Annelated Benzenoid Macrocycles

and Polymerizable Discotic Liquid Crystals

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the degree of Doctor of Philosophy in Chemistry

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Abstract

This dissertation details the efforts towards novel polycyclic aromatic hydrocarbons (PAHs). It begins with an overview of PAHs, liquid crystals, and membrane technologies introducing key concepts pertinent to later discussions, followed by a review on cycloarenes. Then begins discussion on the three projects of my graduate research: the synthesis of septulene, synthetic efforts of towards aromatic belts, and the synthesis and characterization of two polymerizable discotic liquid crystals (DLCs).

Cycloarenes are annelated benzenoid macrocycles that contain C-H bonds pointing into their center cavity. Major interest in this class of compounds stemmed from differing theories about the delocalization of their π electrons. Kekulene, the prototypical cycloarene, was synthesized by Stabb and Diederich after over a decade of attempts. Characterization showed that its π electrons remain delocalized into smaller benzenoid units and not across the entire molecule like with annulenes. This provided proof to the electron delocalization theory of McWeeny and gave support for the Clar bonding model. The synthesis septulene and a hexaazakekulene corroborated these conclusions. Our synthesis of septulene, achieved using ring-closing metathesis (RCM) to "stitch up" bridges on a propenyl substituted cyclometaphenylenylene, was a particularly important addition as it possesses many fundamental structural differences yet similar physical properties. Extensive computational studies tried to quantify the amount of thermodynamic stabilization cycloarenes gain from macrocyclic conjugation, a concept coined as superaromaticity, that ultimately concluded this effect to be negligible.

Aromatic belts are another type of annelated benzenoid macrocycle that possess benzenoid rings oriented perpendicular to the macrocyclic ring, and have yet to be rationally synthesized. Interest in aromatic belts comes from their supramolecular properties and particularly their potential to provide a means for the bottom-up synthesis of carbon nanotubes.
We attempted to synthesize an aromatic belts my using RCM on propenyl substituted cycloparaphenylene (CPPs), in the same manner as our septulene synthesis. While we were successful in making the required small molecule building blocks, macrocyclization attempts using established methods for CPP synthesis proved unsuccessful.

We attempted to synthesize a nanoporous membrane templated by the columnar order within a discotic liquid crystal (DLC) mesophase. This work stemmed from previous work on boronic ester containing DLCs made for solar cell applications. The parent DLCs were found to organized in a columnar hexagonal fashion, just like that needed for the desired membranes. Our monomers were tailored to possess a hydrolytically labile aromatic core, functionalized by peripheral alkyl chains terminated by polymerizable end groups. Triphenylene cores induce crystallinity while the alkyl chains induce fluidity within the liquid crystal mesophase. Acrylate end groups provide a means to lock-in the order of the DLC mesophase while boronic ester linkages provide a means to remove the triphenylene cores post-polymerization. Our first monomer was found to produce a polymerized film that possessed no columnar order, leading us to synthesize a second monomer unit. This second monomer possesses shorter alkyl chains, in hopes to reduce the fluidity of the mesophase and increase stacking of the triphenylene cores. Polarized optical microscopy of our second monomer showed Schlieren textures indicative of a nematic mesophase, and X-ray diffraction of both monomers showed patterns characteristic of a discotic nematic mesophase. While nematic mesophases possess none of the columnar order needed for the desired nanoporous membranes, they are quite rare for discotic mesogens and have LCD applications worth investigating.
Dedication

To my parents, for making me in to the man I am today.
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Chapter 1: Introduction and Overview of Chapters

1.1 Introduction

This dissertation details the efforts towards and synthesis of novel polycyclic aromatic hydrocarbons (PAHs). The compounds of interest are important because they either answer fundamental questions about the nature of aromatic compounds or provide a stepping stone towards making functional materials. While the heart of this work lies in organic synthesis, it incorporates many other scientific aspects including materials science, polymer science, and liquid crystals. By combining these disciplines, we set out to make important and interesting materials with the potential to make an impact on the world.

1.2 Polycyclic Aromatic Hydrocarbons

PAHs are compounds made solely of carbon and hydrogen that contain multiple aromatic rings. Initially discovered as components of coal tar, crude oil, and other petroleum products, many synthetic efforts and analytical characterizations have been performed to better understand these compounds dating back to the late 19th century. Major motivation for these studies stem from environmental concerns and a desire to understand the fundamental concepts behind aromaticity. Many works detail the basic concepts and rich history of PAHs well, a few of which will be used to give a brief summary of some key points on classification and seminal works.\textsuperscript{1-3}

PAHs can be divided into sub-classes in many different ways. Acenes, such as anthracene, contain only linearly fused rings, while phenes, such as phenanthrene, contain at least one angular fusion. Kata-annelated systems, like triphenylene, contain tertiary carbon centers as the fusions between only two rings, while peri-condensed systems, like pyrene, contain some tertiary carbon centers as the fusions between three tings. Larger PAHs can contain aspects of multiple classifications; for these cases, individual regions are classified rather than the entire system.
Alternant versus nonalternat PAHs are two classifications with differences stemming from their electronic structures. If conjugated carbon atoms are divided into two sets, such as those marked with an asterisk and those without, alternant systems can be divided into such a way that no two adjacent atoms are in the same set, while nonalternant systems, require adjacent atoms within the same set (figure 1.2). Alternant hydrocarbons can be further described as even or odd alternant based upon the overall number of conjugated atoms. Even alternant systems have pairs of bonding and anti-bonding orbitals with equal and opposite energies, leading to bonding orbitals completely filled with $\pi$ electrons evenly across all conjugated atoms. Odd alternant systems have these same pairs of bonding and antibonding orbitals, but also have one nonbonding orbital with zero energy. Nonalternant systems have bonding and antibonding orbitals that are not equal and opposite in energy, and therefore unequal charge distributions.

In the early 1900s, Clar, Cook, and Scholl served as pioneers for PAH chemistry. Clar documented his contributions in the two volume series *Polycyclic Hydrocarbons.* Two of his more notable contributions were the Zn-dust melt method as a better way to reduce polycycle quinones and oxygen containing precursors, and the synthesis of pentacene by dehydrogenation. Clar also pioneered the use of UV-Vis spectrophotometry as an analytical tool for the characterization of PAHs. A major application of this was with his synthesis of haxa-peri-
hexabenzocoronene 1 (scheme 1.1), which he confirmed using UV-Vis along with elemental analysis.⁵

![Scheme 1.1. Clar's synthesis of 1.](image)

Cook's work revolved around testing the structural basis for the carcinogenicity of PAHs.³ His early work focused on isolating new PAHs from natural coal sources and developing methods for synthesizing these and previously isolated compounds. Through his efforts he was able to develop more effective structure elucidation techniques and develop new methods to synthesize substituted PAHs that would pave the way for future generations.

![Figure 1.3. Some novel PAHs synthesized by Cook.](image)

One of Scholl's first major contributions was the synthesis of coronene 4 by oxidation of dibenzoperopyrenequinone 2 to carboxylic acid derivative 3 and subsequent decarboxylation (scheme 1.2, top).⁶ His biggest contribution was the development of Lewis acid mediated oxidative cyclodehydrogenation conditions, a reaction that now bears his name. This methodology was applied in his synthesis of bisanthene 5 (scheme 1.2, bottom), but he did not realize its full utility.⁷ Nearly a century later, this methodology is still applied in the synthesis of modern PAHs.
Scheme 1.2. Scholl's syntheses of 4 and 5.

1.3 Liquid Crystals

In 1888, Austrian botanist Friederich Reinitzer described the first observation of what is now known as a liquid crystal. When recording the melting point of cholesteryl benzoate, he observed a "double melting" behavior where the material first formed a cloudy fluid, then upon further heating transformed into a clear liquid. The history of liquid crystals can be divided into three general time periods. The first ranges from Reinitzer's discovery to around 1925 where this new state of matter was being defined and established while meeting much skepticism. Next, from around 1925 to around 1960 lived the period where liquid crystal research interest was low, garnering lots of attention from only a small number of scientists. Finally, the modern age of liquid crystals began around 1960 when technological applications were realized, stimulating a boom in both research interest and financial support.

Mesogens, molecules that exhibit liquid crystalline behavior, spontaneously form an ordered phase between crystalline solids and isotropic liquids, referred to as the mesophase. Mesophases exhibit some degree of long range order, like that of crystals, but maintain some degree of fluidity, like that of liquids. This unique mix of properties allows liquid crystals to be
useful in applications that need the long range order of solids but also the manipulability and self-healing properties of liquids.

Liquid crystals are classified based upon the way the mesophase is formed. Thermotropic liquid crystals are obtained by adjusting temperature while lyotropic liquid crystals are obtained by varying concentration within a solvent. It is worth noting that lyotropic mesophases can be temperature dependent, but that does not also make them thermotropic. Amphotropic mesogens exhibit both lyotropic and thermotropic mesophases. Thermotropic liquid crystals can be further classified based upon the shape of the mesogen: calamitic (rod-like), discotic (disk-like), and bent-core (banana-like).

Figure 1.4. Classifications of liquid crystals.

Mesophases exist with high degrees of directional order but varying degrees of positional order. Nematic phases, the least ordered, have no positional order. Smectic phases possess some positional order where the molecules form layered structures. In columnar mesophases, molecules stack together forming the namesake columns with various degrees of order. B phases are unique sets of mesophases for bent-core mesogens. The lyotropic mesophases are lamellar, columnar, and cubic with one, two, and three dimensions of positional order, respectively.
Figure 1.5. Examples from three of the major thermotropic liquid crystal phases.

In 1977, Chandrasekhar et al. reported the first discotic liquid crystals (DLCs), the benzene hexa-\textit{n}-alkanoates.\textsuperscript{10} The most abundantly studied DLCs are the hexaalkoxytriphenylenes.\textsuperscript{11} As seen with both of these classes, DLCs contain an aromatic core surrounded by peripheral alkyl chains (figure 1.6). The cores give systems their crystallinity, while the alkyl chains give fluidity. Careful tuning of the effects these two regions induce is vital in manipulating mesophase properties. Homeotropic alignment occurs when DLCs align with cores perpendicular to the substrate, while planar alignment occurs when DLCs align with cores parallel to the substrate. Laschat \textit{et al.}\textsuperscript{12} and Kumar\textsuperscript{11} have written excellent reviews detailing DLCs.

Figure 1.6. A benzene hexa-\textit{n}-alkanoate (left) and a hexaalkoxytriphenylene (right) detailing key structural features.
1.4 Membrane Technology

Membrane technologies have existed for as long as living organisms. Biological systems possess very complex membrane systems for a multitude of functions. While much simpler, synthetic membranes work very differently than their biological counterparts. Still, their production and application have developed into a multi-billion dollar industry. This industry contains large dominant divisions, including water purification and hemodialysis, and many smaller niche markets.

Membranes act as a permselective barrier separating two phases: the feed and the permeate (figure 1.7). Membrane separations work by allowing some components of the feed to pass through the membrane better than others, leading to differences in composition between the feed and permeate. To induce flow between the two phases through the membrane, a driving force is needed, such as variances in pressure, concentration, or temperature. Selectivity of membranes is often quantified as its retention; essentially, how well the membrane allows desired components to pass and prevents others from passing.

![Figure 1.7. Schematic representation of a membrane separation process.](image-url)
Porous membranes consist of a solid matrix possessing holes of a specific size. These membranes are generally described by either their average pore diameter or the separation process they are used for (figure 1.8). When classifying pore diameter, macroporous membranes have pores larger than 50 nm, mesoporous membranes have pores between 2 and 50 nm, and microporous membranes have pores smaller than 2 nm. This is often confusing, as membrane processes include microfiltration, where pore sizes are in the 50 nm to 10 µm range, ultrafiltration, where pore sizes are in 1-100 nm range, and nanofiltration, where pore sizes are in the 0.5 to 2 nm range. Nanoporous membranes are a specific type of microporous membrane where the pores are around 1 nm. Figure 1.8 shows a few more membrane processes, some of which use nonporous membranes.

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**Figure 1.8.** Membrane classifications.
1.5 Organization and Scope

This dissertation encompasses three major projects. Chapter 1 provides a general introduction to key concepts along with important background and history. Chapter 2 contains a review of cycloarenes and serves as an expanded introduction to aromaticity and why the synthesis of interesting PAHs is important. Chapters 3-5 each pertain to one of the three projects. Chapter 3 covers the synthesis of septulene and the key concepts learned from its synthesis. Chapter 4 covers efforts towards the synthesis of an aromatic belt. Chapter 5 covers the synthesis and characterization of nanoporous membranes made using DLCs. Chapters 3 and 5 detail projects I joined at various stages, and begin with a description of the major contributions to the project. Chapter 4 covers a project that I, at this point in time, have overseen at all stages.

1.6 References


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Chapter 2: Kekulenes, Cycloarenes, and Heterocycloarenes: A Review

Buttrick, J. C. and King, B. T. Chem. Soc. Rev. accepted for publication.

2.1 Introduction

Cycloarenes are defined as, “polycyclic aromatic compounds in which, by a combination of angular and linear annelations of benzene units, fully annelated macrocyclic systems are present enclosing a cavity into which carbon-hydrogen bonds point.” Figure 2.1 shows some examples of this class of molecule, along with some heterocyclic analogues, for which the synthesis has been attempted. Heterocycloarenes have one or more carbon atoms exchanged for a heteroatom and consequently do not fit the above definition of cycloarenes because they lack inward-facing protons, e.g. 7. Nonetheless, heterocycloarenes are similar in structure and properties to their hydrocarbon cousins and will be reviewed all the same.

Figure 2.1. Cycloarenes and heterocycloarenes, which the synthesis has been attempted.

2.1.1 History

The earliest report of cycloarenes was probably in 1951 when McWeeny discussed the electronic structure of 1. His molecular orbital (MO) calculations suggested that despite the large
conjugated structure of 1, the electrons remain delocalized only into smaller benzene type rings. These calculations contradicted calculations he made using the semi-classical approach of Pauling, which suggest the electrons in 1 are globally delocalized throughout the entire molecule. This set off many attempts to synthesize cycloarenes, in hopes that the physical data collected would answer these and future questions about their molecular and electronic structure.

![Figure 2.2. Key events in the history of cycloarenes.](image)

In 1965, at the Kekulé Centenial in Bonn, Germany, Staab reported the first attempts towards the synthesis of 1. It was at this time 1 was given the name Kekulene, in homage August Kekulé, due to its planar, conjugated nature and D_{6h} symmetry like benzene. Over the next decade the groups of both Staab and Jenny reported many more attempts at the synthesis of 1. It was not until 1978 that Staab and Diederich achieved the first conclusive synthesis of 1.

Peter and Jenny first reported attempts at the synthesis of 2 in the mid-1960s. More attempts were reported by Staab et al. in 1983. The synthesis of 2 was finally achieved by Staab and Funhoff in 1986. Staab and Sauer published attempts at 3 and 4 in 1984, however the
synthesis of these two compounds has yet to be reported. In 2012, Kumar et al. achieved the synthesis of 5, which they named septulene.\textsuperscript{5} In 2016, Müllen and co-workers reported the synthesis of the extended cycloarene 6.\textsuperscript{48}

Heterocyclic analogues of kekulene have also been of interest. Katritzky and Marson reported attempts to synthesize diazakekulene 7 in 1983.\textsuperscript{6} In 1985, Ranshoff and Staab published their attempts at the synthesis of hexaazakekulene 8.\textsuperscript{7} Tatibouët et al. achieved the first conclusive synthesis of a heterocyclic cycloarene with the synthesis of 9 in 1997.\textsuperscript{8}

2.1.2 Naming

Despite the dearth of successful syntheses of cycloarenes, multiple nomenclatures have been suggested. Naming of such large compounds using IUPAC nomenclature gives long and complicated names that do not easily relate any of the structural characteristics of the compounds.\textsuperscript{1} The suggested name for 1 by Peter and Jenny, [12]coronaphene, also does not relay much about the structure or symmetry of the compound and leaves ambiguity.\textsuperscript{12} Consequently, neither of these methods caught on for naming cycloarenes.

Staab and Diederich provided their own nomenclature for cycloarenes, which 1 will be used here as an example.\textsuperscript{1} First, is to indicate the number of benzene annelations present with 1 being called a cyclododecakisbenzene. Next is to indicate the annelation of these benzene units. The letters “a” and “b” are assigned to the preceding annelation, and proceeding clockwise all carbon atoms are labeled continuing with “c”. The letter of the first bond of the next annelation is used to represent that particular annelation type. This gives rise to linear annelations getting a “d” designation (Figure 2.3, highlighted in red) and angular annelations receiving an “e” designation (highlighted in green). Although not specified, they tend to always start with the lower letter designation. Thus 1 would be called cyclo[d.e.d.e.d.e.d.e.d.e.d.e.d.e.d.e.d.e.d.e.]dodecakisbenzene. As a few more examples, 2 would be cyclo[d.e.d.e.d.e.d.e.d.e.e.]dekakisbenzene and 3 would be cyclo[d.e.e.d.e.e.d.e.e.]nonakisbenzene.
Kumar et al. suggested using the corannulene nomenclature developed by Agranat et al. to name cycloarenes.\textsuperscript{5,17} This method uses the name corannulene followed in brackets by a series of numbers each containing another superscripted number. The base number dictates the size of a specified smaller ring while the superscript number indicates the number of carbon atoms within this small ring along the outer perimeter of the overall molecule that are not shared by any other smaller rings. This leads to benzene rings getting a “6” designation with linear annelations getting a superscript “1” (Figure 2.3, highlighted in orange) and angular annelations getting a superscript “2” (highlighted in blue). When determining the numbering of the smaller rings, the carbon atom designated C1 when drawn in standard orientation is chosen as the starting point. This gives 1 the name corannulene[6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1}]. Kumar et al. suggested an abbreviation to this method where 1 is abbreviated as corannulene\((6\textsuperscript{2},6\textsuperscript{1})_6\) with the subscript 6 clearly indicating the six-fold symmetry of 1. 2 could then be named as corannulene\((6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2},6\textsuperscript{1})_2\) and 3 could be named corannulene\((6\textsuperscript{2},6\textsuperscript{1},6\textsuperscript{2})_3\). For consistency, all compounds within this review will be named according to the name used most commonly for that compound in the scientific literature, and for clarity, their structures will be provided.

