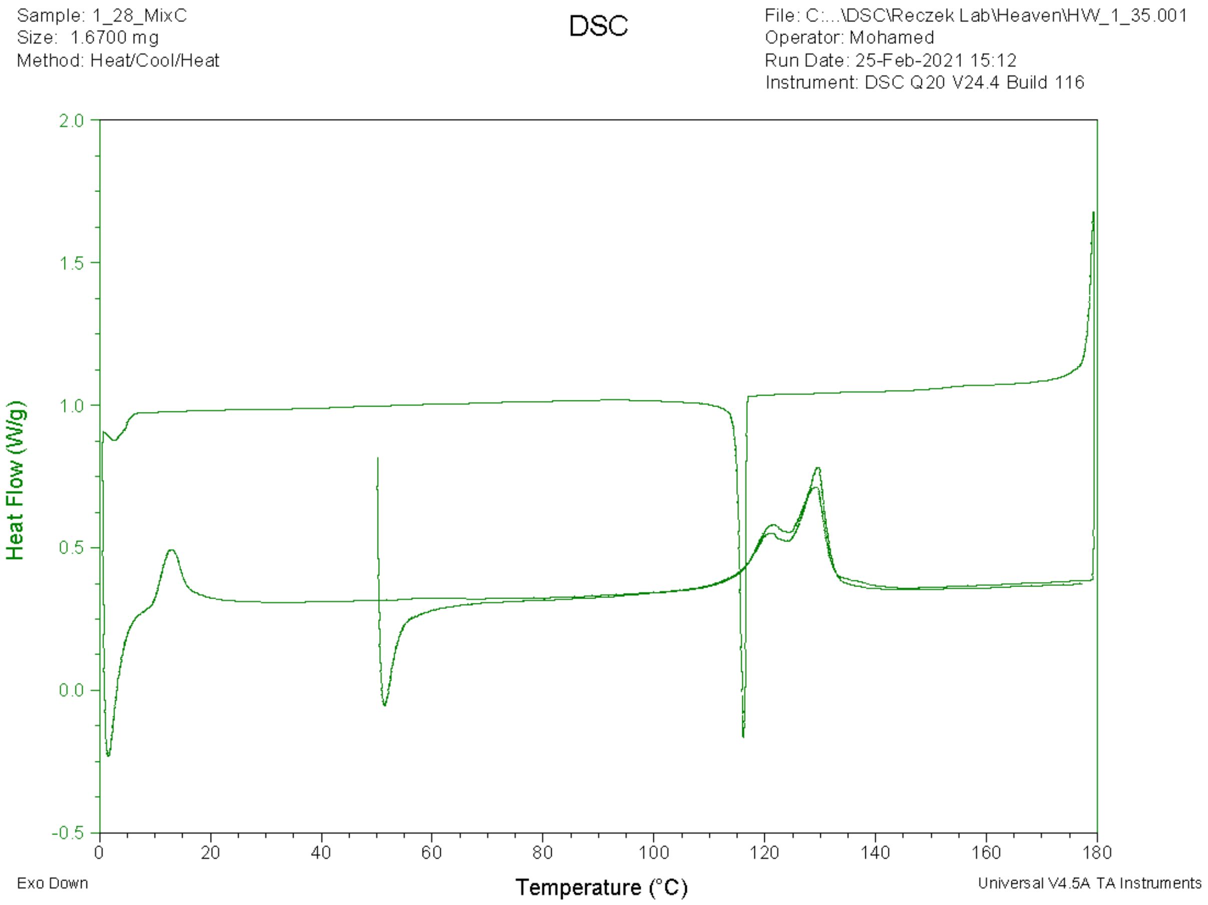
NMR: GP6 1-82 + DAN alcohol

NMR: Octyl NDI + DAN alcohol

