# Synthesis of Liquid Crystals

"Filling Forms with Function"

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**Organic Synthesis of Liquid Crystals: Filling Forms with Function**

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## Abstract

There is much to investigate in the materials science of liquid crystals, and the applications are seemingly endless. In the research conducted, $SmAP_F$ electro-optic translators and a chromatographic stationary phase for the separation of enantiomers using B4 phase were explored. The $SmAP_F$ phase would be able to translate electrical signals to optical signals, and vice versa. One target structure bent unit of the $SmAP_F$ phase was completely synthesized. An imine-free, homo-chiral B4 phase has the potential to give high enantiomer resolution. The B4 phase was completely synthesized, and appeared to establish homo-chirality, but its phase was not officially determined.

## Introduction

Liquid crystals are a material that appears to be fluid to the naked eye but, under a polarized microscope, a texturized, crystalline-like structure appears. This appearance is induced by rigid cores and flexible alkyl tails within the molecule. On the molecular level, these materials exhibit unique phases: isotropic, nematic, and smectic (**Figure 1**). Among these phases, different molecular shapes can be introduced, creating more complex phases.

The isotropic phase is the least ordered phase, in which the liquid crystal phase is actually a liquid. This phase is achieved when heating the liquid crystal until it is completely melted.

The nematic phase of liquid crystals is slightly more ordered than the isotropic phase; the molecules are facing in the same general direction, but they are not aligned any further. From the isotropic phase, the nematic phase can be achieved by cooling. As the material is cooled down, the molecules begin to exhibit directional ordering.

The smectic phase is a more complex and ordered phase, compared to the nematic phase. As the material is cooled even further, the directionally ordered molecules order themselves into layers. There are a smectic layers unique to their alignment; the most well-

known of these phases are the smectic A and C phases. The smectic A phase is a linear phase, in which the molecules are perpendicular to the layers and the smectic C phase is a tilted phase. Within the smectic C phases, there can be different alignment between the layers. The smectic C phase can either have a uniform directional tilt throughout the layers, or can have an alternating tilt direction between layers.

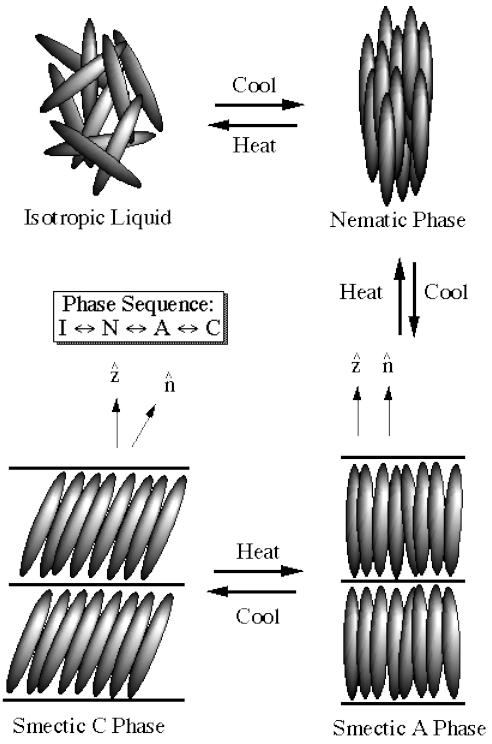



**Figure 1**[1]: The phases that liquid crystals exhibit when heated and cooled down, isotropic, nematic, smectic A and smectic C. In the figure, the molecules are depicted as calamitic (rod-shaped) mesogens.

Liquid crystal phases can also change depending on the shape of the mesogens (liquid crystals), as well. There are three main shapes of mesogens: calamitic, discotic, and banana. The calamitic phase is a rod-shaped (**Figure 1**) mesogen, and the discotic phase is a 2-dimensional sphere (a disc), and the banana phase is a bent phase, in which there is a bend in the middle of the mesogen, creating an angle. The discotic phase can align in which the discs stack on top of one another, creating columnar filaments; these columnar filaments can create their own nematic phase in which they are directionally ordered. The banana phases have distinctive, newly discovered "B" phases.

In the following research conducted, the $SmAP_F$ phase and B4 phase were explored.

**Background: $SmAP_F$ Electro-Optic Translators**

Material exhibiting high second order susceptibility ($\chi^{(2)}$) has high potential to modulate optical signals by applying an electrical field; therefore the material can work as an electro-optic translator. Electronic signals generate data, and optical signals transfer data; this material with high $\chi^{(2)}$ would be able to translate electronic signals to optical signals and vice versa. High $\chi^{(2)}$ is a material property that can be attributed to hyperpolarizability β on a molecular level[1]. A material design with high β would have a strong "push-pull" system, or a system that contains a strong electron donor at one end, a strong electron acceptor at the other end, and a π-conjugated bridge in between the two groups (**Figure 2**).