2.1.3. Bonding models
The initial motivation to prepare cycloarenes was to resolve questions concerning their π-electronic structure. We thus review the two dominant valence-bond models for π-electron distribution.

Representing delocalization of electrons in aromatic systems is a difficult task of which many methods have been developed. The most widely used is using Kekulé structures. Benzene, for example, can be represented as a cyclic arrangement of alternating double and single bonds of which two possible Kekulé structures can be drawn (Figure 2.4). Of course, the actual electronic structure of benzene is said to be neither of these structures but a combination of the two. As aromatic systems grow larger, the number of Kekulé structures increases. Naphthalene, for example has three Kekulé structures, while anthracene has four and phenanthrene has five.

![Figure 2.4. Kekulé structures of benzene.](image)

Another common method is that of Clar’s aromatic sextets. In this method a circle is used to represent the delocalization of six π electrons. The most characteristic Clar structure is that which contains the maximum number of these aromatic sextets, where no two circles are drawn in adjacent rings, and all remaining electrons can be properly represented by typical Kekulé structures. Unlike with Kekulé structures, the number of Clar structures does not always increase with larger structures. For example, anthracene has three proper Clar structures (Figure 2.5) while phenanthrene has only one (Figure 2.6). Each Clar structure represents $2^n$ Kekulé structures where $n$ is the number of aromatic sextets. In many cases, the Kekulé structures represented by the Clar structure have been found to be more dominant representations of the electronic structure of the molecule. For example, X-ray crystal structures of phenanthrene show that the middle ring has a more olefinic character than the outer two rings. Therefore, the
Kekulé structure not represented by the Clar structure (Figure 2.6, top right) does not contribute as significantly to the real molecular and electronic structure of phenanthrene as the other four do.

![Kekulé and Clar structures of phenanthrene.](image)

**Figure 2.5.** Clar structures of anthracene.

![Kekulé and Clar structures of phenanthrene.](image)

**Figure 2.6.** Kekulé and Clar structures of phenanthrene.

These contrasting bonding models relate quite well to the contrasting ideas of Pauling\textsuperscript{10} and McWeeny.\textsuperscript{9} The Kekulé bonding model says nothing about which of the large number of possible structures should contribute most, only which ones are possible; therefore, supporting both delocalization theories equally. The use of the Kekulé model is the only way to depict the global delocalization of electrons described by Pauling. While the local delocalization of electrons described by McWeeny can also be shown using Kekulé structures, Clar structures do a better job. When used in conjunction with cycloarenes, Pauling’s electron delocalization theory does not support the Clar bonding model, only the Kekulé bonding model. McWeeny’s electron delocalization theory, however, supports both bonding models with the Clar model being the better one. Support for the McWeeny theory of electron delocalization goes hand in hand with support for the Clar bonding model. Meanwhile, support for the Pauling theory of electron delocalization undermines the Clar bonding model and vice versa.

### 2.1.4. Diamagnetic Anisotropy
Diamagnetic anisotropy is an interesting phenomenon that is especially evident in aromatic molecules and serves as one of the most easily interpreted markers of aromatic character.\textsuperscript{22} When an aromatic molecule, such as benzene, is placed in an external magnetic field ($B_0$, Figure 2.7, highlighted in blue), the $\pi$ electrons circulate (highlighted in red) creating their own magnetic field ($B_{\text{IND}}$, highlighted in green) that opposes $B_0$ inside the ring. This is commonly observed in nuclear magnetic resonance (NMR) spectroscopy. In $^1\text{H}$ NMR, the protons of benzene exist outside the circulating ring of $\pi$ electrons, and experience a $B_{\text{IND}}$ in the same direction as $B_0$. These two magnetic fields have an additive effect, deshielding the protons to a lower field value (higher ppm chemical shift vs. TMS by convention).

![Diamagnetic anisotropy in aromatic molecules](image)

**Figure 2.7.** Depiction of diamagnetic anisotropy in aromatic molecules. Structures not drawn to scale.

\textsuperscript{18}Annulene, an especially important example, has protons inside and outside of the circulating flow of $\pi$ electrons.\textsuperscript{23} These inner protons experience a $B_{\text{IND}}$ in the opposite direction as $B_0$. These two magnetic fields have a subtractive effect, shielding the protons to a higher field value (lower ppm chemical shift vs. TMS by convention). The outer protons are still deshielded like benzene’s as they still experience a $B_{\text{IND}}$ in the same direction as $B_0$.\textsuperscript{23}
Of major interest with cycloarenes is whether the electrons remain delocalized into smaller benzenoid rings (Figure 2.7, bottom left) as predicted by McWeeny\textsuperscript{9} or if they are globally delocalized across the entire molecule (Figure 2.7, bottom right) as predicted by the methods of Pauling.\textsuperscript{10} The chemical shift of these inner protons makes for a very efficient spectroscopic handle for determining how the $\pi$ electrons are delocalized. If they remain delocalized into benzenoid rings, the inner protons will be deshielded, supporting the electron delocalization theory of McWeeny and the Clar bonding model. If the $\pi$ electrons are globally delocalized the inner protons will be shielded, supporting the electron delocalization theory of Pauling and undermining the Clar bonding model.

### 2.1.5. Superaromaticity

Another concept taught by cycloarenes is superaromaticity, the idea that macrocyclic conjugation in large, cyclic PAHs leads to an increased stabilization of the molecules.\textsuperscript{24–28} That is, delocalization about the “superring” of the cycloarenes affords additional aromatic character. While closely related to electronic structure, this idea was still debated even after the synthesis of 1 showed that electrons are delocalized mostly into only smaller benzenoid rings. The main thought behind these debates was that even though electrons in cycloarenes remain mostly delocalized into benzenoid rings, they could still have minor global delocalization that can give rise to superaromatic character.

### 2.1.6. Significance of Cycloarenes

The contrasting theories based on the ideas of McWeeny\textsuperscript{9} and Pauling\textsuperscript{10} brought about much debate as to how electrons are delocalized in large aromatic systems, and cycloarenes are ideal test cases of these competing hypotheses. This serves as an excellent example as to how the synthesis of complex and interesting molecules can answer fundamental scientific questions. In particular, the $^1$H NMRs of successfully synthesized cycloarenes all exhibited deshielding of the inner protons.\textsuperscript{1–3,5} This deshielding effect showed that electrons in these molecules remain
delocalized in small benzenoid rings, as opposed to being globally delocalized across the entire molecule. This realization shows that the McWeeny electron delocalization theory is the valid one, not the Pauling theory. The Clar bonding model is therefore a more accurate representation for large macrocyclic PAHs than the Kekulé bonding model.

Many computational studies have been carried out in an attempt to quantify superaromaticity in cycloarenes. Although some of these studies have shown that cycloarenes might enjoy some amount of superaromaticity, most studies agree that this is more likely caused by accumulation of errors in the computational methods or that any stabilization cycloarenes might experience due to superaromaticity is just too small compared to the overall energy of the molecule. Because these values are so small, or possibly nonexistent, computational studies of cycloarenes suggest that there is little, if any, need for the concept of superaromaticity.

A more modern application of cycloarenes is that they can serve as models for defects in graphene. Interest in graphene has grown astronomically in recent years due to its remarkable properties and possible applications. Cycloarenes can help us to better understand graphene, how it behaves, and how it can be used. Modern methods for making graphene almost always lead to imperfections of various degrees. 3, for example, is a model of a single point defect in graphene made by the removal of a single carbon atom from the graphene lattice, and 1 is a larger hole model made by removing a full benzenoid unit from the graphene lattice.

4 and 5 are interesting non-graphitic cycloarenes, in that they cannot be excised from a graphene lattice. Graphene can contain defects without six-fold symmetry. These defects lead to altered properties and performance of the system. Scott, Itami, and coworkers have recently shown how large PAHs with non-six membered rings can serve as excellent models for defects in graphene. While their work is a great model for fully carbon defects, cycloarenes are excellent examples for holes that exist in graphene.
2.2 Synthesis

The syntheses of cycloaranes are interesting in their own right. They showcase many cutting edge strategies for the synthesis of PAHs at that time. Most syntheses employ three key steps: macrocyclization, completion of the σ bond framework, and aromatization to the final product. These steps are not always carried out in the same order and in some cases multiple steps are carried out at once. Some of these then state of the art reactions included sulfur extrusion, Suzuki coupling, ring-closing metathesis (RCM), Scholl oxidation, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation reactions.

2.2.1 Kekulene

In 1978, after over a decade of attempts, Staab and Diederich reported the first successful and conclusive synthesis of 1.1,2 This approach (Scheme 2.1) utilized a key sulfur extrusion method in which dibromide 10 was reacted with dithiol 11 to dithiacyclophane 12. Photolysis of 12 then gave macrocycle 13 while Stevens rearrangement and sulfoxide elimination of 12 gave 14. Both 12 and 13 contain the carbon atom skeleton of 1. Although, this is not the first reported synthesis of 13,11 it is the first with a somewhat satisfactory yield.
Scheme 2.1. [a] KOH, benzene, EtOH, high dilution, reflux, 24 hr, 60%. [b] trimethyl phosphite, 20 °C, 450 W, 2 hr, 59%. [c] 1) methyl fluorosulfonate, CH₂Cl₂, 20 °C, 6 hr, 92%. 2) KOtBu, THF, 20 °C, 12 hr, 75%. 3) mCPBA, CH₂Cl₂, −20 °C, 10 min, 95%. 4) 450 °C, 30 min, 43 %.

With sizable quantities of 13 and 14 in hand, many routes of oxidative C-C bond formation to 1 were explored (Scheme 2.2). Overall, two new σ bonds and either four or six new π bonds needed to be formed, with each approach selectively forming only a few of these at a time. The first approach utilized DDQ to selectively dehydrogenate the dihydrophenanthrene type bridges of 13 to give macrocycle 15; however, all attempts to further oxidize 15 to 1 were unsuccessful.

Scheme 2.2. [a] DDQ, toluene, reflux, 24 hr, 81%. [b] DDQ, benzene, reflux, 24 hr, 66%. [c] I₂, benzene, 300 W, 10 min, 70%. [d] DDQ, 1,2,4-trichlorobenzene, 100 °C, 3 d, 91%.
The next approach used DDQ to dehydrogenate 14 to macrocycle 16. Photochemical cyclodehydrogenation attempts of 16 were unsuccessful. This is most likely due to the highly twisted structure of 16 brought on by the steric crowding of the inner protons attached to the carbon atoms between which the new σ bond is desired. This steric crowding does not allow 16 to adopt an appropriate geometry for photochemical cyclization. Photochemical cyclization of 14, however, proceeded well, yielding macrocycle 17. Presumably, the increased flexibility of 14 over 16 contributed to this success. 17 is the first molecule with the complete σ bond network of 1 to be conclusively synthesized. The dehydrogenation of 17 was extremely difficult due to its low volatility and low solubility, but using the uncommon solvent 1,2,4-trichlorobenzene 1 was finally obtained in measurable quantities (45 mg).

Parallel to the efforts of Staab and Diederich, Jenny and coworkers made attempts towards the synthesis of 1 (Scheme 2.3), which they called [12]coronaphene.12,13 Their most successful attempt utilized dichloride 18 to form macrocycle 19. Simultaneous dehydrogenation and halogenation, followed by dehalogenation gave macrocycle 20. Photochemical cyclodehydrogenation attempts of 20 gave mass spectroscopic evidence hinting at the formation of 1, however isolation or further characterization of this desired product was not reported.

![Scheme 2.3](image)

**Scheme 2.3.** [a] Na, THF. [b] NBS. [c] high temp.

### 2.2.2 Other Graphitic Cycloarenes

#### 2.2.2.1. Cyclo[d.e.e.d.e.e.d.e.e.e.e.e.]dekakisbenzene

Peter and Jenny first reported an attempt to synthesize cycloarene 2 in 1966 (Scheme 2.4).15 Dibromide 21 was treated with phenyl lithium to give macrocycle 22, which contained the
carbon atom skeleton of 2. The authors had previously claimed in 1965 that drastic conditions were able to cyclodehydrogenate 22 into 2,[14] however, the claims made in this presentation were not substantiated in the subsequent publication a year later.[15]

Scheme 2.4. [a] bromobenzene, Li, ether, benzene, 60-70 °C, 30 min, 3%. [b] AlCl₃, CS₂, Pd/C, CO₂, 320-340 °C.

In 1983, Staab et al. reported an attempted synthesis of cycloarene 2 (Scheme 2.5), taking a disconnection similar to that of the synthesis of 1.[16] Dibromide 21 and dithiol 23 reacted to give dithiacyclophane 24. Two different sulfur extrusion methods applied to 24 produced macrocycles 22 and 25. Scholl reaction of 22 was only successful in installing one of the two required σ bonds. Similarly, photochemical cyclodehydrogenation of 25 was also successful in installing only one of the two required σ bonds.

Scheme 2.5. K₂CO₃, EtOH, t-BuOH, toluene, reflux, 3 hr, 61%. [b] trimethyl phosphite, 500 W, 6 hr, 73 %. [c] 1) methyl fluorosulfonate, CH₂Cl₂, 20 °C, 6 hr, 94%. 2) KOtBu, THF, RT, 20 °C, 12 hr, 60%. 3) methyl fluorosulfonate, CH₂Cl₂, 20 °C, 6 hr, 94%. 4) KOtBu, THF, RT, 20 °C, 12 hr, 20%. 
Staab and Funhoff reported the first successful approach to 2 in 1986 (Scheme 2.6) utilizing a similar approach to the previous one but incorporating more flexibility in the macrocycles, the same trick that was applied in the successful synthesis of 1.\(^3\) Dibromide 26 and diisothiouronium salt 27 reacted to produce dithiacyclophane 28, which then yielded macrocycle 29 via sulfur extrusion. Photochemical cyclization gave a mixture of isomers that could then be dehydrogenated to give 2 for the first time in a measurable quantity.

**Scheme 2.6.** [a] KOH, toluene, MeOH, reflux, 30%. [b] 1) methyl fluorosulfonate 2) KOrBu, THF, 96% over 2 steps. 3) mCPBA, CH\(_2\)Cl\(_2\), –25 °C. 4) 170 °C, 6 hr, 17% 2 steps. [c] 1) nPropylamine, h\(_v\), –32 °C, 6.5 hr, 35%. 2) DDQ, \(m\)-xylene, 90 °C, 54 hr, 13%.

**2.2.2.2 Cyclo[d.e.e.d.e.e.d.e.e.]nonakisbenzene (attempt)**

Staab and Sauer reported the attempt to synthesize cycloarene 3 in 1984 (Scheme 2.7).\(^4\) In much the same manner as Staab’s approach to 1 and 2, dibromide 30 was reacted with dithiol 31 to give dithiacyclophane 32. Two different sulfur extrusion methods on 32 yielded either macrocycle 33 or macrocycle 34. All attempts to cyclodehydrogenate either of these two compounds to 3 were unsuccessful.
Scheme 2.7. [a] K$_2$CO$_3$, benzene, THF, MeOH, 20 °C, 5 hr, 58%. [b] 1) mCPBA, CHCl$_3$, 20 °C, 2.5 hr. 2) 450 °C, 10$^{-5}$ torr, 15 min, 62%. [c] 1) methyl fluorosulfonate, 1,1,2,2-tetrachloroethane, 20 °C, 8 hr, 96%. 2) KOtBu, THF, 20 °C, 3 d, 79%. 3) mCPBA, CH$_2$Cl$_2$, −25 °C, 25 min, 88%. 4) mesitylene, 165 °C, 50 hr, 18%.

2.2.3 Non-graphitic Cycloarenes

2.2.3.1 Cyclo[\textit{d.e.d.e.d.e.d.e.d.e.}]dekakisbenzene (attempt)

Staab and Sauer also reported the attempt to synthesize cycloarene 4 in 1984 (Schemes 2.8 and 2.9). Again following Staab’s approach to 1 and 2, dithiol 35 and dibromide 36 were reacted to form dithiacyclophane 37. Two different sulfur extrusion methods yielded either macrocycle 38 or macrocycle 39. 38 and 39 were oxidized to the more rigid macrocycles 40 and 41 respectively. All cyclodehydrogenation attempts of compounds 38, 39, 40 or 41 to 4 were unsuccessful.
Scheme 2.8. [a] KOH, AcOH, benzene, EtOH, 75 °C, 24 hr, reflux 1 hr, 49%. [b] trimethyl phosphite, 125 W, 6 hr, 48%. [c] 1) methyl fluorosulfonate, CH₂Cl₂, 20 °C, 12 hr, 93%. 2) KOtBu, THF, 20 °C, 12 hr, 59%. 3) mCPBA, CH₂Cl₂, −25 °C, 30 min, 98%. 4) mesitylene, 48 hr, reflux 35%.

Scheme 2.9. [a] DDQ, toluene, reflux, 4.5 hr, 22%. [b] DDQ, toluene, reflux, 20 hr, 71%.

2.2.3.2 Septulene

Kumar et al. reported the synthesis of 5 (Scheme 2.10) in 2012, which they named septulene to imply its sevenfold symmetry and similarity to kekulene 1. This was the first successful synthesis of a non-graphitic cycloarene. Their synthesis began with the highly functionalized monomer unit 42. This AB type Suzuki polymerization monomer contained olefin groups to be used later for a RCM reaction as the key step in their synthesis. Propenyl substituents were chosen to reduce styrene-type polymerizations and were deuterated at the β positions to provide a spectroscopic handle for the progress of the RCM. Suzuki polymerization of 41 under dilute conditions gave a mixture of linear 43 and cyclic 44 polymers. RCM of this mixture gave a mixture of products from which 5 was isolated in a 3% yield over the two steps. The authors note
that this low yield is more likely do to the unselective nature of the polymerization and not the effectiveness of the RCM.

Scheme 2.10. [a] Pd\{P(p-tol)\}_4, K_2CO_3, toluene, THF, H_2O, high dilution, 20 °C, 3d. [b] Grubb’s 2nd generation catalyst, 1,2,4-trichlorobenzene, toluene, 70 °C, 3 d, 3% over 2 steps.