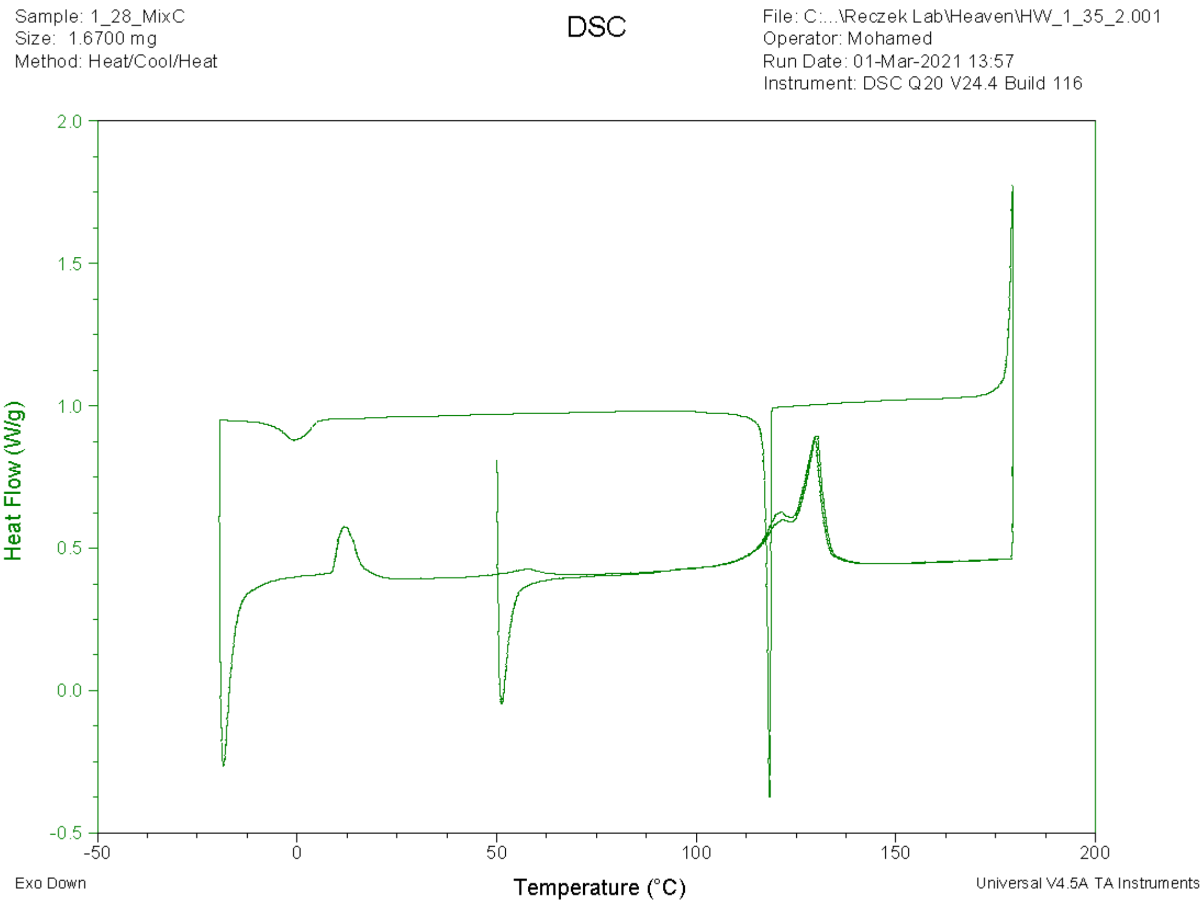


NMR: Octyl NDI

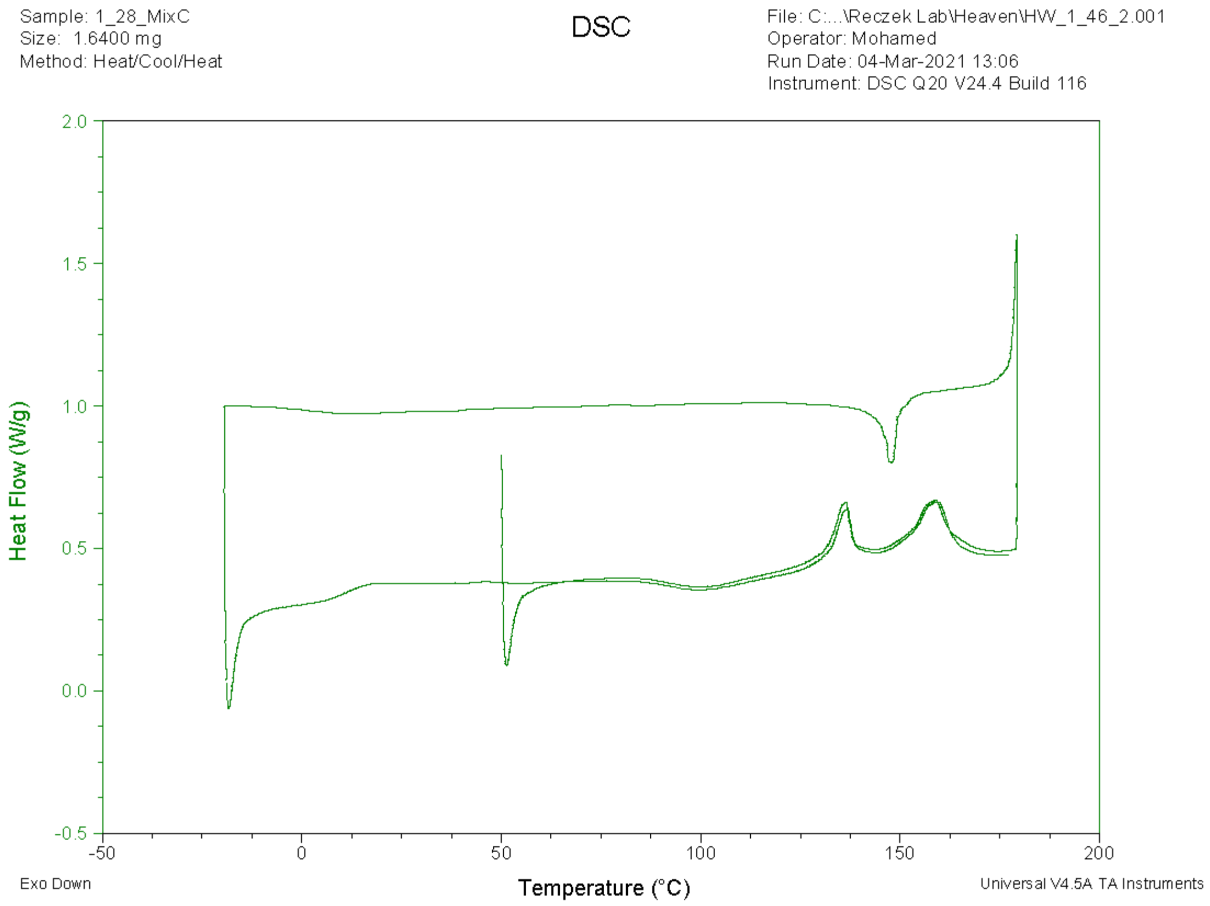