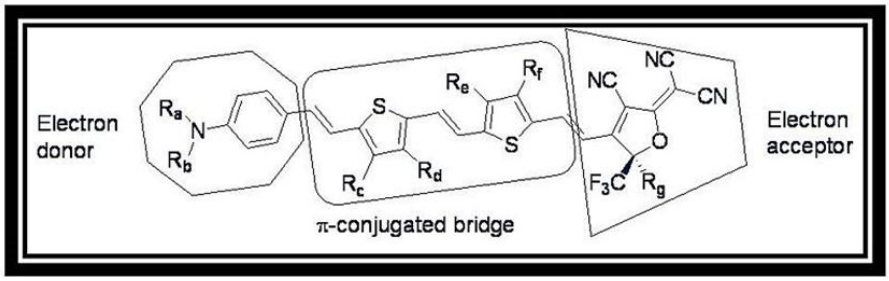



**Figure 2** [2]: An example of a common material that exhibits high β.

However, high β does not necessarily equal to high $\chi^{(2)}$ because of alignment of molecules, non-polar and polar alignment. In non-polar alignment, the molecules of different layers are facing in opposite directions, therefore cancelling each other out to obtain an $\chi^{(2)}$ equal to zero (**Figure 3**). Whereas, in polar alignment, the molecules of different layers are facing in the same direction and obtaining a high $\chi^{(2)}$ (**Figure 3**)..

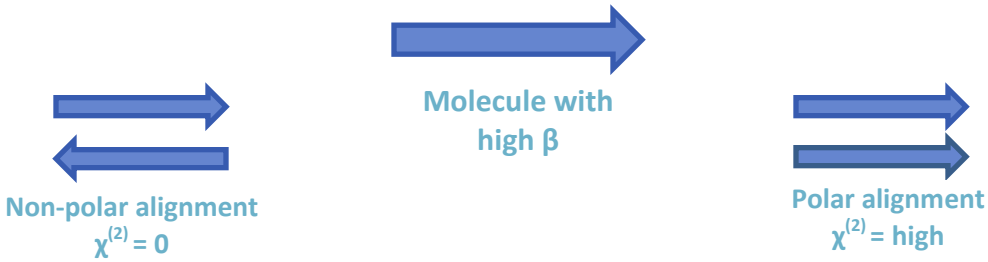



**Figure 3**: The arrows (molecules) that are facing in opposite directions are aligned non-polar and have a $\chi^{(2)}$ equal to zero. The arrows that are facing in the same direction have a polar alignment and have a high $\chi^{(2)}$.

A platform that has a high potential for high $\chi^{(2)}$are the ferroelectric bent-core liquid crystals. Bent-core liquid crystals are advantageous to the calamitic liquid crystals because their "push-pull" or donor-acceptor system is along the long molecular axis and perpendicular to the bent unit; therefore, maintaining a relatively high percentage of polar alignment of the dipoles (**Figure 4**).

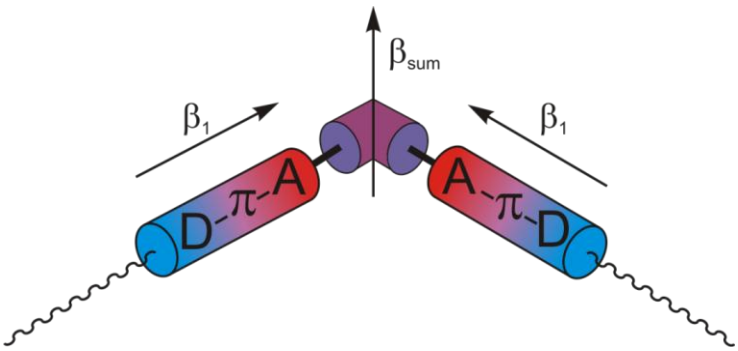



**Figure 4**[3]: The electron donor-acceptor system along the long molecular axis of a bent-core mesogen; this "push-pull" system is perpendicular to the bent unit.

The $SmAP_F$ phase (linear, polar alignment, **Figure 5**) of bent-core mesogens is advantageous to the $SmCP_F$ phase (tilted, polar alignment) for three reasons:

1) One chain per molecule increases the density of the molecules within the layers. The tails at the end of the molecules "whip" around, and disallow the surrounding molecules to be "packed" in close to it; thus, by having one tail instead of two would increase the amount of molecules per layer.
2) The alignment of the molecules in $SmAP_F$ on a substrate (i.e. glass) is better than the tilted phases.
3) $SmAP_F$ has higher intrinsic order parameter, compared to tilted phases; since the molecules are not tilted, they have a higher percentage of alignment within the layer.