2.2.4 Multi-stranded Cycloarenes

In 2016, Müllen and co-workers reported the synthesis of the extended cycloarene 6 (Scheme 11).\(^\text{48}\) Sonogashira coupling of hexa-\(m\)-phenylene 45 with TIPS-acetylene produced macrocycle 46 which was subsequently deprotected to give 47. Six-fold Diels-Alder cycloaddition with 2,3,4,5-tetraphenylcyclopenta-2,4-dienone yielded dendrimer 48. Cyclodehydrogenation of 48 then produced a material that suggested evidence of 6 by mass spectroscopy. Structural characterization to exclude rearrangements\(^\text{49,50}\) was not provided.\(^\text{48}\)
Scheme 2.11. [a] TIPS-acetylene, CuI, PPh₃, piperidine, Pd(PPh₃)₄, 80 °C, 3 d, 62%. [b] TBAF, THF, 1 hr, 78%. [c] 2,3,4,5-tetraphenylcyclopenta-2,4,-dienone, o-xylene, 300 W microwave, 160 °C, 24 hr, 66%. [d] FeCl₃, CH₃NO₂, CH₂Cl₂, 3 d, 84% (crude).

2.2.5 Heterokekulenes

2.2.5.1 18,21-Diazakekulene (attempt)

In 1983, Katritzky and Marson reported the attempt at a nitrogen-containing cycloarene, 18,21-diazakekulene 7 (Scheme 2.11).⁵ Condensation between diketone 49 and dialdehyde 50 gave the dioxa-macrocycle 51; however, no attempts to convert this to the desired diaza-macrocycle were discussed. An alternative condensation method between 49 and 50 showed mass spectroscopic evidence of what the authors believed to be 7; however, isolation or further characterization of this compound was not described.
**Scheme 2.12.** [a] TfOH, 100 °C, 2 hr, 86%. [b] KOEt 2) NH$_4$OAc, acetamide, DMF.

2.2.5.2 19,20,21,22,23,24-Hexaazakekulene (attempt)

Ranshoff and Staab reported an attempt to synthesize 19,20,21,22,23,24-hexaazakekulene 8 in 1985 (Scheme 2.12) that was similar to the previously discussed attempt at 7. Self-condensation of compound 52 gave the dioxa-macrocycle 53, which was then converted to the desired hexaaza-macrocycle 54 by treatment with ammonia. At the time of publication, attempts to dehydrogenate 54 to form 8 were said to be in progress; however, neither details nor results from these attempts have been reported.

**Scheme 2.13.** [a] AcOH, perchloric acid, 20 °C, 2.5 hr, 94%. [b] NH$_3$, ACN, reflux, 18 hr, 3%.

2.2.5.3 3,9,15,19,21,23-Hexaazakekulene

In 1997, Tatibouët *et al.* reported the first successful attempt at a nitrogen-containing cycloarene, 3,9,15,19,21,23-hexaazakekulene 9 (Scheme 2.13). Condensation of two equivalents of protected proflavine 55 with one equivalent of formaldehyde to yield protected diamine 56, which was then deprotected to give diamine 57. Condensation using one equivalent each of 57 and proflavine 58 with two equivalents of formaldehyde gave 9, the first conclusive synthesis of a heterocyclic cycloarene analogue.
Scheme 2.14. [a] Paraformaldehyde, HCl, 50 °C, 3 weeks, 84%. [b] NaOH, EtOH, 90 °C, 24 hr, 68 %. [c] Proflavin 58, paraformaldehyde, HCl, 50 °C, 7 d.

2.3 Molecular and Electronic Structure

The molecular and electronic structure of cycloarenes has long been of interest. The highly conjugated nature of cycloarenes gives rise to an extraordinarily high amount of Kekulé structures. In stark contrast, there exist a low number of Clar structures with the maximum number of aromatic sextets. 1, for example, has been determined to have 200 different Kekulé structures while it has only one Clar structure with six aromatic sextets (Figure 2.8). Of particular interest of these 200 Kekulé structures are those like 1a where the structure is composed of two concentric annulenes bridged by radial single bonds, and those like 1b where the structure is composed of six angularly annelated bezenoid rings, just like in the Clar model 1c. 2 is of interest because it can also be represented as two concentric annulenes 2a yet it has nine different Clar representations with a maximum number of aromatic sextets, two of which are shown in 2b and 2c. 5 is of interest because it cannot be represented as two concentric annulenes, instead requiring at least one radial double bond as seen in 5a. As with 1, however, 5 also has only one Clar structure with seven aromatic sextets as seen in 5b. Multiple computational studies have been performed but give contrasting results. The semi-classical approach of Pauling\textsuperscript{10} suggests structures more like 1a while MO calculations by McWeeny\textsuperscript{9} were the first to suggest structures more like 1b and 1c.
Figure 2.8. Kekulé and Clar structures of some synthesized cycloarenes.

2.3.1 $^1$H NMR

One way to elucidate the electronic structure of these cycloarenes would be to use nuclear magnetic resonance (NMR) spectroscopy. Structures like 1a would exhibit a different diamagnetic anisotropy than those like 1b and 1c. 1a, being comprised of two concentric [4n+2] annulenes, allows for the delocalization of electrons across the entire molecule and would exhibit $^1$H NMR chemical shifts similar to [18]annulene, where the outer protons are deshielded and the inner protons are shielded due to the flow of electrons in the molecule. In contrast, structures like 1b and 1c would contain only localized ring currents, so both the inner and outer protons would be deshielded. All NMR chemical shifts discussed are reported in ppm vs. TMS.

The acquisition of the $^1$H NMR of 1 in 1978 was difficult due to its extremely low solubility in all organic solvents. The first suitable spectrum was reported to have been taken in [d$_3$]-1,3,5-trichlorobenzene (Table 2.1, column 1) at about 200 °C in an 80 MHz instrument for about 50,000 scans. Three reproducible signals were seen with an intensity ratio of 2:1:1 at 7.94, 8.37, and 10.45 ppm for the outer vinyl, outer aryl, and inner type protons respectively. No
signals were seen shifted upfield. In 1983, spectra in [d2]-1,2,4,5-tetrachlorobenzene (Table 2.1, column 2) at 155 °C were reported with similar signals at 8.01, 8.45, and 10.47 ppm.\textsuperscript{1,35} The downfield shift of the inner protons suggests that the electronic structure is indeed more like that of 1b and 1c than 1a.

**Table 2.1.** Experimental and calculated proton chemical shifts of 1. All values in ppm.

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<th>2</th>
<th>3</th>
<th>4</th>
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</tbody>
</table>

Many calculations have predicted chemical shifts for 1 that also support an electronic structure like 1b and 1c (Table 2.1). Using the methods of McWeeny,\textsuperscript{9} Wilcox calculated the chemical shifts of 1 (column 3).\textsuperscript{35} In 1972, Ege and Vogler calculated the chemical shifts of 1 using a modified Hückel Molecular Orbital (HMO) theory (column 4).\textsuperscript{36} Staab et al. reported the chemical shifts of 1 calculated using a similar method to Ege and Vogler but also took into account additional van der Waals deshielding (column 5).\textsuperscript{35} In 1979, Vogler calculated chemical shifts of 1 with the coupled Hartree-Fock (HF) perturbation theory (column 6).\textsuperscript{37} In 2001, Steiner et al. predicted the chemical shifts of 1 using current-density maps (column 7).\textsuperscript{38} These last calculations also suggested that the higher deshielding seen of the inner protons over the outer protons is due to a paramagnetic rotating ring current around the inner “hub” of 1 and not from just van der Waals deshielding.

The experimental results for 2 and 5 also suggest electronic structures more like 2b, 2c, and 5b.\textsuperscript{3,5} The \textsuperscript{1}H NMR of 2 in [d2]-1,2,4,5-tetrachlorobenzene exhibited chemical shifts of 8.11, 8.11, 8.29, and 8.65 ppm for the outer protons and 9.56 ppm for the inner protons. The \textsuperscript{1}H NMR of 5 in [d4]-1,2-dichlorobenzene exhibited chemical shifts of 7.86 and 8.63 ppm for the outer protons and 10.19 ppm for the inner protons. Because the spectra of 1, 2, and 5 were recorded in
different solvents they cannot be directly compared; however, all three show evidence of a benzenoid over an annulenoid type electronic structure.

2.3.2 X-Ray Crystallography

The crystal structures of two cycloarenes, 1 and 5, are known.\textsuperscript{5,35,39} The average unique C-C bond lengths (Figure 1.9) tell much about the electronic structure of these compounds. These bond lengths can be grouped into three categories that fit quite well with their Clar representations. The first group (highlighted in green) agrees with typical bond lengths of benzenoid rings. The second group (highlighted in blue) is much longer and indicates a high single-bond character. The final group (highlighted in red) is very close to that of normal C-C double bonds.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{unique_bond_lengths.png}
\caption{Unique C-C bond lengths for 1 and 5.}
\end{figure}

The crystal structures of 1 and 5 reveal just how similar these two compounds are. The C-C bond lengths of these two compounds are indeed essentially the same. Additionally, despite the planar nature of 1 versus the non-planar nature of 2, the two compounds have surprisingly similar three-dimensional packings (Figure 2.10). Both compounds were found to pack into slipped stacks that make up a herringbone pattern. The similarity in the molecular structure of 1 and 5 further suggests that the Clar model, which is also similar for the two compounds, is a better representation than the Kekulé model, which has some drastic differences such as total number of
Kekulé structures and 5 requiring at least one radial double bond in all Kekulé structures while 1 does not.

![Diagram of Kekulé structures]

**Figure 2.10.** The crystal packing of 1 (top) and 2 (bottom). Figure reproduced with permission from reference 5.

### 2.3.3 Electronic Spectra

The fluorescence and phosphorescence of 1 were recorded in a polycrystalline matrix of 1,2,4,5-tetrachlorobenzene at 1.3 K using the method of Shpol’skii. Despite being both symmetry and spin-forbidden, 0-0 bands are observed in the fluorescence and phosphorescence spectra. This has been attributed to an external heavy atom effect and a reduction in symmetry of first excited singlet and triplet states brought about by the chosen solvent. Because these 0-0 bands are observed with high intensity in the phosphorescence spectrum, it was possible to obtain optical detection magnetic resonance (ODMR) spectra, where the optical measurement is combined with electron spin resonance spectroscopy. With ODMR, the zero field splitting parameters |D| and |E| were determined. Of particular interest were the |D| values, which measure the dipolar coupling of the triplet electrons. By definition, |D| values are a function of the inverse average distance between these electrons; therefore, they should decrease with the increase in size of a π system. Anthracene, for example has a much smaller value than
naphthalene, which has a much smaller value than benzene (Table 2.2). The |D| value of 1 was found to be surprisingly high, and in fact, is close to that of phenanthrene. This data suggests that the electrons in 1 are not coupled over long distances, and instead are localized into smaller regions, as depicted by the Clar model.

**Table 2.2.** |D| values of various PAHs.

| Compound       | |D| (cm⁻¹) |
|----------------|------------------|
| Benzene        | 0.1581           |
| Naphthalene    | 0.0994           |
| Anthracene     | 0.0694           |
| Phenanthrene   | 0.1053           |
| 1              | 0.1039           |

### 2.3.4 Nucleus independent chemical shifts

Nucleus independent chemical shifts (NICS) values are a standard method for calculating the aromaticity of compounds.⁴² Values at ring centers can be easily computed and are useful in that they are not highly dependent on the size of the system and can probe effects within individual rings of a polycyclic system. NICS-1 values differ from standard NICS values in that the probe is placed 1 Å above the ring center, and are regarded as a better measure of aromaticity. The more negative this value the more aromatic character (−9.7 ppm for benzene), the more positive this value, the more antiaromatic character (27.6 ppm for cyclobutadiene), and values close to zero show a more nonaromatic character (−2.2 ppm for cyclohexane).²⁶ The NICS-1 values calculated for 1 and 5 validate the X-ray crystallographic data by showing more aromatic character of the benzenoid rings with higher values of −11.5 ppm for 1 and −11.3 ppm for 5 and showing less aromatic character for the olefinic rings with lower values of −6.3 ppm for 1 and −5.8 ppm for 5.⁵ These results also suggest the Clar model is a better representation for the electronic structure of 1 and 5 than the Kekulé model.

### 2.4 Superaromaticity
Many attempts have tried to quantify the thermodynamic stabilization, if any, from macrocyclic conjugation in cycloarenes, also known as superaromaticity. These attempts are all alike in that they first calculate the overall aromaticity of the system, then determine superaromaticity by subtracting the aromaticity of a superaromaticity free reference. The methods differ in the way aromaticity is computed and how the superaromaticity free reference is defined.

2.4.1 Additive Nodal Increments

In 1991, Ciodlowski et al. attempted to use an additive nodal increment (ANI) approach to determine the superaromatic stabilization energy of 1. Benzenoid hydrocarbons can be represented as molecular graphs $G$ (Figure 2.11). A corresponding “dualist” $G'$ can be created for this graph by replacing each hexagonal ring with a dot and connecting each dot with a straight line. $G'$ can be broken up into its different types of vertices, called nodes. Benzo[a]anthracene 59, for example can be represented as the graph $G_{59}$ and its dualist $G_{59}'$. Splitting apart $G_{59}'$, three types of nodes are formed: two of type 1, one of type 2, and one of type 3. Similarly, 1 can be represented by the graph $G_{1}$ and its dualist $G_{1}'. Splitting up $G_{1}'$ gives twelve total nodes: six of type two and six of type three. Isonodal hydrocarbons have been shown to be of about the same Hückel total $\pi$-electron energy, $E_{\pi}$. These energies can be approximated by Equation 2.1:

$$E_{\pi} \approx \sum_{i=1}^{12} n_{i}E_{i}$$  \hspace{1cm} (2.1)

where $n_{i}$ is the number of nodes of type $i$, and $E_{i}$ is the nodal energy increment for nodes of type $i$. $E_{\pi}$ should then, in theory, be additive.
Figure 2.11. Molecular graphs of 59 and 1, their dualists, and corresponding nodes.

Ciodlowski et al. were able to approximate the energy of the desired nodes using the calculated energies of some small PAHs. The energy for node type 2 for example could be calculated by subtracting the energy of anthracene from that of tetracene, since anthracene has two type 1 nodes and one type 2 nodes while tetracene also has two type 1 nodes but has two type 2 nodes. By calculating the total HF energy, $E_{HF}$, for anthracene, phenanthrene, tetracene, 59, and chrysene, they were able to approximate the energy of nodes type 1, 2, and 3 using Equation 2.2:

$$E_{HF} \approx n_1E_1 + n_2E_2 + n_3E_3 \quad (2.2)$$

From these values (Table 2.3) the ANI energy, $E_{ANI}$, of 1 could be approximated using Equation 2.3:

$$E_{ANI} = 6E_2 + 6E_3 \quad (2.3)$$

Since $E_{ANI}$ was determined from non-superaromatic PAHs, the difference between $E_{HF}$ and $E_{ANI}$ should represent a molecule’s superaromatic stabilization energy (SSE). Thus 1 was determined to have a SSE of 52.4 mhartree (32.9 kcal/mol) at the STO-3G level of theory and 40.5 mhartree (25.4 kcal/mol) at the 6-31G** level of theory (Table 2.4).
Table 2.3. Nodal HF energy increments. All energies in atomic units. Values of the fitted total energies in parentheses.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>HF/STO-3G</th>
<th>HF/6-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>-529.4725 (-529.4724)</td>
<td>-536.0167 (-536.0167)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-529.4874 (-529.4875)</td>
<td>-536.0277 (-536.0278)</td>
</tr>
<tr>
<td>Tetracene</td>
<td>-680.2535 (-680.2564)</td>
<td>-688.6601 (-688.6625)</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>-680.2770 (-680.2714)</td>
<td>-688.6783 (-688.6736)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-680.2838 (-680.2865)</td>
<td>-688.6824 (-688.6847)</td>
</tr>
<tr>
<td>Nodal Energy Increments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Node Type 1</td>
<td>-189.3442</td>
<td>-191.6854</td>
</tr>
<tr>
<td>Node Type 2</td>
<td>-150.7840</td>
<td>-152.6459</td>
</tr>
<tr>
<td>Node Type 3</td>
<td>-150.7990</td>
<td>-152.6570</td>
</tr>
<tr>
<td>Error Values</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rms Error / Ring</td>
<td>0.0008</td>
<td>0.006</td>
</tr>
<tr>
<td>Maximal Error / Ring</td>
<td>0.0014</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

Table 2.4. Determined energies of 1. All energies in atomic units.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>HF/STO-3G</th>
<th>HF/6-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF energy</td>
<td>-1809.5502</td>
<td>-1831.8168</td>
</tr>
<tr>
<td>ANI energy</td>
<td>-1809.4978</td>
<td>-1831.8573(^a)</td>
</tr>
<tr>
<td>SSE</td>
<td>-0.0524</td>
<td>-.0405</td>
</tr>
<tr>
<td>Rms error</td>
<td>0.0092</td>
<td>0.0077</td>
</tr>
<tr>
<td>Maximal error</td>
<td>0.0168</td>
<td>0.0141</td>
</tr>
</tbody>
</table>

\(^a\)Corrected value. See reference 24 for details.

In 1992, Aihara suggested that these differences in energy are more likely due to an accumulation of errors in the energy increments that increase as the molecules get larger. This suggestion comes from the fact that acyclic PAHs 60 and 61 (Figure 2.12), which are similar in size to 1 but cannot be superaromatic, also were found to have a difference between \( E_{HF} \) and \( E_{ANI} \) similar to that of 1.
2.4.2 Conjugated Circuits

PAHs contain many cyclic paths throughout their structures. If there exists a Kekulé structure in which one of these paths is composed of alternating single and double bonds, this path is known as a conjugated circuit. In 1977, Randić demonstrated that all \((4n+2)\) conjugated circuits lower the energy of the system, while \(4n\) conjugated circuits raise the energy of the system.\(^{43}\) Aihara applied this concept of conjugated circuits in an attempt to explain superaromaticity in \(1.\)\(^{25}\) All calculations in this section are performed at the HMO level of theory.

The conjugated circuits in \(1\) are all \((4n+2)\) and can be divided into two types. Type 1 circuits are those that contain one or more consecutive benzene rings while type 2 circuits are those that surround the inner cavity. \(1\) has been determined to contain 132 type 1 circuits and 4096 type 2 circuits. Figure 2.13 outlines a few examples of these.