Appendix II: DSC



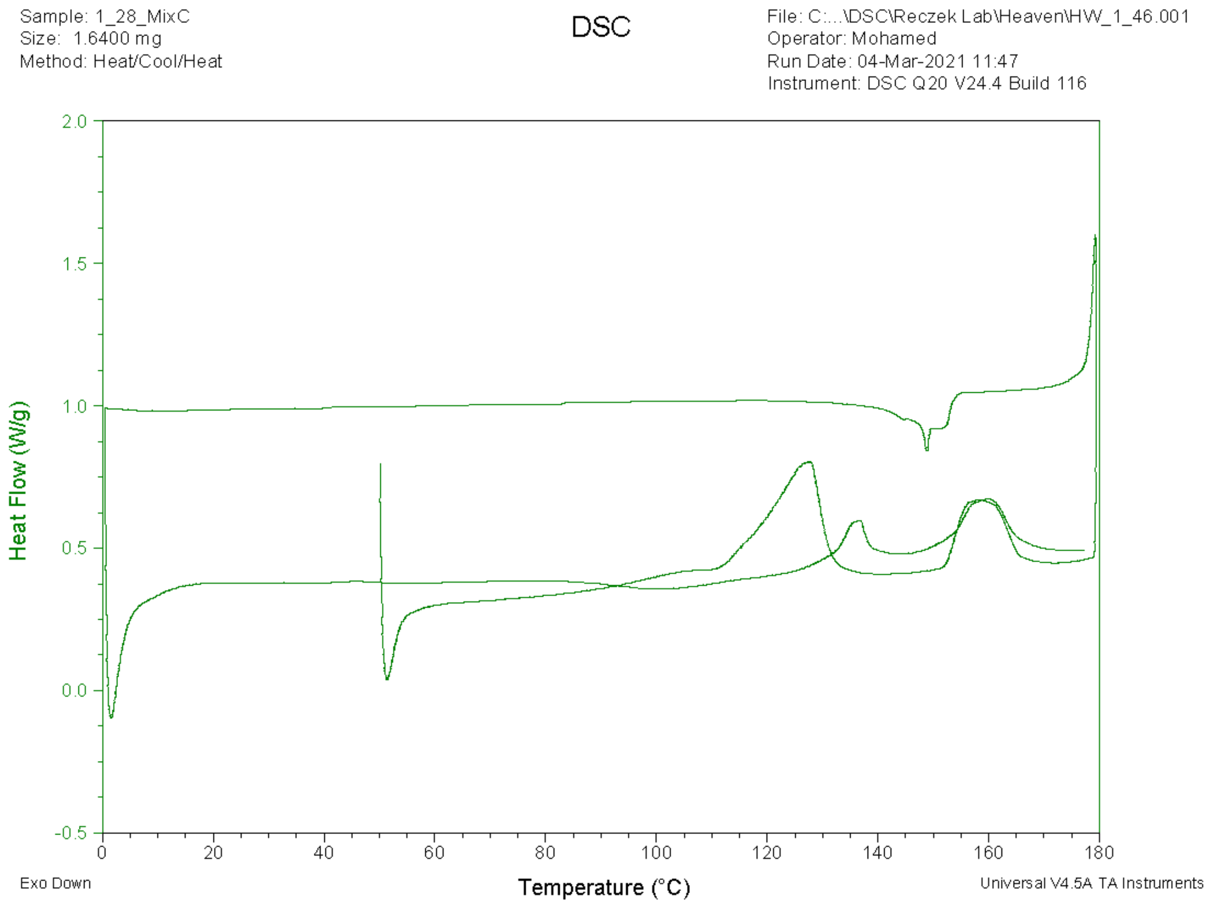
DSC of Octyl NDI + DAN alkene (0°C)