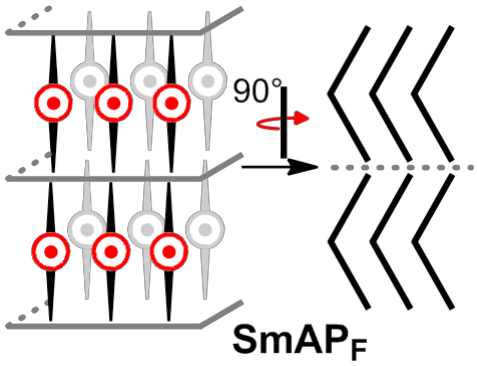



**Figure 5**: In the $SmAP_F$ phase for bent-core mesogens is non-tilted with the molecules pointing in the same direction in every layer, therefore establishing polar alignment.

Therefore, the design of the $SmAP_F$ electro-optic translator is as illustrated in **Figure 6.**

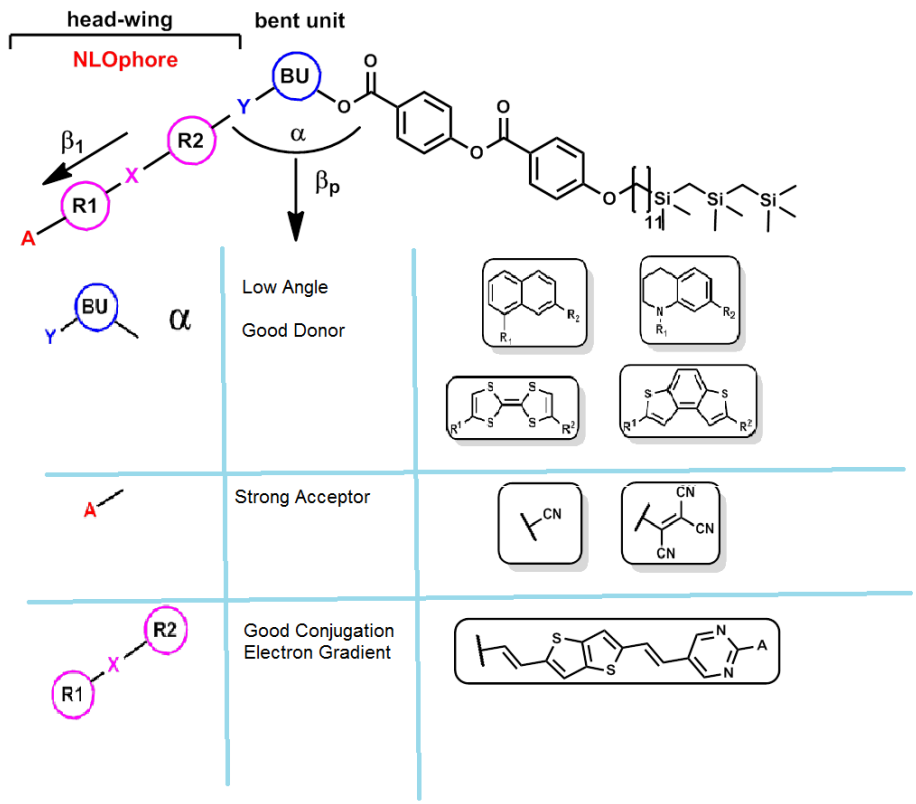



**Figure 6**: The design of the electro-optic translator, $SmAP_F$ phase. It should have a good donor with low angle, a strong acceptor, and good conjugation electron gradient. The target structures are listed in the right column of the chart.

## Background: B4 Phase as Stationary Phase for Chromatography

The B4 phase of bent-core liquid crystals is a unique phase that are stacks of smectic layers, twisted with negative curvature; thus, forming a helical shape[1-2] (**Figure 7**). These helical filaments are found on the nanometer scale[3]; therefore, considered to be a part of nanotechnology. The helical shape of these filaments creates chirality on a supramolecular level, even when the molecules composing the filaments are usually achiral.[2] The B4 phase remains to be the only bent-core mesogen phase that establishes chirality on a macroscopic scale[2],and this unique attribute to the B4 phase can be applied to the broad field of nanotechnology—one application in this field is the separation of enantiomers via chromatography.