![Conjugated Circuits](image)

**Figure 2.12.** Acyclic PAHs similar to \(1.\)

**Figure 2.13.** Some conjugated circuits in \(1.\) Double bonds omitted for clarity.

Herndon\(^{44}\) and Randić\(^{43}\) have shown that the Dewar resonance energy (DRE) can be expressed in terms of conjugated circuits, and that smaller circuits, such as six and ten-membered
ones, are more relevant than the larger circuits, such as eighteen or larger membered ones. Using Randić’s conjugated circuit method,\textsuperscript{43} \textit{I} was estimated to have a DRE of 145.8 kcal/mol,\textsuperscript{25} which is in good agreement with the calculated DRE of 141.4 kcal/mol. The largest contribution of any type 2 conjugated circuit is only 0.02 kcal/mol from that of eighteen membered circuit \textit{d}. Since any SSE experienced by \textit{I} must come from type 2 conjugated circuits, and the total contribution of these circuits to the overall aromatic character of \textit{I} is so low, Aihara concluded that using this method \textit{I} appears to not be superaromatic.

Another approach of Aihara to explain the superaromaticity of \textit{I} using conjugated circuits, compared the circuit resonance energies (CREs) of the conjugated circuits within \textit{I}.\textsuperscript{25} CREs have been shown to approximately measure the contribution of a conjugated circuit to the overall aromaticity of a system.\textsuperscript{45} CREs of the conjugated circuits in \textit{I} (Table 2.5), show that the smaller type 1 conjugated circuits contribute much more to the aromaticity of \textit{I} than the superaromatic type 2 conjugated circuits.\textsuperscript{25} This is in accordance with the findings using the methods of Randić.

\textbf{Table 2.5.} CREs of circuits from figure 2.13. All energies in $|\beta|$.

<table>
<thead>
<tr>
<th>Circuit</th>
<th>CRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.1400</td>
</tr>
<tr>
<td>b</td>
<td>0.0446</td>
</tr>
<tr>
<td>c</td>
<td>0.0327</td>
</tr>
<tr>
<td>d</td>
<td>0.0036</td>
</tr>
<tr>
<td>e</td>
<td>0.0017</td>
</tr>
<tr>
<td>f</td>
<td>−0.0002</td>
</tr>
</tbody>
</table>

Aihara also showed how ring currents can be used to determine superaromaticity within \textit{I}.\textsuperscript{25} It has been shown that ring currents of individual conjugated circuits can be added up to give the overall ring current of the system. When \textit{I} is placed in an external magnetic field, the overall ring current can, therefore, be said to be comprised of the ring current of all type 1 and type 2 conjugated circuits. The ring currents due to just type 2 conjugated circuits can be summed up to
give the superaromatic ring currents. By definition, diamagnetic ring currents are drawn clockwise. A comparison of the calculated ring currents (Figure 2.14) shows that the superaromatic ring currents in 1 are much smaller than the overall ring currents in 1, and therefore do not contribute much to the overall aromaticity of 1.

![Ring currents](image)

**Figure 2.14.** Overall (A) and superaromatic type 2 (B) ring currents within 1. Clockwise currents are diamagnetic.

### 2.4.3 Polynomial References

Secular polynomials are graph theoretically defined equations that are constructed using the mathematical equivalencies of graphs, secular matrices, and characteristic polynomials. For chemical compounds, a graph of a compound is broken apart into smaller subgraphs that are then compiled to construct the overall secular polynomial of the compound. A polynomial reference can then be constructed by deleting specific components of the overall secular polynomial. Secular polynomials have been shown to be useful in determining the standard aromaticity of compounds. By deriving the secular polynomial of a compound and deleting the cyclic components, the reference polynomial is obtained. The difference in energy between these two polynomials gives the aromatic stabilization energy of the compound.

In 1995, Zhou tried to determine the superaromaticity of 1 using hardness indices. He claims this to be a superior method because it is much less sensitive to deviations caused by poor reference structures. This is important because the superaromaticity, if any, is so much smaller compared to traditional benzenoid aromaticity than the calculated values for superaromaticity,
which are too close to the potential error of the previous methods. Superaromaticity was determined by topologically defining a secular polynomial reference structure derived from the secular polynomial of the molecule of interest. Derivation of this reference polynomial was said to be straightforward yet tedious. Superaromaticity \( \eta^S \) could then be determined using equation 2.4:

\[
\eta^S = \eta - \eta^S_{ac}
\]

where \( \eta \) is the hardness of the molecule of interest and \( \eta^S_{ac} \) is the hardness of the superaromaticity free reference. A positive \( \eta^S \) indicates superaromaticity while a negative \( \eta^S \) indicates superantiaromaticity. 1 was determined to have a \( \eta^S \) of 0.0266 \(|\beta|\), much smaller than that of 0.0744 \(|\beta|\) for coronene and 0.1031 \(|\beta|\) for corannulene tetraanion. From this relatively small value compared to the overall hardness for 1 of 0.4372, 1 was claimed to experience some slight superaromatic stabilization.

Aihara et al. also used polynomial defined references to determine superaromaticity within cycloarenes in 2013.\(^{28}\) Again this method has been claimed to determine SSE with a high degree of precision. Using HMO theory, they determined the total \( \pi \)-binding energy for many different macrocyclic PAHs, some of which are given in table 2.6. Subtracting out the graph-theoretically exact polynomial reference, SSE was also determined for these compounds. The SSE for 1 and 5 was determined to be minimal, in agreement with previous methods. It is worth noting, however, that evenly stranded variants such as 62 and 63 showed much greater SSE.

Table 2.6. SSE of some macrocyclic PAHs determined using polynomial defined references.

| Compound | Total \( \pi \)-binding energy (|\( \beta \)|) | SSE (|\( \beta \)|) |
|----------|-----------------------------------------------|------------------|
| 1        | 68.610210                                    | 0.003483         |
| 5        | 80.041176                                     | 0.000002         |
| 62       | 132.513299                                    | 0.048368         |
| 63       | 185.085176                                    | 0.028038         |
2.4.4 Aromatic Stabilization Energy and Diamagnetic Susceptibility

In 1996, Jiao and Schleyer attempted to quantify the SSE of 1 in a method similar to the ANI approach of Ciodlowski et al. Jiao and Schleyer’s approach was to calculate the aromatic stabilization energy (ASE) of 1, which measures the cyclic electron delocalization, and therefore the aromacity, of a molecule. The SSE of 1 would therefore be the difference between the ASE of 1 and its smaller, non-superconjugated benzenoid hydrocarbon components. Using benzene, anthracene, phenanthrene, naphthalene, and 1,2.7,8-dibenzanthracene as reference compounds, the non-superaromatic ASE of 1 can be determined using homodesmotic equations 2.5a, 2.5b, and 2.5c.

\[
3[\text{anthracene} + \text{phenanthrene} - 2 \text{benzene}] = \text{kekulene} \quad (2.5a)
\]

\[
6[\text{anthracene} + \text{phenanthrene} - 2 \text{naphthalene}] = \text{kekulene} \quad (2.5b)
\]

\[
6[1,2.7,8\text{-dibenzanthracene} - \text{phenanthrene}] = \text{kekulene} \quad (2.5c)
\]

The calculated ASEs (Table 2.7) paired with equations 2.5a, 2.5b, and 2.5c provide the SSE of 1 summarized in Table 2.8. These values are much smaller than those determined by Ciodlowski et al. with equation 4c actually giving slightly positive values. Based on these findings, it was concluded that 1 does not experience any significant extra stabilization due to superaromaticity.
Table 2.7. Energies calculated for 1 and reference compounds and their magnetic susceptibility anisotropies. All energies in Hartree. Both $\chi_{\text{anis}}$ and $\Lambda$ in ppm cgs and calculated at the Becke3LYP/6-31G level of theory.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E (HF/3-21G)</th>
<th>E (HF/3-21G)</th>
<th>$\chi_{\text{anis}}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1821.55153</td>
<td>-1821.55153</td>
<td>-769.7</td>
<td>-227.8</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-533.00347</td>
<td>-533.00347</td>
<td>-203.1</td>
<td>-56.1</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-533.01572</td>
<td>-533.01572</td>
<td>-190.5</td>
<td>-52.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-381.21581</td>
<td>-381.21581</td>
<td>-135.0</td>
<td>-36.5</td>
</tr>
<tr>
<td>1,2,7,8-dibenzanthracene</td>
<td>-836.60869</td>
<td>-836.60869</td>
<td>-56.1</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>-229.41945</td>
<td>-229.41945</td>
<td>-69.8</td>
<td>-16.7</td>
</tr>
</tbody>
</table>

Table 2.8. Determined SSE of 1. All energies in kcal/mol. Both $\chi_{\text{anis}}$ and $\Lambda$ in ppm cgs and calculated at the Becke3LYP/6-31G* level of theory.

<table>
<thead>
<tr>
<th>Equation</th>
<th>SSE (HF/3-21G)</th>
<th>SSE (Becke3LYP/6-31G*)</th>
<th>Extra $\chi_{\text{anis}}$</th>
<th>Extra $\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>-6.7</td>
<td>-3.3</td>
<td>-7.7</td>
<td>-3.7</td>
</tr>
<tr>
<td>4b</td>
<td>-16.4</td>
<td>-11.6</td>
<td>-28.1</td>
<td>-11.2</td>
</tr>
<tr>
<td>4c</td>
<td>3.9</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similarly, Jiao and Schleyer used diamagnetic susceptibility exaltation ($\Lambda$) and diamagnetic susceptibility anisotropy ($\chi_{\text{anis}}$) to determine the superaromaticity of 1. The extra $\Lambda$ and $\chi_{\text{anis}}$ of 1 can be determined using equations 5a and 5b as done with ASE. These values (Table 2.8) were found to be small for the large size of 1 and therefore imply no superaromatic stabilization.

### 2.5 Conclusions

Cycloarenes have taught us much about some fundamental concepts in chemistry. Their preparation demonstrated that their electrons tend to remain delocalized into benzenoid rings as predicted by McWeeny and they are best depicted using Clar structures. Computational studies of cycloarenes have shown that they do not gain much, if any, superaromatic stabilization from macocyclic conjugation. Thus, superaromaticity is not a relevant concept, at least for cycloarenes. Their potential use as models for defects in graphene has only just been looked into. While not
many examples within this interesting class of molecules have been synthesized, especially in recent years, cycloarenes still have very much to teach us and should continue to be of intense interest.

2.6 References


Chapter 3: Septulene


### 3.1 Contributions

This project spanned many years with multiple key contributors. Dr. Margel Bonifacio began by developing a first generation monomer synthesis and determining the viability for implementation of ring-closing metathesis (RCM) to make polycyclic aromatic hydrocarbons. Dr. Ruth Viboh continued this work to develop the final monomer synthesis, optimize the polymerization and RCM reactions, and begin characterization. Dr. Bharat Kumar completed this work by continuing to refine synthetic methods, isolating and purifying septulene, and performing a majority of the characterization. My contributions to this project mainly dealt with making septulene using the previously developed and optimized methods and assisting with its purification and characterization. As such, this chapter will focus on the synthesis of septulene and the key concepts learned from its synthesis. Many computational studies were also performed but will not be discussed here.

### 3.2 Introduction

The synthesis of kekulene 2 by Staab and Deiderich

1–4 answered a long-standing, fundamental question about arenes and their electronic structure. Pauling

5 and McWheeny

6 developed contradicting theories about how π electrons are delocalized in these systems. Pauling’s theory, best depicted by the Kekulé bonding model (figure 3.1, top right), suggested that 2 should behave as two concentric annulenes, and that the inner protons should be strongly shielded, as in [18]annulene.

7 McWheeny’s theory, best depicted using Clar’s aromatic sextets (figure 3.1 bottom right),

8 suggests localized ring currents, and that the inner protons should be...
deshielded as in benzene. Experimental results showed that these inner protons are deshielded and resonate with a chemical shift above 7 ppm, in support of McWheeny’s electron delocalization theory. Our synthesis of septulene 1, reinforced these conclusions.

![Kekulé and Clar structures of septulene 1 and kekulene 2. Arrow indicates the unique radial bond in the Kekulé structure of 1.](image)

**Figure 3.1.** Kekulé and Clar structures of septulene 1 and kekulene 2. Arrow indicates the unique radial bond in the Kekulé structure of 1.

The properties of 1 and 2 are extraordinarily similar, despite them possessing fundamentally different Kekulé structures (figure 3.1, top). This difference arises from the odd number of carbon atoms in both the inner and outer annuli of 1, necessitating a radial double bond in its Kekulé structures. Another underlying difference is that 2 is alternant while 1 is non-alternant. The similar properties of 1 and 2, in light of these differing fundamentals suggests that consideration of a few Kekulé structures provides little insight into the chemistry of condensed arenes.

Our approach to the synthesis of 1 (scheme 3.1) was to first synthesize an olefin substituted cyclometaphenylene then use ring closing metathesis (RCM) to form phenanthrene type bridges, “stitching-up” the gaps.9–11 This cyclometaphenylene network was produced as a minor side product in the polymerization of monomer 3. Propenyl substituents were chosen over
vinyl ones to prevent styrene type polymerizations and deuterium was incorporated on these to provide a spectroscopic handle to monitor the RCM as the loss of the C-D stretch could be easily seen with IR spectroscopy.

3.3 Results and Discussion

Monomer 3 was produced in 3 steps from known material in a 44% overall yield (Scheme 3.1). First, a Wittig reaction of dialdehyde 4 using CH₃CD₂PPh₃Br to give dibromide 5 as a mixture of EE, EZ, and ZZ isomers. 5 was isomerized into solely the EE isomer by photoirradiation in the presence of diphenyldisulfide. While the isomerization was not essential, it greatly increased clarity in spectroscopic characterization. It is also worth noting, this radical isomerization is unpredictable and the yields are inconsistent. Recent work has suggested using a larger excess of potassium tert-butoxide in the previous Wittig reaction may directly yield the EE isomer as the sole product. Application of this can be seen in chapter 4 but has not been performed with this substrate. Finally, borylation with n-BuLi and isopropyl pinacol borate gave monomer 3.

![Scheme 3.1. Synthesis of septulene 1. [a] CH₃CD₂PPh₃Br, tBuOK, THF [b] Ph₂S₂, THF, 100 W [c] nBuLi, isopropyl pinacol borate, THF, -78 °C [d] Pd[P(ρ-tol)]₃, K₂CO₃, THF/H₂O, toluene, 80 °C [e] Grubb’s catalyst (2nd generation), 1,2,4-trichlorobenzene, toluene, 70 °C.

Polymerization of 3 under standard Suzuki conditions produced a mixture of linear polymers and macrocyclic oligomers as evidenced by MALDI-TOF mass spectrometry. Performing the polymerization under dilute conditions, the yield of macrocycles increased with
cycloheptamer 6 being the most abundant. RCM of the polymer mixture using Grubb’s 2nd generation catalyst was monitored by IR spectrometry, observing the disappearance of the C-D stretch. 1 crystalized from THF upon workup and was purified using HPLC. The low yield of 1, 3% in two steps from 3, can be attributed to 6 only being a minor side product of the polymerization reaction and not the effectiveness of the RCM reaction.

The synthesis of 1 showed its copious physical similarities to 2. 1 is insoluble in common organic solvents, with slight solubility in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene (~1 mg / 20 mL at 100 °C). 1 possesses a melting point > 500 °C and is quite stable, showing no signs of decomposition under ambient conditions for months. 1 forms as yellow crystals from 1,2-dichlorobenzene and 1,2,4-trichlorobenzene that have a light green fluorescence.

1 and 2 also possess similar NMR properties. The 1H NMR spectrum of 1 in d₄-1,2-dichlorobenzene (referenced to TMS) showed three singlets at 7.86, 8.36 and 10.19 ppm in the ratio 2:1:1 (see experimental). The 1H NMR spectrum of 2 in d₃-1,2,4-trichlorobenzene also showed three singlets at 7.94, 8.37, and 10.45 ppm, in a 2:1:1 ratio. Although the spectra were recorded in different solvents and cannot be directly compared, they do show striking similarities.

The "extraordinarily difficult" acquisition of the 1H NMR spectrum for 2 by Staab and Diederich in 1978 set a high standard, prompting us to obtain the 13C NMR for 2. This required 14 hours on an 800 MHz spectrometer equipped with a cryo probe. The spectrum, obtained in d-bromoform, showed five peaks at 131.7, 130.4, 129.8, 128.2 and 118.0 ppm.

The optical absorbance of 1 (figure 3.2) showed three transitions (λₓᵧₙ 339 nm, log ε 4.90; 365 (sh), 4.45; 396, 4.04) slightly red-shifted from those of 2 (λₓᵧₙ, 326 nm, log ε 4.93; 347 (sh), 4.74; 388, 4.22). Their fluorescence spectra were also similar, with 1 showing peaks at 453, 466, 486 and 517 nm and 2 showing peaks at 453, 468, 483, and 513 nm (± 5 nm).
Figure 3.2. UV/Vis and fluorescence spectra of 1. Reproduced with permission from reference 18.

Surprisingly, the X-ray crystal structure of 1 showed that it has a chair-type structure (figure 3.3), and not a saddle shape as predicted by gas phase density functional theory calculations. The average unique C-C bond lengths of both 1 and 2 can be grouped into three categories that fit quite well with their Clar representations (figure 3.4).2,4 The first group (highlighted in green) agrees with typical bond lengths of benzenoid rings. The second group (highlighted in blue) is much longer and indicates a high single-bond character. The final group (highlighted in red) is interestingly very close to that of normal C-C double bonds. Additionally, despite the planar nature of 1 versus the non-planar nature of 2, the two compounds have surprisingly similar three-dimensional packings, where both compounds were found to pack into slipped stacks that make up a herringbone pattern (figure 3.5).
Figure 3.3. The solid-state conformation of 1. Views from the top and the side with the least squares molecular plane in translucent grey. Atomic displacement parameters are drawn at 50% probability and H atoms omitted for clarity. Reproduced with permission from reference 18.

Figure 3.4. Unique C-C bond lengths for 1 and 2.
Figure 3.5. The crystal packing of 1 (top) and 2 (bottom). Reproduced with permission from reference 18.

The synthesis of 1 was important because it not only reinforced the conclusions made from the synthesis of 2, but also proved that the fundamental differences between the two have little effect on their physical properties. The exclusion of certain possible Kekulé for 1, particularly that it cannot be drawn as two concentric annulenes, and that 1 is nonalternant while 2 is alternant are among the most notable differences; however, the non-planarity of 1 is its only significant physical difference from 2.