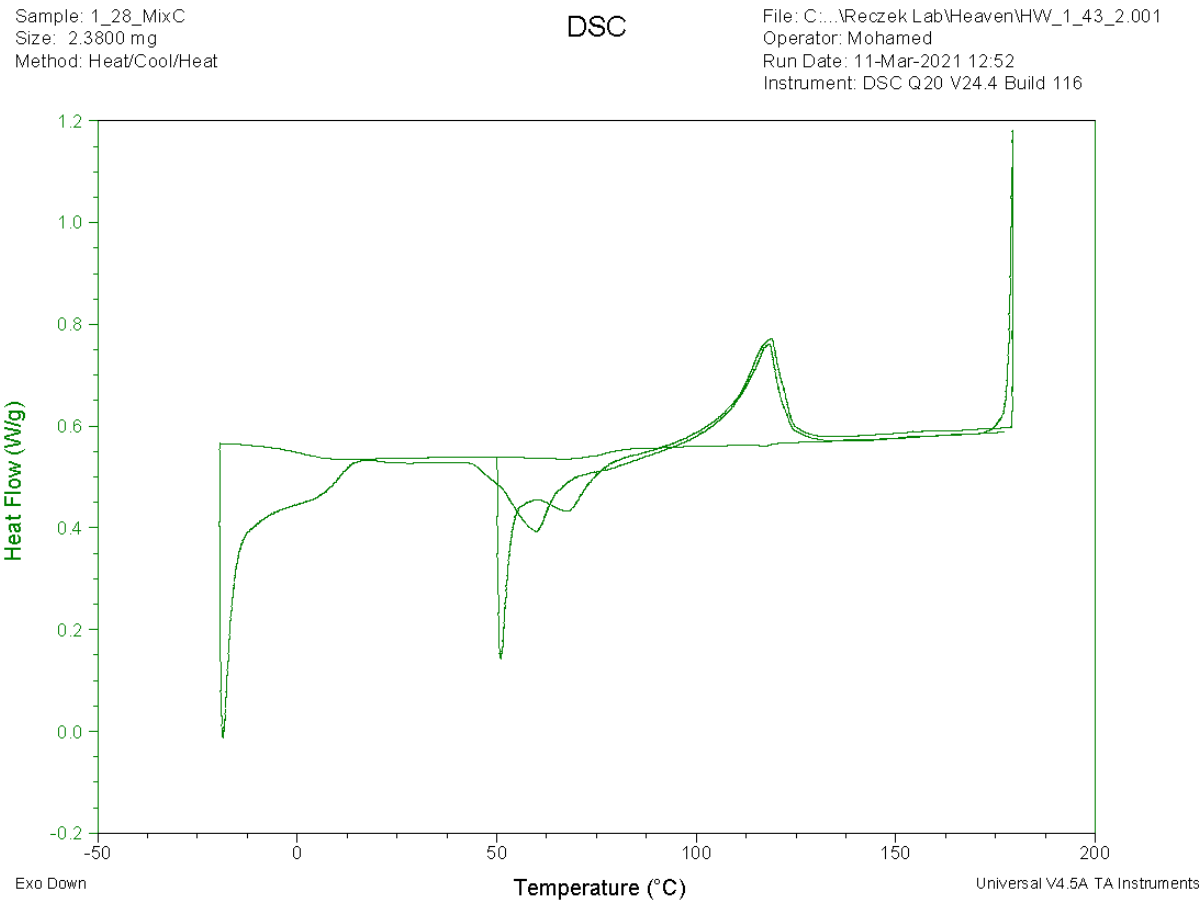
DSC of Octyl NDI + DAN alkene (-20°C)