3.4 Conclusions

The synthesis of 1 confirmed many of the conclusions made after the synthesis of 2. The two compounds demonstrated that the π electrons of arenes tend to remain localized into benzenoid rings as predicted by McWheeny and not delocalized throughout the entire system. These conclusions also show the Clar bonding model to be the best method for depicting arenes, an idea that has yet to catch on with most of the chemical community.

3.5 Experimental

3.5.1 Methods

All materials were used without further purification unless otherwise specified. THF was distilled from sodium and benzophenone. Most NMRs were recorded on Varian spectrometers (MR 400 MHz, V 400 MHz, V 500 MHz). Most mass spectra were recorded on an Agilent 6230 TOF-LC/MS using either electrospray ionization or atmospheric pressure photoionization in positive mode. All IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR ATR surface with 4 cm⁻¹ resolution as thin films. The mass spectrum of septulene was recorded using a MALDI-TOF mass spectrometer. ¹³C{¹H} NMR spectrum of septulene was recorded on a Bruker 800 MHz spectrometer with a cryoprobe.
**4,6-Dibromobenzene-1,3-dicarbaldehyde (4).** Synthesized according to literature procedure.\(^9\)

**1,1-2H)-Ethyltriphenylphosphonium bromide.** Triethylamine (5 drops) was added to a solution of ethyltriphenylphosphonium bromide (3.55 g, 9.56 mmol) in deuterium oxide (10 mL). The mixture was refluxed 16 hours and the solvent was removed under reduced pressure to give CH\(_3\)CD\(_2\)PPh\(_3\)Br as a white solid in 90% yield.

\(^1\)H NMR [CDCl\(_3\), 400 MHz]: \(\delta 7.91 – 7.76\) (m, 8H), 7.70 (ddd, \(J = 2.5, 3.4, 7.6, 5\)H), 1.39 (d, \(J = 20.1, 3\)H) ppm.

\(^13\)C\(_{\{1\}H}\) NMR [CDCl\(_3\), 100 MHz]: \(\delta 131.5, 131.0, 133.6, 130.6, 130.4, 118.3, 117.5, 6.6\) ppm.

\(^31\)P NMR [CDCl\(_3\), 400 MHz]: \(\delta 27.4\) ppm.

HRMS [ESI-TOF]: C\(_{20}\)H\(_{18}\)D\(_2\)P calculated 293.1428, found 293.1422.

**1,5-dibromo-2,4-bis(2-2H)propenylbenzene (5).** Potassium tert-butoxide (2.83 g, 25.2 mmol) was added to a solution of 4 (9.87 g, 26.5 mmol) in dry tetrahydrofuran (350 mL). The orange solution was degassed and stirred at room temperature for 20 min. A solution of CH\(_3\)CD\(_2\)PPh\(_3\)Br (3.50 g, 12.0 mmol) in dry THF (200 mL) was slowly added to the reaction mixture. The solution was stirred for 18 hours at room temperature. The solvent was evaporated, the residue extracted with hexane and purified by flash chromatography with hexane to give 5 as a yellow liquid in 85% yield (mixture of EE, ZZ, EZ isomers).

\(^1\)H NMR [CDCl\(_3\), 400 MHz]: \(\delta 7.80\) (s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.52 (s, 1H), 7.36 (s, 1H), 7.25 (s, 1H), 7.21 (s, 1H), 6.62 (d, \(J = 11.6, 3\)H), 6.38 (d, \(J = 8.1, 3\)H), 1.90 (s, 6H), 1.77 (s, 12H) ppm.

\(^13\)C\(_{\{1\}H}\) NMR [CDCl\(_3\), 100 MHz]: \(\delta 136.9, 136.5, 136.4, 135.7, 135.5, 131.9, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.1, 124.3, 122.4, 122.2, 121.1, 121.0, 87.7, 18.6, 14.5, 14.4, 14.3 ppm.

**1,5-dibromo-2,4-di[(1E)-2-2H]propenylbenzene (5EE).** Diphenyl disulfide (0.17 g, 0.78 mmol) was added to a solution of 5 (mixture of stereoisomers, 1.38 g, 4.34 mmol) in unstabilized
tetrahydrofuran (150 mL). The solution was irradiated for 18 hours using a 100 W lamp. The solvent was evaporated, residue dissolved in hexane and purified by flash chromatography with hexane to give 5EE as white crystals in 80% yield.

$^1$H NMR [CDCl$_3$, 400 MHz]: $\delta$ 7.68 (s, 1H), 7.52 (s, 1H), 6.60 (s, 2H), 1.90 (s, 6H) ppm.

$^{13}$C $^1$H NMR [CDCl$_3$, 100 MHz]: $\delta$ 136.9, 135.7, 129.1, 128.8, 124.3, 121.0, 18.5 ppm.

FT-IR [ATR, cm$^{-1}$]: 3025, 2966, 2929, 2909, 2842, 2723, 2244, 1628, 1427, 1371.

HRMS [APPI-TOF]: C$_{12}$H$_{10}$D$_2$Br$_2$ calculated 315.9413, found 315.9401.

2-{5-bromo-2,4-di[(1E)-(2-2H)prop-1-enyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3). 5EE (3.20 g, 10.1 mmol) was dissolved in dry THF (145 mL), stirred for 5 min. then cooled to $-78$ °C. n-BuLi (6.5 mL, 10.4 mmol) was added dropwise, the solution stirred for 10 min, and isopropyl pinacol borate was added (2.11 g, 11.3 mmol). The reaction mixture was warmed to room temperature, the solvent was evaporated, and the residue was purified by flash chromatography with dichloromethane. This crude product was recrystallized from absolute ethanol to afford 3 as a yellow solid in 65% yield.

$^1$H NMR [CDCl$_3$, 400 MHz]: $\delta$ 7.87 (s, 1H), 7.59 (s, 1H), 7.06 (s, 1H), 6.69 (s, 1H), 1.94 – 1.82 (m, 6H), 1.37 – 1.28 (m, 12H) ppm.

$^{13}$C $^1$H NMR [CDCl$_3$, 100 MHz]: $\delta$ 143.2, 139.9, 139.6, 130.8, 130.0, 122.9, 120.8, 83.8, 24.9, 18.6 ppm.

FT-IR [ATR, cm$^{-1}$]: 2961, 2932, 2909, 2236, 1634, 1584, 1476, 1384, 1331, 1246, 1138, 1068, 964, 910, 859, 682.

HRMS [APPI-TOF]: C$_{18}$H$_{20}$D$_2$BrBO$_2$ calculated 363.1215, found 363.1299.

Poly(4,6-di[(1E)-(2-2H)propenyl])-m-phenylene. A solution of 3 (1.0 g, 2.78 mmol) and [Pd{P(p-tol)$_3$}]$_3$ (10 mg, 3.0 mol%) in dry toluene (50 mL) was added via syringe pump over 3 days to a boiling mixture of [Pd{P(p-tol)$_3$}]$_3$ (10 mg, 3.0 mol%) in 2N aqueous Na$_2$CO$_3$ (180 mL), THF (200 mL), and toluene (100 mL). The phases were separated, and the organic phase
was washed with water, the solvent removed, and solids purified by flash chromatography with dichloromethane. Methanol (100 mL) was added and the solids were filtered to give a polymer mixture in 90% yield that was used without further purification.

$^1$H NMR [CDCl$_3$, 400 MHz]: $\delta$ 7.68 (br, 1H), 6.87 (br, 1H), 6.18-6.11 (br, d, 2H, $J = 28$ Hz), 1.74-1.52 (br, 6H) ppm.

FT-IR [ATR, cm$^{-1}$]: 3016, 2959, 2909, 2850, 2727, 2232, 1634, 1469, 1445, 1373, 906, 865, 678.

**Septulene (1).** The Poly(4,6-di[(1E)-(2-2H)-propenyl])-m-phenylene mixture (0.50 g, 3.17 mmol) and 2,6-dichloro-1,4-benzoquinone (0.03 g, 0.158 mmol) were dissolved in distilled, degassed 1,2,4-trichlorobenzene (10 mL) and toluene (10 mL). The solution was heated to 70 °C, Grubbs catalyst (2nd generation) (120 mg, 0.022 mmol) was added in three batches over three days. The reaction was monitored by IR spectroscopy. The extent of the reaction was determined by the disappearance of C-D stretch at 2236 cm$^{-1}$. Ethylene glycol monovinyl ether (0.8 mL) was added to quench the catalyst and reaction was poured into methanol (100 mL). The green solid residue (790 mg) was filtered, dried on high vacuum, and dissolved in 1,2,4-trichlorobenzene (10 mL). To the solution, triethylamine (1.0 mL), silica gel (1.0 g) and tris(hydroxymethyl)phosphine (1.0 g) were added. The mixture was heated to 70 °C for 28 hours and purified by flash chromatography with 1,2,4-trichlorobenzene (100 mL). The solvent was removed under reduced pressure, the residue washed with unstabilized THF (20 mL), then purified by HPLC to give clean 1 in 3% yield.

$^1$H NMR [d$_4$-1,2-dichlorobenzene, 400 MHz]: $\delta$ 8.09 (s, 14H), 8.59 (s, 7H), 10.41 (s, 7H) ppm.

$^{13}$C{$^1$H} NMR [CDBr$_3$, 200 MHz]: $\delta$ 131.7, 130.4, 129.8, 128.2, 118.0 ppm.

FT-IR [ATR, cm$^{-1}$]: 3038, 2989, 2952, 1587, 1434, 1109, 894, 743, 690, 529, 492, 438.

HRMS [MALDI-TOF]: C$_{56}$H$_{28}$ calculated 700.2191, found 700.2186.
3.5.2 Spectra

3.5.2.1 NMR

(1,1-2H)-Ethyltriphenylphosphonium bromide.
1,5-dibromo-2,4-bis(2H)propenylbenzene (5).
1,5-dibromo-2,4-di[(1E)-2H|propenylbenzene (5E).
2-{5-bromo-2,4-di[(1E)-(2-2H)prop-1-enyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).
Poly(4,6-di[(1E)-(2-2H)-propenyl])-m-phenylene.
Septulene (1).
3.5.2.2 Mass Spectra

(1,1-2H)-Ethyltriphenylphosphonium bromide.

1,5-dibromo-2,4-di[(1E)-2-2H]propenylbenzene (5EE).
2-\{5-bromo-2,4-di[(1E)-(2-2H)prop-1-enyl]phenyl\}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).

Septulene (1).
3.5.2.3 IR

1,5-dibromo-2,4-di[(1E)-2-2H]propenylbenzene (5EE).

2-[5-bromo-2,4-di[(1E)-(2-2H)prop-1-enyl]phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).
Poly(4,6-di[1E-(2-2H)-propenyl])-m-phenylene.

Septulene (1).
3.6 References


Chapter 4: Synthetic Efforts Towards Aromatic Belts

4.1 Introduction

Aromatic belts have garnered attention for decades.\(^1\) Aside from their potentially interesting supramolecular and electronic properties, scientists believe they may serve as a stepping-stone towards the bottom up synthesis of carbon nanotubes (CNTs). A universally accepted definition for aromatic belts has yet to be established, but most agree that they must be fully conjugated and include upper and lower edges that do not coincide. A major flaw with most definitions lies with a lack of distinction between large aromatic belts and short nanotubes. Many sub-classes of aromatic belts exist that have better defined guidelines such as cycloacenes, cyclophenacenes, Schlüter belts, and Vögtle belts (figure 4.1). Despite decades worth of efforts, the bottom up synthesis of any aromatic belt has yet to be conclusively accomplished. We set out to synthesize compounds within a new sub-class of aromatic belts. Similar to cycloacenes and cyclophenacenes, our belts are comprised solely of six membered rings and every atom is contained in either the upper or lower strand.

![Schlüter Belt](image1.png)

![Vögtle Belt](image2.png)

![Our Target](image3.png)

Figure 4.1. Some examples of aromatic belts including one of our targets.

Cycloparaphenylene (CPPs) are another class of aromatic molecules that have garnered much attention in the past decade.\(^2\) The three major synthetic routes to CPPs all incorporate some
corner unit to induce curvature and overcome strain in the systems. In 2008, Jasti et al. utilized cyclohexadiene moieties to induce curvature, followed by a late stage aromatization to synthesize their CPPs.\textsuperscript{3} In 2009, Itami and co-workers utilized \textit{cis}-cyclohexane moieties to induce curvature, followed by a late stage dehydration/aromatization to synthesize their CPPs.\textsuperscript{4} In 2010, Yamago et al. utilized a tetranuclear platinum complex to overcome strain, followed by reductive elimination to yield their CPPs.\textsuperscript{5}

\begin{center}
\textbf{Scheme 4.1.} Established routes to CPPs.
\end{center}

Ring-closing metathesis (RCM) has proven to be a useful tool in the synthesis of polycyclic aromatic hydrocarbons (PAHs).\textsuperscript{6–9} This approach forms phenanthrene type bridges from adjacent olefin substituents. RCM reactions are known to be reversible, allowing the process to anneal any defects that may occur from side reactions such as cross metathesis or acyclic diene metathesis polymerizations. RCM reactions tend to favor the synthesis of PAHs over other side reactions due to the gain of resonance stabilization from the newly formed aromatic ring(s).

Our approach to aromatic belts involves the implementation of two key strategies: first to synthesize propenyl substituted CPPs, then use RCM to “stitch-up” the bridges between the phenylene units to complete the aromatic belts.
4.2 Results and Discussion

We have taken two routes towards synthesizing an aromatic belt. Our first route utilized the methods of Itami and co-workers, which required the synthesis of two monomer units, 1 and 2. Synthesis of 1 was achieved in 3 steps from commercially available material. 1,4-dibromo-2,5-dimethylbenzene was oxidized to tetraacetate 3 using chromium trioxide then hydrolyzed to dialdehyde 4 under acidic conditions by known methods. Subsequent Wittig reaction yielded 1 in a 20% overall yield.

Literature methods for the synthesis of 4 worked well and scaled nicely. The only major issue towards the synthesis of 1 was obtaining it as single isomer. Standard Wittig conditions typically yielded 1 as a mixture of EE, EZ, and ZZ isomers. While having 1 as a single isomer is not essential, it makes characterization and purification much simpler; therefore, many attempts were made to isomerize this mixture of isomers to solely the EE one. Photochemical isomerization with PhSSPh and Cp₂TiCl₂ catalyzed isomerizations both typically showed only a negligible change in isomer ratios. A Pd(MeCN)₂Cl₂ catalyzed method led to undesired side reactions, leading to a complex mixture of products. It was serendipitously discovered that use of excess t-BuOK in the Wittig reaction afforded 1 predominantly as the EE isomer (≥80% de) eliminating the need for isomerization. Thompson has since improved conditions for t-BuOK catalyzed isomerization of aryl-propenyl groups.
**Scheme 4.3.** Synthesis of 1. [a] CrO₃, H₂SO₄, AcOH, Ac₂O, 0 °C, 18 h, 52%. [b] H₂SO₄, EtOH, H₂O, reflux, 18 h, 78%. [c] t-BuOK, EtPPh₃Br, THF, reflux, 18 h, 50%.

Our first approach to synthesize 2 began by allylating dimethyl 1,4-cyclohexanedicarboxylate to yield compound 5 as a mixture of isomers. All attempts to decarboxylate 5 to 2 using acid catalyzed, base catalyzed, or Krapcho conditions were unsuccessful.

**Scheme 4.4.** Attempt at 2. [a] Allyl bromide, K₂CO₃, NaI, acetone, reflux, 72 h, 74%.

Based upon the work of Stoltz and co-workers, we took a second approach to 2. A Fischer esterification of succinic acid with allyl alcohol yielded diallyl succinate 6. A Claisen-Dieckman self-condensation of 6 then yielded bis(b-ketoester) 7 and palladium catalyzed decarboxylative allylation of 7 afforded 2 as a mixture of isomers in a 17% yield over 3 steps. All attempts to epimerize 2 to a single isomer using acid or base catalyzed methods were unsuccessful. While having 2 as a single isomer would help purification and characterization of future steps, it was not essential so the mixture of isomers was deemed sufficient. It is also worth noting that the alkenes in 2 are not in the correct place, but rather than identifying a positional isomerization method at this time, we wanted to first determine if CPP synthesis using these two monomers was possible.
Scheme 4.5. Synthesis of 2. [a] TsOH, allyl alcohol, benzene, reflux, 12 h, 90%. [b] NaH, allyl alcohol, toluene, 95 °C, 10 h, 32%. [c] Pd(PPh₃)₄, DMF, RT, 30 min, 60%.

The next step in Itami’s route involves the CeCl₃ addition of monomer 1 to monomer 2 to form trimer 8, the L-shaed unit needed for cyclization. Any attempts to perform this addition gave a complex mixture of which 8’s presence could not be confirmed, let alone isolated. This may possibly be attributed to the difficult nature of the reaction combined with the sixteen possible stereoisomers of 8. Even with a successful reaction, there is no guarantee that the four desired stereoisomers could be isolated from the other twelve. Additionally, the late stage dehydration-aromatization in this route requires strongly acidic conditions with typically high temperatures that could prove detrimental to our olefins. Due to the lack of success with the CeCl₃ addition and the lack of certainty that our substrates would survive dehydration-aromatization conditions, we decided to abandon this route.

Scheme 4.6. First attempt at a propenyl functionalized CPP.

Our second route towards an aromatic belt was to utilize the methods of Yamago and co-workers. This route began by dimerizing monomer 1 to biphenyl 9. Among known dimerization methods, we identified two that could work well with olefins and extra bromide substituents. Fe(OTf)₃ mediated dimerization from the Grignard reagent of 1 showed mono- and di- reduction
of bromides as the major products.\textsuperscript{16} CuCN mediated dimerization via the Lipshutz cuprate yielded 9 reproducibly in acceptable yields.\textsuperscript{17} The only major downside of this method was that the use of \( t \)-BuLi made scaling up problematic. From 9 we envisioned two possible substrates for the platinum cyclizations: stannylated biphenyl 10 based upon Yamago’s cyclizations and borylated biphenyl 11 based upon similar cyclizations by Isobe and co-workers.\textsuperscript{18} Both 10 and 11 were synthesized using palladium-catalyzed methods, as these proved more reproducible than using metal halogen exchange.\textsuperscript{19,20} Any attempts to cyclize 10 or 11 using the methods of Yamago or Isobe yielded a complex mixture of which palladium macrocycle 12 could not be identified. On the chance 12 was present but not discernable, these mixtures were subjected to ligand exchange conditions to form macrocycle 13 and reductive elimination conditions to CPP 14. This final reaction mixture showed none of the brightly colored fluorescence expected if 14 was indeed present. The long, linear nature of this synthesis, combined with the low yields even in the simpler cases, led to us abandoning this route after multiple failed attempts at producing a platinum-containing macrocycle.

\textbf{Scheme 4.7.} Second attempt at a propenyl functionalized CPP. [a] i) \( t \)-BuLi, THF, -78 °C, 1.5 h. ii) CuCN, RT, 30 min, 1,4-benzoquinone, RT, 18 h, 50%. [b] PdCl\(_2\)(dppf)-CH\(_2\)Cl\(_2\), bis(pinacolato)diboron, KOAc, toluene, 100 °C, 24 h, 50%. [c] (Me\(_3\)Sn)\(_2\), Pd(PPh\(_3\))\(_4\), toluene, reflux, 2 h, 90%.

The lack of success synthesizing a propenyl substituted CPP led to us attempting to develop conditions for the synthesis of an aromatic belt directly from a methyl substituted CPP.
To develop this methodology, we used the transformation of 2,2'-dimethylbiphenyl \( \text{15} \) into dihydrophenanthrene \( \text{16} \) as model cases.

\[ \text{Scheme 4.8. Benzylic oxidation attempts at dihydrophenanthrene} \ \text{16}. \]  
[a] 1) NBS, CCl\(_4\), 460 nm hv, 18 h. 2) Potassium ethyl xanthate, acetone, RT, 1 h 37\% (2 steps).  
[b] \( n\)-BuLi, \( t\)-BuOK, HTMP, THF, 1,2-dibromoethane -78 °C, 56\% (GC-MS).

We first tried to reproduce the work of Eisch and co-workers, where they converted \( \text{15} \) to \( \text{16} \) using \( \text{Zr(OEt)}_2(\text{Bu})_2 \), but our attempts were unsuccessful\(^{21} \). Our second attempt utilized \( \text{Na}_4\text{W}_{10}\text{O}_{32} \) in the presence of UV light\(^{22} \). After 12 hours, GC-MS showed a small amount of \( \text{16} \); however, additional irradiation failed to produce any further conversion. Our third attempt was to use a chain transfer agent to act as a masked benzylic radical, which could then react with a neighboring benzylic radical. Xanthate \( \text{17} \) was synthesized in 2 steps from \( \text{15} \); however, all attempts to convert this to \( \text{16} \) were unsuccessful\(^{23} \). Our final attempt utilized \( n\)-BuLi, \( t\)-BuOK, and HMTP to generate dianion \( \text{18} \) and oxidize this to \( \text{16} \).\(^{24} \) Screening of various oxidants showed that 1,2-dibromoethane gave \( \text{16} \) in moderate yields. We then set out to apply this method on an extended case; however, all attempts to transform tetramethylterphenyl \( \text{19} \) into \( \text{20} \) were unsuccessful. With only one method to effectively oxidize adjacent benzylic methyl groups, and no ways to apply this to even a slightly extended case, we deemed the likely hood of “stitching-
up” the six or more gaps needed to make an aromatic belt from a methyl-substituted CPP to be out of reach.


Synthesis of large PAHs is often difficult because it involves reactions that require harsh conditions, are sensitive to outside stimuli such as moisture and oxygen, and give low yields. Harsh conditions, such as high and low pH or strongly oxidative or reductive, can all prove detrimental to olefins and needed to be minimalized in our approach. Incorporation of these olefins also added multiple steps to an already low yielding process, meaning quantities were limited and scales kept low. These compounding difficulties made our approach seem more unattractive with each unsuccessful step, until we finally deemed that our efforts might be better spent elsewhere.

Towards the end of our work on this project, we met with Prof. Jasti, one of the world leaders of CPP synthesis. He shared many tips on making CPPs, but we still seemed unable to make them with our propenyl substituents. We also shared our experiences with using RCM to make PAHs with him. Recently, Jasti and co-workers have made some progress towards aromatic belts using their systems and RCM. While they have not made a fully annelated system to date, they have incorporated up to six vinyl substituents on their CPPs through a long, stepwise process and shown that RCM can be used to form the desired phenanthrene type bridges.

4.3 Conclusions

We have made progress along two routes towards the synthesis of aromatic belts. Small molecule building blocks 1, 2, 10, and 11 are key to these routes and have been synthesized in acceptable yields. L shaped unit 8 and macrocycle 12 remain the elusive intermediates to date.
Further spectroscopic analysis to understand the reasons these reactions are unsuccessful may be helpful. Additionally, any advancements in the synthesis of CPPs are worth monitoring for potential application with our proposed approach. It is worth noting that the success of RCM in the synthesis of septulene and the recent work by Jasti gives hope that should one of the elusive fully-olefin substituted CPPs be synthesized, an aromatic belt will follow.

4.4 Experimental

4.4.1 Methods

All materials were used without further purification unless otherwise specified. THF was distilled from sodium and benzophenone. NMRs were recorded on Varian spectrometers (MR 400 MHz, V 400 MHz, V 500 MHz). IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR ATR surface with 4 cm\(^{-1}\) resolution as thin films. GCMS data was recorded on an Agilent 7890A spectrometer.

2,5-dibromo-1,4-bis(acetyloxyethyl)benzene (3). Procedure modified from published method.\(^{10}\) 1,4-dibromo-2,5-dimethylbenzene (16.0 g, 60.6 mmol) was added to a mixture of acetic acid (80 mL) and acetic anhydride (160 mL). This suspension was cooled to 0 °C, then conc. H\(_2\)SO\(_4\) (56 mL) was added dropwise. CrO\(_3\) (24 g) was slowly added in small portions to ensure that the reaction mixture never rose above 10 °C, and the green slurry was allowed to stir for 18 hours. The reaction mixture was slowly poured into ice water. The precipitate was collected and washed with water (200 mL) followed by cold methanol (100 mL). The white to yellowish solid was collected in 52% yield and used without further purification. Spectroscopic data matched previously published results.

\(^1\)H NMR [CDCl\(_3\), 400 MHz]: \(\delta\) 2.15 (s, 12H), 7.74 (s, 2H), 7.84 (s, 2H) ppm.

2,5-dibromobenzene-1,4-dicarbaldheyde (4). Procedure modified from published method.\(^{10}\) Tetraacetate 3 (32.9 g, 70 mmol) was added to a mixture of ethanol (400 mL) and water (400 mL). Conc. H\(_2\)SO\(_4\) (40 mL) was added dropwise, and the reaction was allowed to reflux for 18
hours. The mixture was diluted with water (400 mL) and the precipitate was recrystallized from CH₂Cl₂ to give a pale yellow solid in 78% yield. Spectroscopic data matched previously published results.

\(^1\)H NMR [CDCl₃, 400 MHz]: \(\delta\) 10.34 (s, 2H), 8.15 (s, 2H) ppm.

**1,4-dibromo-2,5-dipropenylbenzene (1).** Potassium \(t\)-butoxide (4.0 g, 35 mmol) was added to a suspension of CH₃CH₃PPh₃Br (10.8 g, 29 mmol) in THF (300 mL) and the mixture was stirred for 20 min at room temperature. A solution of 4 (3.5 g, 12 mmol) in THF (200 mL) was transferred via cannula to the orange phosphonium ylide mixture, and allowed to reflux for 18 hours. The solvent was evaporated and the residue was dissolved in hexanes (200 mL) and the insoluble materials were removed. The mother liquor was concentrated then purified by flash chromatography with hexanes to yield the EE isomer of 1 as a white solid in 50% yield with >80% de.

\(^1\)H NMR [CDCl₃, 500 MHz]: \(\delta\) 1.91 (s, 6H), 6.18 (m, 2H), 6.61 (d, 2H), 7.62 (s, 2H) ppm.

\(^{13}\)C\(^{\{1\}H}\) NMR [CDCl₃, 125 MHz]: \(\delta\) 18.82, 121.94, 128.71, 129.82, 130.47, 137.51 ppm.

GC-MS: C₁₂H₁₂Br₂ (M⁺, 100%) calculated 316.03, found 315.90.

**Dimethyl 1,4,-diallyl-2,5-dioxocyclohexane-1,4-dicarboxylate (5).** A mixture of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (2.8 g, 12 mmol), allyl bromide (4.0 g, 33 mmol), K₂CO₃ (2.5 g, 14 mmol), and NaI (220 mg, 1.5 mmol) in dry acetone (15 mL) was refluxed for 72 hours. The insoluble materials were filtered, the solvent evaporated, and the solid recrystallized from diethyl ether:methanol (1:9 v/v) to give 5 in 74% yield as a mixture of isomers.

\(^1\)H NMR [CDCl₃, 500 MHz]: \(\delta\) 2.65 (m, 4H), 2.81 (d, 2H), 3.03 (d, 2H), 3.73 (s, 6H) 5.13 (m, 4H), 5.66 (m, 2H) ppm.

GC-MS: C₁₆H₂₀O₆ (M⁺, 0.65%) calculated 308.33, found 308.11.

**Diallyl succinate (6).** Procedure modified from published method.\(^{15}\) TsOH (0.021 g, 1.2 mmol) was added to a solution of succininc acid (4.0 g, 33.9 mmol) in benzene (30 mL). 70 mL of allyl
alcohol was added and the reaction refluxed for 12 hours under Dean-Stark conditions. The reaction was then quenched with aq. NaHCO₃ and the phases were separated. The organic layer was washed with aq. NaHCO₃ and brine, and then dried over MgSO₄. The solvent was evaporated to afford 6 as a colorless liquid in 90% yield, which was used without further purification. Spectroscopic data matched previously published results.

1H NMR [CDCl₃, 500 MHz]: δ 2.67 (s, 4H), 4.60 (m, 4H), 5.28 (m, 4H), 5.91 (m, 2H) ppm.

GC-MS: C₇H₉O₃ (M − OC₃H₅, 79.19%) calculated 141.14, found 141.00.

**Diallyl succinylsuccinate (7).** Procedure modified from published method.⁵ Allyl alcohol (0.2 mL, 2 mmol) was added dropwise to a mixture of NaH (0.76 g, 32 mmol) in toluene (6.3 mL) with vigorous stirring. After gas evolution ceased, 6 (2.5 g, 15 mmol) was added dropwise and the reaction was heated to 95 °C. After 15 minutes, more toluene was added (6.3 mL) and the heating and stirring continued for 10 hours. The solvent was evaporated, the solids suspended in CH₂Cl₂, and acidified with 2 M HCl (18 mL). This mixture was stirred for 2 hours, the phases separated, and the aqueous layer extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered, and the solvent was evaporated. The crude orange solid was recrystallized from a mixture of petroleum ether and acetone to afford 7 as a white solid in 32% yield. Spectroscopic data matched previously published results.

1H NMR [CDCl₃, 500 MHz]: δ 3.23 (s, 4H), 4.69 (m, 4H), 5.32 (m, 4H), 5.94 (m, 2H), 12.11 (s, 2H) ppm.

GC-MS: C₁₀H₈O₄ (M − COOC₃H₅, 4.40%) calculated 192.17, found 192.00.

**2,5-diallylcyclohexane-1,4-dione (2).** Pd(PPh₃)₄ (205 mg, 180 µmol) was added to a solution of 7 (512 mg, 1.8 mmol) in DMF (10 mL) and stirred at room temperature for 30 minutes. The solvent was evaporated and the residue purified by flash chromatography with CH₂Cl₂ to afford 2 as a mixture of isomers in 60% yield.
\(^1\)H NMR [CDCl\(_3\), 500 MHz]: \(\delta\) 2.21 (m, 2H), 2.39 (m, 2H), 2.55 (m, 2H), 2.78 (m, 4H), 5.08 (m, 4H), 5.71 (m, 2H) ppm.

GC-MS: C\(_{12}\)H\(_{16}\)O\(_2\) (M+, 3.84%) calculated 192.25, found 192.10.

**4,4’-dibromo-2,2’,5,5’-tetrapropenylbiphenyl (9)**. A solution of tert-butyl Lithium in hexanes (4.0 mL, 6.4 mmol) was added to a solution of 1 (2.0 g, 6.3 mmol) in THF (200 mL) at -78 °C. The reaction mixture was allowed to stir at -78 °C for 1.5 hours then copper(I) cyanide (375 mg, 4.2 mmol) was added, and the mixture was allowed to stir for another 30 minutes. The reaction mixture was then slowly warmed to room temperature and stir until all the copper(I) cyanide dissolved. 1,4-Benzoquinone (1.0 g, 9.3 mmol) was added and the mixture stirred overnight. An aqueous work up with ethyl acetate gave a crude material that was purified by flash chromatography with toluene. The resulting oil was then recrystallized from CH\(_2\)Cl\(_2\) to yield 9 as an off white solid in a 50 % yield.

\(^1\)H NMR [CDCl\(_3\), 500 MHz]: \(\delta\) 1.73 (dd, 6H), 1.90 (dd, 6H), 5.93 (dd, 2H), 6.14 (m, 4H), 6.73 (dd, 2H), 7.21 (s, 2H), 7.73 (s, 2H) ppm.

\(^{13}\)C\(\{^1\)H\}\) NMR [CDCl\(_3\), 125 MHz]: \(\delta\) 18.77, 18.84, 122.56, 127.83, 127.87, 128.37, 128.85, 129.09, 129.44, 135.59, 136.85, 137.59 ppm.

GC-MS: C\(_{24}\)H\(_{24}\)Br\(_2\) (M+, 57.37%) calculated 472.25, found 472.00.

**4,4’-bispinacolato-2,2’,5,5’-tetrapropenylbiphenyl (10)**. A mixture of 9 (900 mg, 1.6 mmol), bis(pinacolato)diboron (1.2 g, 4.7 mmol), PdCl\(_2\)(dpdf)-CH\(_2\)Cl\(_2\) (60 mg, 73 µmol), and KOAc (630 mg, 6.4 mmol) in toluene (30 mL) was heated to 100 °C and stirred for 24 hours. An aqueous work up with chloroform gave a crude material that was purified by flash chromatography with dichloromethane. The resulting oil was then recrystallized from methanol to yield 10 as an off white solid in 50% yield.

\(^1\)H NMR [CDCl\(_3\), 500 MHz]: \(\delta\) 1.39 (s, 24H), 1.69 (dd, 6H), 1.87 (dd, 6h) 6.01 (dd, 2H), 6.15 (m, 4H), 7.17 (dd, 2H), 7.29 (s, 2H), 7.95 (s, 2H) ppm.
\[ ^{13}C\{^1H\} \text{NMR [CDCl}_3, 125 \text{ MHz]: } \delta 18.75, 18.96, 25.07, 83.80, 126.14, 126.39, 126.46, 128.96, 131.32, 132.46, 134.20, 141.89, 141.94 \text{ ppm.} \]

**4,4’-bistrimethyltin-2,2’,5,5’-tetrapropenylbiphenyl (11).** A mixture of 9 (657 mg, 1.4 mmol), hexamethylditin (1.5 g, 4.6 mmol) and Pd(PPh\(_3\))\(_4\) (370 mg, 320 µmol) in toluene (100 mL) was refluxed for 2 h. The solvent was evaporated and the residue purified by flash chromatography with hexanes:ethyl acetate (3:1). The resulting oil was then recrystallized from acetonitrile to yield 11 as an off white solid in 90% yield.

\[ ^1H \text{NMR [CDCl}_3, 500 \text{ MHz]: } \delta 0.28 (s, 18H), 1.63 (dd, 6H), 1.75 (dd, 6H), 5.97 (3, 4H), 6.03 (d, 2H), 6.36 (dd, 2H), 7.18 (s, 2H), 7.55 (s, 2H) \text{ ppm.} \]

**Xanthate (17).** 2,2’-dimethylbiphenyl (100 mg, 0.55 mmol) and NBS (100 mg, 0.56 mmol) were dissolved in CCl\(_4\) and stirred for 18 hours under a blue LED (460 nm). Solvent was evaporated and crude mixture was purified by column chromatography with hexanes to give 2-Bromomethyl-2’-methylbiphenyl in 40% yield that was used without further purification.

\[ ^1H \text{NMR [CDCl}_3, 500 \text{ MHz]: } \delta 2.08 (s, 3H), 4.29 (dd, 2H), 7.14 (dd, 1H), 7.31 (m, 5H), 7.54 (dd, 1H) \text{ ppm.} \]

A solution of potassium ethyl xanthate (80 mg, 0.50 mmol) in 2 mL dry acetone was added dropwise to a stirred solution of 2-Bromomethyl-2’-methylbiphenyl in 1.5 mL dry acetone and allowed to stir at room temperature for 1 hour. The solution was filtered, the solvent evaporated, and the residue purified by column chromatography with 9:1 hexanes:ethyl ether to give 17 in 93% yield.

\[ ^1H \text{NMR [CDCl}_3, 500 \text{ MHz]: } \delta 1.37 (t, 3H) 2.08 (s, 3H), 4.17 (dd, 2H), 4.58 (q, 2H) 7.14 (m, 2H), 7.28 (m, 5H), 7.51 (m, 1H) \text{ ppm.} \]

**Dihydrophenanthrene (16).** N-BuLi (0.38 mL, 1.6 M in hexanes) was added to a solution of 2,2’-dimethylbiphenyl (91 mg, 0.50 mmol) in 15 mL THF and stirred for 5 min at –78 °C. A solution of tBuOK (67 mg, 0.60 mmol) in 0.6 mL THF was added dropwise followed by HTMP
(84 µL, 0.50 mmol) and allowed to stir for 15 min. 1,2-Dibromoethane (0.13 mL, 1.5 mmol) was added and the mixture stirred for another 5 min then allowed to warm to room temperature. The crude mixture contained 16 in 56% yield (GC/MS).

GC-MS: C_{14}H_{12} (M+, 100%) calculated 180.25, found 180.10.
4.4.2 Spectra

4.4.2.1 NMR

2,5-dibromo-1,4-bis(acetyloxy)methyl)benzene (3).

![NMR spectrum of 2,5-dibromo-1,4-bis(acetyloxy)methyl)benzene (3).]

2,5-dibromobenzene-1,4-dicarbaldehyde (4).

![NMR spectrum of 2,5-dibromobenzene-1,4-dicarbaldehyde (4).]
1,4-dibromo-2,5-dipropenylbenzene (1).
Dimethyl 1,4-diallyl-2,5-dioxocyclohexane-1,4-dicarboxylate (5).