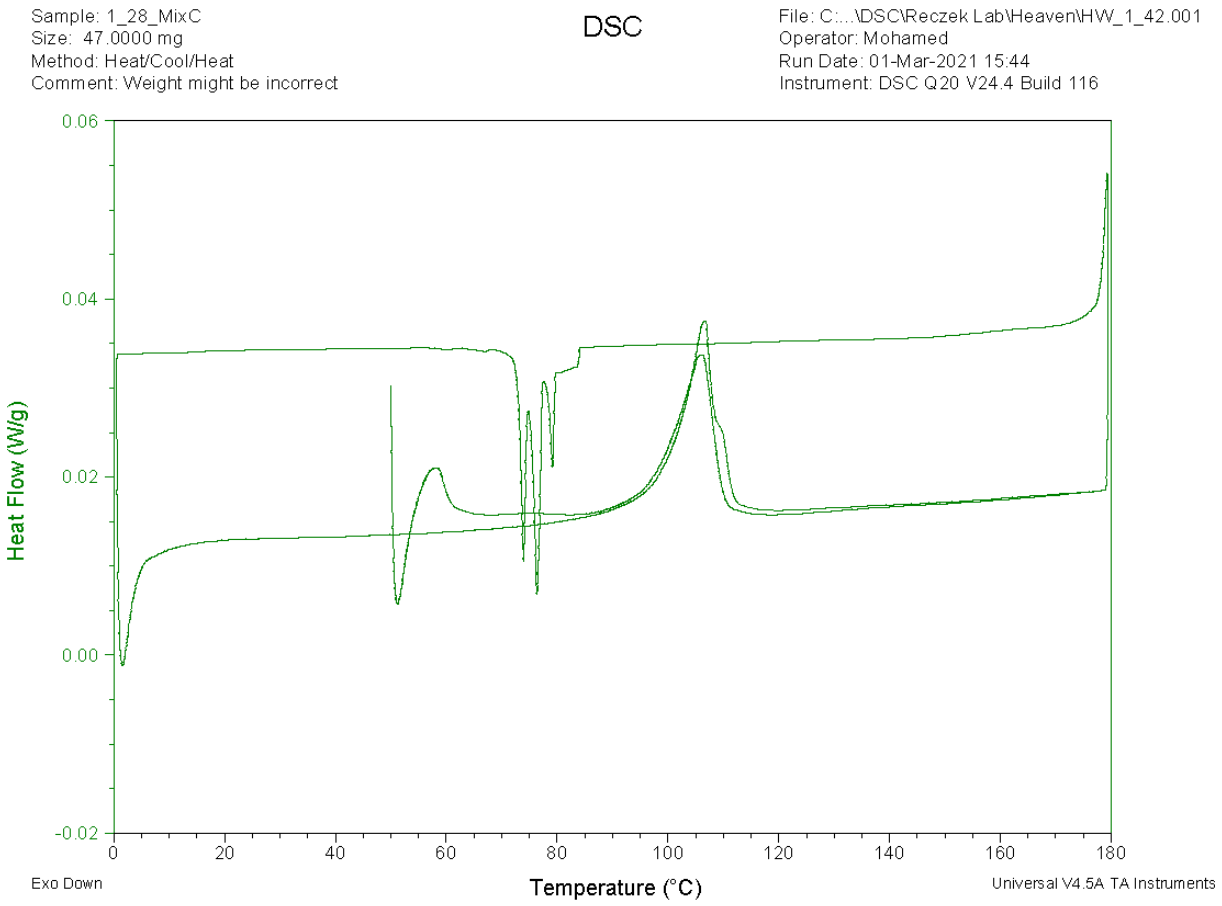
DSC Octyl NDI + DAN alcohol (-20°C)