Diallyl succinate (6).
Diallyl succinylsuccinate (7).

2,5-diallylcyclohexane-1,4-dione (2).
4,4’-dibromo-2,2’,5,5’-tetrapropenylbiphenyl (9).
4,4'-bispinacolato-2,2',5,5'-tetrapropenylbiphenyl (10).
4,4'-bistrimethyltin-2,2',5,5'-tetrapropenylbiphenyl (11).

![Chemical structure of 4,4'-bistrimethyltin-2,2',5,5'-tetrapropenylbiphenyl](image)

2-Bromomethyl-2'-methylbiphenyl

![Chemical structure of 2-Bromomethyl-2'-methylbiphenyl](image)
Xanthate (17).

4.4.2.2 Mass Spectra

1,4-dibromo-2,5-dipropenylbenzene (1).
Dimethyl 1,4-diallyl-2,5-dioxocyclohexane-1,4-dicarboxylate (5).

Diallyl succinate (6).
Diallyl succinylsuccinate (7).

2,5-diallylcyclohexane-1,4-dione (2).
4,4'-dibromo-2,2',5,5'-tetrapropenylbiphenyl (9).

Dihydrophenanthrene (16).
4.5 References


Chapter 5: Polymerizable Discotic Liquid Crystals

5.1 Contributions

This project began under Dr. Luke Tatum, stemming from his work on electron deficient discotic liquid crystals. He developed the synthetic route to our first monomer, made the first polymer and apo-polymer samples, and began characterization. I took over, optimizing synthetic methods of the monomers, polymer, and apo-polymer and continued characterization. Harrison Root also helped with much of the synthesis and characterization.

5.2 Introduction

Nanoporous membranes are a specific type of semipermeable membrane possessing holes on the nanometer scale. These membranes provide a means to manipulate or separate materials on the atomic scale, and therefore have a multitude of applications including water desalination and gas separation. Functional membranes must be mechanically stable to endure the rigorous nature of separation processes and have uniform pore sizes to maintain adequate selectivity; additionally, flux through the membrane should be maximized to minimize the resources needed to perform separations. To achieve higher fluxes, large surface area, thin membranes with high pore density and low pore tortuosity are crucial.

Nanoporous membranes fabricated using the microphase separation of block copolymers has met with much success. This method uses specifically designed systems to form microdomains that can then be locked in by crosslinking. Removal of the minor domains reveals pores in the membrane. Although narrow pore distributions and high pore densities have been achieved, these systems still suffer from high pore tortuosity and a lower pore size limit of about 5 nm, making them unattractive for water purification and gas separations.

Polymerizable liquid crystal (LC) systems have shown promise in accessing membranes with sub 1 nm pores. This approach utilizes the order within a LC mesophase as a template that
gets locked in upon crosslinking, providing a mechanically robust polymer film that maintains the order of the LC mesophase. In 2001, Kim and coworkers were the first to use a discotic liquid crystal (DLC) to template a nanoporous membrane (scheme 5.1). They used a triimidazole core hydrogen bonded to three trialkoxy-benzoic acids; photopolymerization of terminal acrylates followed by acidic removal of the cores provided a porous material that maintained the columnar hexagonal order of the DLC mesophase. While providing a good basis for future work, characterization of their system was lacking and failed to provide anything other than stated X-ray diffraction patterns to corroborate order in their membrane.

Scheme 5.1. Kim and coworkers’ route to a nanoporous membrane.

Osuji, Gin, and coworkers recently reported well-ordered membranes templated by both lyotropic and thermotropic columnar mesophases of a trialkyl sodium benzoate salt (scheme 5.1). By rotating these systems in an applied magnetic field, a remarkable increase was seen in the long range order of the LC mesophases, which was maintained after polymerization.
Transmission electron microscopy (TEM) images showed the membranes possessed exceptional long-range order of 1 nm pores in high density with very low tortuosity. Furthermore, they demonstrated that the same systems could be made using soft confinement of thin (<28 µm) samples without the need for an applied magnetic field.\textsuperscript{10}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme.png}
\end{center}

**Scheme 5.2.** Osuji, Gin, and coworkers’ magnetically aligned membrane.

Our approach relies on columnar mesophases of DLCs to template linear, homeotropic pores. Our monomers are based upon boronic ester containing DLCs previously reported by Tatum \textit{et al.}, that are known to form columnar mesophases.\textsuperscript{1} Network polymerization of acrylate-bearing side arms on a monomer crosslinks the DLCs to form the polymer while preserving the essential columns. The boronic ester linkages are then hydrolyzed, freeing the aromatic cores from the polymerized film and producing the desired membrane, called the apo-polymer. Our approach hopes to make membranes with a tight pore size distribution, and pores that are linear and aligned due to the preorganization of our DLCs.
5.3 Results and Discussion

Our first monomer 1 was tailored to contain a hydrolytically labile aromatic core functionalized with peripheral alkyl chains terminated by polymerizable end groups (figure 5.1). 1 was synthesized in four steps with a 26% overall yield from commercially available material (scheme 5.3). Starting with 5-bromoresorcinol, a Williamson ether synthesis using 10-bromodecanol produced alkylated aryl bromide 2. Molander’s direct borylation using Buchwald’s second generation Xphos preformed palladium catalyst then gave boronic acid 3. Schotten-Baumann esterification of 3 with acryloyl chloride yielded boronic acid 4. Finally, condensation between 2,3,6,7,10,11-hexahydroxypentaphenylene (HHTP) and three equivalents of 4 produced 1.

![Figure 5.1. Monomer 1 detailing key structural features.](image)
Scheme 5.3. Synthesis of 1. [a] K₂CO₃, DMF, reflux, 18 h, 70%. [b] Pd-XPhos-G2, XPhos, B₂(OH)₄, KOAc, EtOH, 70 °C, 3 h, 90%. [c] NEt₃, acryloyl chloride, THF, RT, 3 h, 75%. [d] HHTP, MeCN, RT, 24 h, 53 %.

The major complications throughout this synthetic procedure lied with purification. With each step, the product gains new features that hinder purification. Compound 2 cannot be recrystallized, boronic acid 3 becomes difficult to chromatograph and is no longer volatile enough to distil, acrylate-containing 4 becomes sensitive to acid, base and light, and monomer 1 becomes sensitive to hydrolysis and nucleophilic solvents such as alcohols. It is, therefore, imperative to clean each product as best as possible before moving on to make a new product that will only be harder to purify. Compound 2 was purified by vacuum distillation as incorporation of the alkyl chains hindered the ability to perform recrystallizations or column chromatography. During the recrystallization, only the highly pure middle fraction was collected, choosing to dispose of some product to ensure a high degree of purity. Also, performing the Williamson reaction under more concentrated conditions increased reaction yields, leading to fewer impurities that needed to be removed.

The palladium catalyzed borylation initially proved to be a fickle reaction, going through periods of working then not working without a modification in procedure. It was eventually discovered that residual boric acid in the commercially available B₂(OH)₄ hindered the reaction. Trituration with dioxane was found to provide sufficiently clean B₂(OH)₄ that was stored under N₂ to prevent decomposition. Traditionally, phenyl boronic acids are converted into their pinacol or MIDA protected analogues for purification; however, removal of these protecting groups is not trivial and was found to not produce sufficient quantities of purified 3. It was
discovered that \( \textbf{3} \) could simply be washed with hot acetonitrile to provide sufficiently clean product in adequate yields. Presumably, this occurs through formation of highly insoluble boroxines or boronic ester network polymers, as evidenced by IR spectroscopy.\(^{14}\)

The Schotten-Baumann esterification to produce \( \textbf{4} \) always contained significant amounts of unreacted \( \textbf{3} \), even when over 10 equivalents of acryloyl chloride was used. Different solvents such as dioxane or \( \text{CH}_2\text{Cl}_2 \) did not improve conversion, nor did incorporation of DMAP, which is known to promote similar reactions.\(^{15}\) Adding additional batches of acryloyl chloride was found to improve conversion to \( \textbf{4} \) in sufficient quantities. The presence of BHT was critical to prevent unwanted polymerizations beginning with work up and purification of \( \textbf{4} \) and continued through monomer synthesis. Like most boronic acids, \( \textbf{4} \) “streaks” badly on silica gel making chromatography difficult. Compound \( \textbf{4} \) showed negligible movement on silica gel using \( \text{CH}_2\text{Cl}_2 \) as an eluent, while incorporation of 10% methanol into the mobile phase flushed the product of well. From these observations, flash chromatography conditions were developed where crude \( \textbf{4} \) was loaded onto the silica gel with minimal \( \text{CH}_2\text{Cl}_2 \), the plug washed with a copious amount of \( \text{CH}_2\text{Cl}_2 \) to elute less soluble impurities, then the column flushed with 9:1 \( \text{CH}_2\text{Cl}_2\text{:MeOH} \) to collect sufficiently clean \( \textbf{4} \). Washing with acetonitrile proved successful in removing remaining impurities; however, it did not produce a highly insoluble mixture. In fact, \( \textbf{4} \) is much more soluble in acetonitrile than \( \textbf{3} \), and if any partially esterified material is present from poor conversion of the Schotten-Baumann reaction then washing with acetonitrile worsens the ratio of product to partially reacted material.

Condensation between \( \textbf{4} \) and HHTP \( \textbf{1} \) proceeds well at room temperature in acetonitrile, as \( \textbf{1} \) falls out of solution upon production. While these conditions showed an upper limit in yield around 60\%, attempting to drive the reaction to further conversion by azeotropic distillation of water produced product that was not as clean and therefore deemed insufficient. Purification of \( \textbf{1} \) proved difficult due to its reactive nature. Sensitivity to acid, base, water, alcohols, light, and heat
meant common techniques like silica gel chromatography and distillation could not be performed. Dissolving 1 in a minimal amount of chloroform followed by precipitation with acetonitrile produced samples that were sufficiently clean. The major impurities are believed to come from peripheral alkyl chains terminated with hydroxyl groups instead of the desired acrylates; however, this had no negative effects towards the properties of the forthcoming polymers.

Differential scanning calorimetry (DSC) revealed a mesophase from <30-55 °C for 1 and that polymerization occurs from around 150 °C. 1 was found to align with what we believed to be a high degree of homeotropicity because it produces a mostly black image when viewed under polarized optical microscopy (POM) (scheme 5.4, middle left). To confirm that 1 was indeed aligned in a LC mesophase and not in some isotropic or amorphous state, a push test was performed where the sample is manually disturbed while observed under cross polarizers. The appearance of birefringence in the sample during this disturbance indicates the presence of a LC mesophase, which was the case with 1.
**Scheme 5.4.** Membrane synthesis with corresponding POM (middle) images. Differential interference contrast images (bottom) show sample present under POM.

1 was aligned between glass slides then irradiated under ambient conditions for 72 hours with 300 nm light. Initial samples were simply prepared by placing a small amount 1 on a borosilicate slide, covering with a coverslip, heating above the clearing temperature and slowly cooling to the LC mesophase. This led to polymer samples that were too thick and brittle, causing surface cracks upon removal from the substrate. Degree of polymerization was also poor as the borosilicate glass blocked most of the UV light. A polymerization cell was then designed using one quartz slide to allow transmission of UV light and one borosilicate slide to keep cost lower (figure 5.2). The slides are separated by a spacer to regulate film thickness and held in place with hot melt adhesive. Placing a small amount of 1 along an open edge and heating above its clearing temperature allowed the material to wick in to the cell. Slow cooling then produced an aligned sample ready for irradiation. Standard printer paper was found to be an adequate spacer leading to films about 120 µm thick; use of a smaller spacer proved unsuccessful, as 1 is too viscous to wick in.

![Polymerization cell design](image1)

**Figure 5.2.** A) Polymerization cell design: glass slides (grey), paper spacers (green), adhesive (purple), monomer placement (red), and capillary action flow (blue arrow). B) Actual cell.

Like 1, Polymer 5 also showed a mostly black image by POM (scheme 5.4, center). The film can be manually removed from one or both glass surfaces to produce either a supported or freestanding film depending on what is desired. IR of 5 showed greater than 95% polymerization.
Soaking 5 in a 0.1 M solution of HCl in methanol for 3 days at 40 °C freed the aromatic cores from the polymer membrane, yielding apo-polymer 6. Subsequent washings with 0.1 M aqueous HCl then water ensured the pores were free from any methanol and lined with free boronic acids. The amount of hexahydroxytriphenylene that was removed from the membrane was quantified by UV-vis spectrophotometry, showing 65% core removal. After 3 days of soaking in the 0.1 M HCl:MeOH solution, core removal was negligible, even with a fresh acid solution. Use of 0.01 M or 1.0 M acid solutions led to lower yields of core removal. Films of 6 showed significant curling after core removal; to combat this samples of 5 were sandwiched between polyethylene washers held together with a plastic paper clip.

Films of 6 maintained similar visual appearance via POM as 1 and 5 but with slightly more imperfections (scheme 5.4, middle right). The entire polymerization and core removal process was easily monitored via IR spectroscopy (figure 5.3). TEM of polymer 5 showed what appeared to be random order in contrast to what we now know to be misinterpreted POM and X-ray diffraction data (figure 5.4). Combining the random order seen by TEM with the signs of liquid crystallinity by POM, we hypothesized that 1 may organized into a nematic mesophase. This motivated us to prepare a new monomer with shorter alkyl chains, reducing the induced fluid character and hopefully lead to a more ordered material.
Figure 5.3. IR monitoring of polymerization and core removal. A reduction in the peaks at 1634 cm\(^{-1}\) (orange, acrylate C=C stretch) and 808 cm\(^{-1}\) (red, acrylate =CH\(_2\) wag) indicate polymerization of end groups upon photo irradiation of monomer 1 (top) to form polymer 5 (middle). The appearance of a broad O-H stretch peak centered around 3430 cm\(^{-1}\) (blue) and loss of peaks at 1238 cm\(^{-1}\) (purple, triphenylene C-O stretch) and 837 cm\(^{-1}\) (green, triphenylene C-H out of plane bend) indicate removal of the triphenylene core from polymer 5 (middle) to form apo-polymer 6 (bottom).
Figure 5.4. TEM of polymer 5.

Monomer 7 was synthesized according to a similar procedure as 1 in 11% yield over four steps (scheme 5.5). Monomer 7 possesses a mesophase from 45-85 °C, and POM showed a Schlieren texture indicative of nematic mesophases, which are quite rare for DLCs. While Schlieren textures were not seen in POM of 1, X-ray data for both 1 and 7 show them to be low-ordered materials (see experimental). Each possesses a broad small angle peak (corresponding to the core diameter) and a very broad wide-angle peak (corresponding to lateral core spacing), characteristic of a discotic nematic (N_D) mesophase.
**Scheme 5.5.** Synthesis of 7. [a] K₂CO₃, DMF, reflux, 18 h, 77%. [b] Pd-XPhos-G2, XPhos, B₂(OH)₄, KOAc, EtOH, 70 °C, 3 h, 75%. [c] NEt₃, acryloyl chloride, THF, RT, 3 h, 48%. [d] HHTP, MeCN, RT, 24 h, 38%.

**Figure 5.5.** POM of 7 showing Schlieren texture.

While not useful for nanoporous membranes, polymerizable N₉D materials have applications in display technologies (LCDs).¹⁷,¹⁸ Polymerizable triphenylene hexabenzoates make hybrid aligned films that widen the viewing angle of thin film transistor LCDs. Further investigation of our monomers will tell if they can be coaxed into the desired hybrid alignment and possess the photopolymerization speed and thermal stability required for such applications.

Incorporation of a larger core, such as hexa-peri-hexabenzocoronene (HBC) (figure 5.6), could yield a material that possesses the columnar mesophase needed to produce a nanoporous membrane. By incorporating a larger core, greater core-core interactions will be present and could lead to a more ordered film. HBC DLCs form columnar mesophases with well defined helical structures and wide temperature ranges.¹⁹ Polymerizable HBC DLCs have been made where the films can be thermally polymerized in the columnar mesophase to produce films that maintain order.²⁰ The convergent nature of our synthesis means that development of a dodecahydroxy-HBC core is all that would be required for condensation with either 4 or 10.
Figure 5.6. Example of a dodecahydroxyhexa-\textit{peri}-hexabenzocoronene core.

5.4 Conclusions

We have successfully synthesized two novel polymerizable discotic molecules that exhibit liquid crystalline mesophases. Monomer 7 exhibits Schlieren textures by POM characteristic of a nematic mesophase, while both 1 and 7 show X-ray diffraction patterns indicative of a N\textsubscript{D} mesophase. While not useful for the nanoporous membranes we set out to make, polymerizable N\textsubscript{D} materials have commercial applications worth further investigation.

5.5 Experimental

5.5.1 Methods

All materials were used without further purification unless otherwise specified. THF was distilled from sodium and benzophenone. NMRs were recorded on Varian spectrometers (MR 400 MHz, V 400 MHz, V 500 MHz. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR ATR surface with 4 cm\textsuperscript{-1} resolution as thin films. HRMS data was recorded on an Agilent G6230A TOF-MS with an ESI source in positive mode. MALDI-TOF data was recorded on a Bruker spectrometer in reflective positive mode. XRD spectra were recorded on a Bruker D8 diffractometer equipped with a variable temperature stage.

\textit{3,5-di(decan-10-oloxo)bromobenzene} (2). 3,5-dihydroxybromobenzene (5 g, 23 mmol), 10-bromodecanol (13 g, 55 mmol), potassium carbonate (12 g, 87 mmol), and 100 mL dimethylformamide were added to a round bottom flask. The reaction was then degassed, put under N\textsubscript{2}, and refluxed for 24 hours. Aqueous workup with ethyl acetate yielded an amber oil that
was purified by flash chromatography with ethyl acetate resulting in an off white oil. This product was then distilled under reduced pressure (10-100 mTorr) collecting the fraction between 200-300 °C to produce a white solid in 70% yield.

$^1$H NMR [CDCl$_3$, 400 MHz]: δ 1.31 (m, 20 H), 1.43 (m, 4 H), 1.57 (m, 4 H), 1.75 (m, 4 H), 3.64 (t, $J = 6.6$ Hz, 4 H), 3.89 (t, $J = 6.5$ Hz, 4 H), 6.36 (t, $J = 2.2$ Hz, 1 H), 6.63 (d, $J = 2.2$ Hz, 2 H) ppm.

$^{13}$C ($^1$H) NMR [CDCl$_3$, 100 MHz]: δ 25.7, 26.0, 29.1, 29.3, 29.4, 29.45, 29.5, 32.8, 63.0, 68.3, 100.6, 110.2, 122.8, 160.7 ppm.

FT-IR [ATR, cm$^{-1}$]: 3328, 2923, 2851, 1597, 1575, 1437, 1384, 1326, 1277, 1161, 1050, 988, 903, 832, 802, 722, 672.

HRMS [ESI-TOF, M+Na$^+$] C$_{26}$H$_{45}$BrO$_4$Na calc. 523.2399, found 523.2396.

3,5-di(decan-10-olox)benzene boronic acid (3). Absolute ethanol was degassed by bubbling N$_2$ through it for 30 min. Pd-XPhos-G2 (12 mg, 0.05 mmol), XPhos (14 mg, 0.10 mmol), B$_2$(OH)$_4$ (1.6 g, 17 mmol) were added to a dry, degassed 3-neck round-bottom flask under a N$_2$ atmosphere. 2 (3.0 g, 6 mmol) and KOAc (1.76 g, 18 mmol) were added to the flask and the solids left under vacuum for 30 min. 60 mL ethanol was added, the reaction vessel degassed under reduced pressure, put under N$_2$, then heated to 70 °C for 3 hours after which an orange solution was present. The reaction mixture was concentrated then purified by flash chromatography with 9:1 ethyl acetate: methanol. The off white oil was then washed with hot acetonitrile to yield 2 as a mixture of the boronic acid and its boroxine derivative in 90% yield.

$^1$H NMR [CD$_3$OD, 500 MHz]: δ 1.33 (m, 20 H), 1.46 (m, 4 H), 1.52 (m, 4 H), 1.74 (m, 4 H), 3.53 (t, $J = 6.7$ Hz, 4 H), 3.93 (t, $J = 6.5$ Hz, 4 H), 6.47 (t, $J = 2.3$ Hz, 1 H), 6.67 (d, $J = 2.0$ Hz, 2 H) ppm.

$^{13}$C ($^1$H) NMR [CD$_3$OD, 100 MHz]: δ = 26.95, 27.19, 30.45, 30.52, 30.59, 30.66, 30.70, 33.68, 63.02, 65.72, 68.98, 103.789, 112.37 ppm.
FT-IR [ATR, cm$^{-1}$]: 3340, 2919, 2850, 1587, 1425, 1336, 1304, 1154, 1053, 1021, 875, 842, 704, 660.

HRMS [ESI-TOF, M+Na$^+$] C$_{26}$H$_{47}$BO$_6$Na calc. 488.3400, found 488.3465.

3,5-di(10-acryloyldecanoxy)benzene boronic acid (4). 3 (1.7 g, 3.6 mmol), triethylamine (2.5 mL, 18 mmol), and 125 mL THF were added to a round bottom flask equipped with a dropping funnel containing acryloyl chloride (1.5 mL, 18 mmol), and 15 mL THF. If 3 did not completely dissolve, 1-2 drops of distilled water were added to shift equilibrium away from boroxine formation. The reaction was degassed and put under N$_2$. The acryloyl chloride solution was added dropwise over approximately 1 hour and the reaction left to stir for 3 hrs. A small aliquot was removed, purified by aqueous workup with CH$_2$Cl$_2$, and used to monitor the reaction progress via $^1$H NMR. If starting material remains, more triethylamine was added to the reaction mixture and another THF solution of acryloyl chloride was added via the dropping funnel as before. Upon completion, aqueous workup with ethyl acetate resulted in an amber oil. The crude boronic acid was purified using flash chromatography by first eluting with CH$_2$Cl$_2$ to remove the less polar impurities then 9:1 CH$_2$Cl$_2$:MeOH to collect the product. Washing the yellow oil with a minimal amount of acetonitrile afforded 4 as a mixture of the boronic acid and its boroxine derivative in 75% yield.

$^1$H NMR [CD$_3$OD, 500 MHz]: $\delta$ = 1.35 (m, 20 H), 1.47 (m, 4 H), 1.67 (m, 4 H), 1.75 (m, 4 H), 3.95 (t, $J$ = 6.6 Hz, 4 H), 4.14 (t, $J$ = 6.4 Hz, 4 H), 5.86 (dd, $J$ = 10.4, 1.5 Hz, 1 H), 6.15 (dd, $J$ = 17.4, 10.5 Hz, 1 H), 6.36 (dd, $J$ = 17.3, 1.5 Hz, 1 H), 6.48 (t, $J$ = 2.2 Hz, 1 H), 6.67 (d, $J$ = 2.2 Hz, 2 H) ppm.

$^{13}$C($^1$H) NMR [CD$_3$OD, 100 MHz]: $\delta$ = 27.01, 27.16, 29.71, 30.32, 30.43, 30.45, 30.55, 30.59, 65.76, 68.92, 103.83, 104.89, 112.42, 129.67, 131.30, 161.20, 167.78 ppm.

FT-IR [ATR, cm$^{-1}$]: 3455, 2927, 2852, 1722, 1701, 1584, 1426, 1406, 1343, 1302, 1198, 1160, 1052, 982, 849, 807, 703.
HRMS [ESI-TOF, M+Na]\(^{+}\) C\(_{32}\)H\(_{51}\)BO\(_{8}\)Na calc. 596.3612, found 596.3620.

**Monomer (1).** 2,3,6,7,10,11-Hexahydroxytriphenylene (363 mg, 1.1 mmol), 4 (1.99 g, 3.5 mmol), 2,6-di-tert-butyl-4-methylphenol (7.7 mg, 0.035 mmol), and 275 mL acetonitrile were added to a round bottom flask. The reaction was degassed, put under N\(_{2}\), and stirred in the dark at room temperature for 24 hours. The precipitate was filtered, washed three times with warm acetonitrile, and dried under high vacuum. The brown solid was dissolved in a minimal amount of CHCl\(_{3}\) and passed through a pad of celite. Acetonitrile was added to precipitate 1 in 53% yield.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 1.36 (m, 60 H), 1.50 (m, 12 H), 1.70 (m, 12 H), 1.82 (m, 12 H), 3.96 (t, \(J = 6.4\) Hz, 12 H), 4.17 (t, \(J = 6.7\) Hz, 12 H), 5.82 (dd, \(J = 10.4, 1.5\) Hz, 6 H), 6.13 (dd, \(J = 17.3, 10.4\) Hz, 6 H), 6.41 (dd, \(J = 17.3, 1.5\) Hz, 6 H), 6.58 (t, \(J = 2.1\) Hz, 3 H), 7.11 (d, \(J = 2.1\) Hz, 6 H), 8.09 (s, 6 H) ppm.

\(^13\)C\({}^{1}\)H\) NMR [CDCl\(_3\), 125 MHz]: \(\delta = 26.12, 26.28, 28.80, 29.44, 29.58, 29.67, 29.68, 29.72, 64.86, 68.20, 105.70, 106.40, 112.61, 125.64, 128.79, 130.58, 148.29, 160.28, 166.48 ppm.

FT-IR [ATR, cm\(^{-1}\)]: 2920, 2846, 1721, 1583, 1490, 1429, 1401, 1356, 1316, 1292, 1263, 1237, 1190, 1158, 1053, 980, 837, 808, 692.

MS [MALDI-TOF]: C\(_{114}\)H\(_{155}\)O\(_{24}\)B\(_3\) calc. 1940.107, found 1940.549.

**Polymer (5).** In a dust free environment, a quartz slide and a borosilicate glass slide were separated by paper spacers and held in place using high temperature hot melt adhesive. 1 was placed along one opening and allowed to wick in to this polymerization cell at 80 °C. The entire system was slowly cooled to 35 °C and irradiated with 300 nm light for 3 days to produce a flimsy brown film.

FT-IR [ATR, cm\(^{-1}\)]: 2923, 2850, 1729, 1583, 1490, 1425, 1397, 1352, 1312, 1239, 1154, 1041, 976, 890, 850, 826, 753, 693, 607.
Apo-polymer (6). The polymer film was soaked in a 0.1 M HCl in methanol solution for 4 days. The membrane was then soaked in 0.1 M HCl in water for 1 hour, washed with water and dried under high vacuum.

FT-IR [ATR, cm\(^{-1}\)]: 8430, 2919, 2850, 1725, 1583, 1429, 1340, 1255, 1158, 1049, 842, 704, 656.

3,5-di(hexan-6-ol)oxy)bromobenzene (8). 3,5-dihydroxybromobenzene (5 g, 23 mmol), 6-bromohexanol (10 g, 55 mmol), potassium carbonate (12 g, 87 mmol), and 100 mL dimethylformamide were added to a round bottom flask. The reaction was then degassed, put under N\(_2\), and refluxed for 24 hours. Aqueous workup with ethyl acetate yielded a brown oil that was purified by flash chromatography with ethyl acetate resulting in an amber oil. This product was then distilled under reduced pressure (10-100 mTorr) collecting the fraction between 150-250 °C to produce a yellow oil in 77% yield.

\(^1\)H NMR [CDCl\(_3\), 400 MHz]: \(\delta\) 1.44 (m, 8 H), 1.57 (m, 4 H), 1.76 (m, 4 H), 3.64 (t, \(J = 6.6\) Hz, 4 H), 3.89 (t, \(J = 6.5\) Hz, 4 H), 6.35 (t, \(J = 2.2\) Hz, 1 H), 6.62 (d, \(J = 2.2\) Hz, 2 H) ppm.

\(^{13}\)C\{\(^1\)H\} NMR [CDCl\(_3\), 125 MHz]: \(\delta\) 25.59, 25.92, 29.16, 32.72, 62.87, 68.24, 100.70, 110.37, 122.92, 160.77 ppm.

FT-IR [ATR, cm\(^{-1}\)]: 3341, 2928, 1594, 1572, 1436, 1385, 1326, 1296, 1274, 1157, 1043, 911, 826, 804, 727, 672.

HRMS [ESI-TOF, M+Na\(^+\)] C\(_{18}\)H\(_{29}\)BrO\(_4\)Na calc. 411.1147, found 411.1171.

3,5-di(hexan-6-ol)oxy)benzene boronic acid (9). Absolute ethanol was degassed by bubbling N\(_2\) through it for 30 min. Pd-XPhos-G2 (12 mg, 0.05 mmol), XPhos (14 mg, 0.10 mmol), B\(_2\)(OH)\(_4\) (1.6 g, 17 mmol) were added to a dry, degassed 3-neck round-bottom flask under a N\(_2\) atmosphere. 8 (2.3 g, 6 mmol) and KOAc (1.76 g, 18 mmol) were added to the flask and the solids left under vacuum for 30 min. 60 mL ethanol was added, the reaction vessel degassed under reduced pressure, put under N\(_2\), then heated to 70 °C for 3 hours after which an orange solution was present. The reaction mixture was concentrated then purified by flash
chromatography with 9:1 ethyl acetate: methanol. The off white oil was then washed with hot acetonitrile to yield 9 as a mixture of the boronic acid and its boroxine derivative in 75% yield.

$^1$H NMR [CD$_3$OD, 500 MHz]: $\delta$ 1.43 (m, 4 H), 1.50 (m, 4 H), 1.57 (m, 4 H), 1.77 (m, 4 H), 3.57 (t, $J = 6.6$ Hz, 4 H), 3.95 (t, $J = 6.4$ Hz, 4 H), 6.48 (t, $J = 2.3$ Hz, 1 H), 6.68 (s, 2 H) ppm.

$^{13}$C $^1$H NMR [CD$_3$OD, 125 MHz]: $\delta =$ 26.7, 27.00, 30.41, 33.56, 62.88, 68.85, 112.79, 118.10, 161.15 ppm.

FT-IR [ATR, cm$^{-1}$]: 3336, 2932, 2855, 1579, 1429, 1326, 1300, 1157, 1047, 841, 760, 705, 660.

3,5-di(6-acryloyldhexanoloxy)benzene boronic acid (10). 9 (2.1 g, 6 mmol), triethylamine (4 mL, 30 mmol), and 200 mL THF were added to a round bottom flask equipped with a dropping funnel containing acryloyl chloride (2.5 mL, 30 mmol), and 15 mL THF. If 9 did not completely dissolve, 1-2 drops of distilled water were added to shift equilibrium away from boroxine formation. The reaction was degassed and put under N$_2$. The acryloyl chloride solution was added dropwise over approximately 1 hour and the reaction left to stir for 3 hrs. A small aliquot was removed, purified by aqueous workup with CH$_2$Cl$_2$, and used to monitor the reaction progress via $^1$H NMR. If starting material remains, more triethylamine was added to the reaction mixture and another THF solution of acryloyl chloride was added via the dropping funnel as before. Upon completion, aqueous workup with ethyl acetate resulted in an amber oil. The crude boronic acid was purified using flash chromatography by first eluting with CH$_2$Cl$_2$ to remove the less polar impurities then 9:1 CH$_2$Cl$_2$:MeOH to collect the product. Washing the yellow oil with a minimal amount of acetonitrile afforded 10 as a mixture of the boronic acid and its boroxine derivative in 48% yield.

$^1$H NMR [CD$_3$OD, 500 MHz]: $\delta =$ 1.47 (m, 4 H), 1.54 (m, 4 H), 1.72 (m, 4 H), 1.79 (m, 4 H) 3.97 (t, $J = 6.4$ Hz, 4 H), 4.18 (t, $J = 6.6$ Hz, 4 H), 5.87 (dd, $J = 10.4$, 1.5 Hz, 1 H), 6.15 (dd, $J = 17.3$, 10.4 Hz, 1 H), 6.37 (dd, $J = 17.3$, 1.5 Hz, 1 H), 6.49 (t, $J = 2.3$ Hz, 1 H), 6.68 (d, $J = 2.4$ Hz, 2 H) ppm.
\(^{13}\)C\(^{1}\)H\(^{1}\) NMR [CD\(_3\)OD, 125 MHz]:  \(\delta = 25.42, 25.47, 28.27, 28.92, 64.30, 67.40, 111.26, 128.27, 129.98, 159.78, 166.40\) ppm.

FT-IR [ATR, cm\(^{-1}\)]: 2937, 2860, 1714, 1635, 1620, 1579, 1438, 1405, 1339, 1295, 1270, 1186, 1164, 982, 843, 810, 730, 705, 668.

**Monomer (7).** 2,3,6,7,10,11-Hexahydroxytriphenylene (100 mg, 0.3 mmol), 4 (450 mg, 0.1 mmol), 2,6-di-\textit{tert}-butyl-4-methylphenol (0.2 mg, 0.001 mmol), and 50 mL acetonitrile were added to a round bottom flask. The reaction was degassed, put under N\(_2\), and stirred in the dark at room temperature for 24 hours. The precipitate was filtered, washed three times with warm acetonitrile, and dried under high vacuum. The brown solid was dissolved in a minimal amount of CHCl\(_3\) and passed through a pad of celite. Acetonitrile was added to precipitate 1 in 38% yield.

\(^{1}\)H NMR (CDCl\(_3\), 400 MHz):  \(\delta = 1.53\) (m, 24 H), 1.76 (m, 12 H), 1.88 (m, 12 H), 4.00 (t,  \(J = 6.4\) Hz, 12 H), 4.22 (t,  \(J = 6.7\) Hz, 12 H), 5.84 (dd,  \(J = 10.4, 1.5\) Hz, 6 H), 6.16 (dd,  \(J = 17.3, 10.4\) Hz, 6 H), 6.44 (dd,  \(J = 17.4, 1.6\) Hz, 6 H), 6.60 (t,  \(J = 2.3\) Hz, 3 H), 7.15 (d,  \(J = 2.3\) Hz, 6 H), 8.16 (s, 6 H) ppm.

\(^{13}\)C\(^{1}\)H\(^{1}\) NMR [CDCl\(_3\), 125 MHz]:  \(\delta = 25.83, 25.87, 28.64, 29.27, 64.59, 67.87, 105.58, 106.27, 112.50, 125.53, 128.61, 130.59, 148.14, 160.07, 166.37\) ppm.

FT-IR [ATR, cm\(^{-1}\)]: 2937, 2864, 1715, 1635, 1616, 1584, 1492, 1449, 1427, 1409, 1358, 1317, 1292, 1266, 1241, 1186, 1161, 1055, 978, 887, 858, 832, 807, 759, 730, 690, 668, 606.

MS [MALDI-TOF]: \(C_{90}H_{105}O_{24}B_{3}\) calc. 1602.728, found 1602.562.
5.5.2 Spectra

5.5.2.1 NMR

3,5-di(decan-10-oloxy)bromobenzene (2).
3,5-di(decan-10-oloxy)benzene boronic acid (3).
3,5-di(10-acryloyldecanoloxy)benzeneboronic acid (4).
Monomer (1).
3,5-di(hexan-6-oloxy)bromobenzene (8).
3,5-di(hexan-6-ol)benzene boronic acid (9).
3,5-di(6-acryloyldhexanolxy)benzene boronic acid (10).
Monomer (7).
5.5.2.2 Mass Spectra

3,5-di(decan-10-ol-oxy)bromobenzene (2).

3,5-di(decan-10-ol-oxy)benzene boronic acid (3).

3,5-di(10-acryloydecanoloxy)benzene boronic acid (4).
Monomer (1).

3,5-di(hexan-6-oloxy)bromobenzene (8).
Monomer (7).
5.5.2.3 IR

3,5-di(decan-10-oloxy)bromobenzene (2).

3,5-di(decan-10-oloxy)benzene boronic acid (3).
3,5-di(10-acryloyldecanoloxy)benzene boronic acid (4).

Monomer (1).
Polymer (5).

[Graph showing IR spectrum for Polymer (5)].

Apo-polymer (6).

[Graph showing IR spectrum for Apo-polymer (6)].
**3,5-di(hexan-6-oloxy)bromobenzene (8).**

![Graph of 3,5-di(hexan-6-oloxy)bromobenzene](image1)

**3,5-di(hexan-6-oloxy)benzene boronic acid (9).**

![Graph of 3,5-di(hexan-6-oloxy)benzene boronic acid](image2)
3,5-di(6-acryloyldhexanolxy)benzene boronic acid (10).

Monomer (7).
5.5.2.4 XRD

Monomer (1). [35 °C]

Monomer (7). [35 °C]
5.6 References