DSC Octyl NDI + DAN alcohol (0°C)



DSC: GP6 1-82 NDI + DAN alcohol

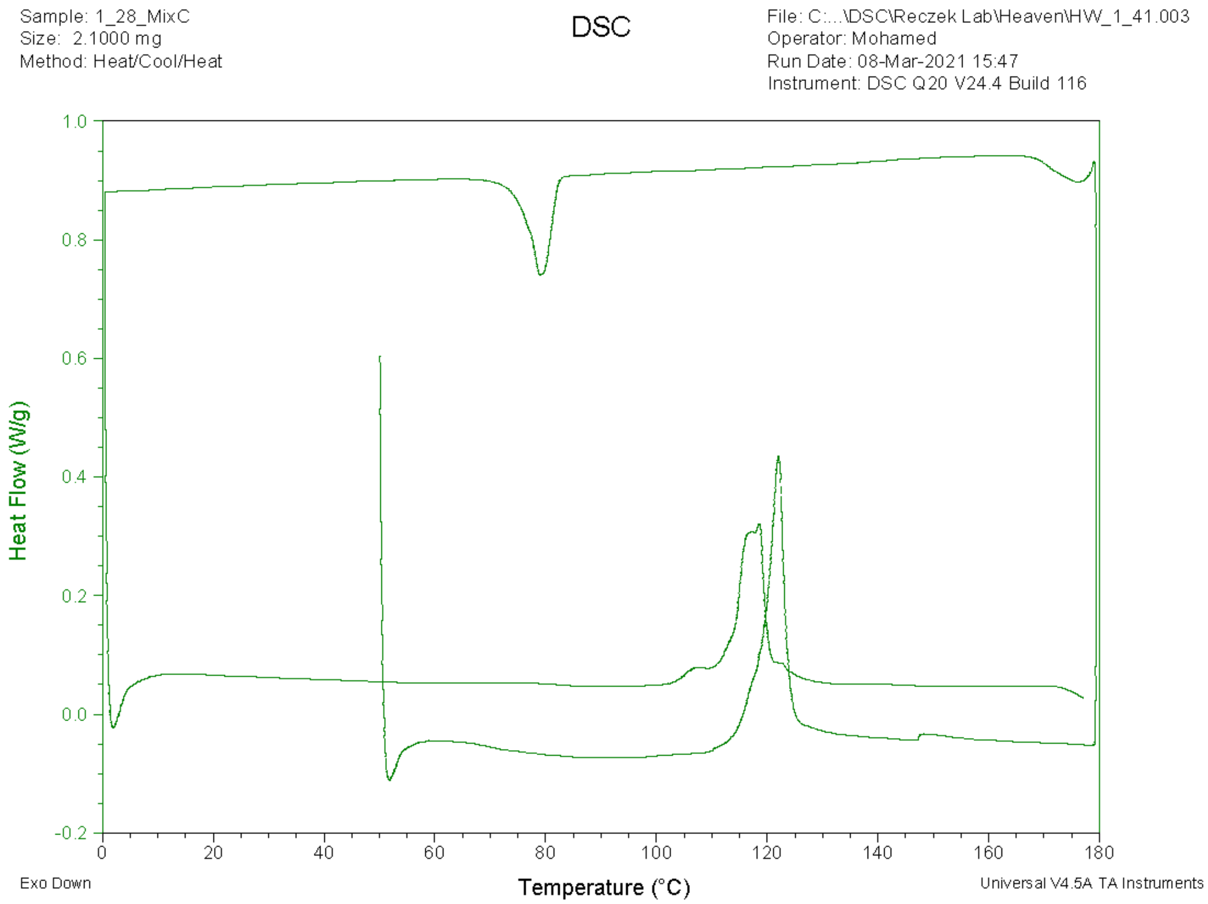


Sample: 1_28_MixC
Size: 47.0000 mg
Method: Heat/Cool/Heat
Comment: Weight might be incorrect

DSC

File: C:...\DSC\Reczek Lab\Heaven\HW_1_42.001
Operator: Mohamed
Run Date: 01-Mar-2021 15:44
Instrument: DSC Q20 V24.4 Build 116

DSC: GP6 1-82 + DAN alkene



DSC: GP6 1-82 + DAN ether