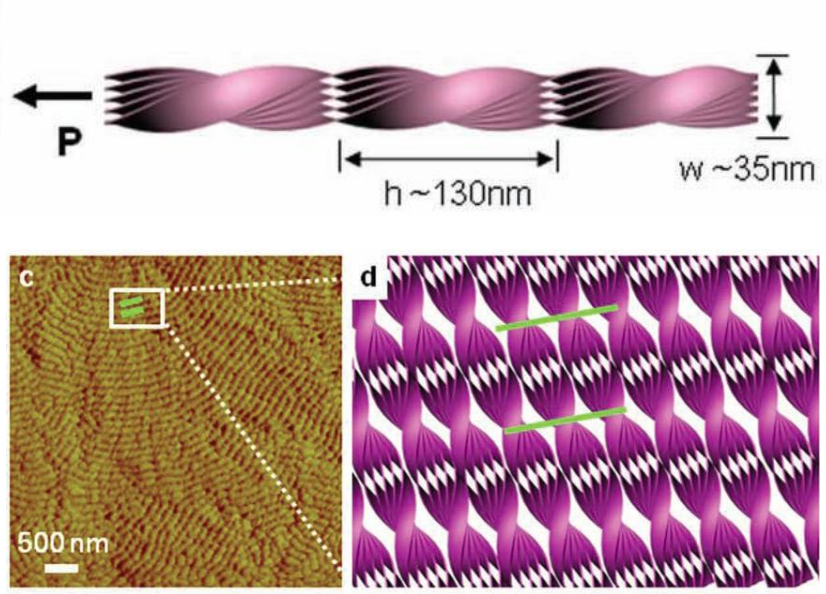



**Figure 7**[4] (above) The size and shape of a B4 phase helical filament. One pitch is about 130nm in length, and the width of the filament is about 35nm. (below) The texture of the B4 phase under a polarized microscope.

For the separation of enantiomers, HPLC (High-Performance Liquid Chromatography) is among the most favored and commercially used techniques but, nanotechnologies are becoming more advanced in the methodologies of enantioselective separation. [4] In order to differentiate enantiomers, an asymmetric environment is needed; this environment is induced by homochiral molecules, the chiral selector.[4] The chiral selector interacts with the right and left enantiomer by creating transitory diastereomeric adsorbates due to weak interactions such as hydrogen bonding, charge-transfer, and ionic or dipolar interactions.[4] Since the B4 phase creates chirality macroscopically, it could be a good candidate for high enantiomer resolution in the stationary phase of chromatography. However, the composition of nearly all B4 phases contains imines (**Figure 8**). Imines would be inefficient when applied to chromatography, because when an imine is introduced to water, or water-containing solvents, it will undergo hydrolysis and break down into an aldehyde and an amine (**Figure 9**). Solvents containing water could not be used for chromatography, because the stationary phase would be broken down and unusable.

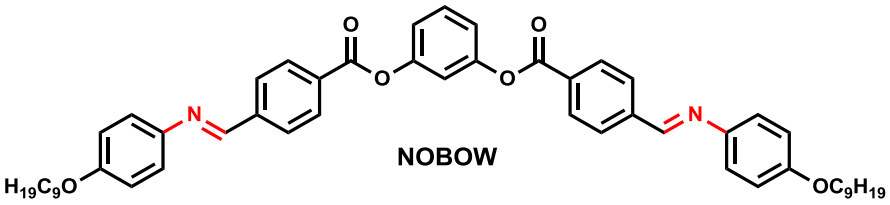



**Figure 8**: A typical B4 phase, which contains imines (highlighted in red).

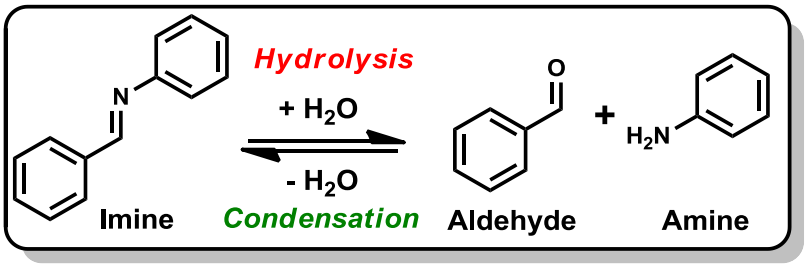



**Figure 9**: The hydrolysis of an imine into an aldehyde and amine. This would cause a problem in the stationary phase of chromatography because solvents containing water could not be used.

However, the proposed B4 phase that is imine- free, the W513, (**Figure 10**) would be a good potential candidate for enantiomer separation, except for the requirements of homochirality. Therefore, the synthesis of a homochiral version (**Figure 11**) of the W513 would obtain a likely B4 phase that would fit the requirements of an enantioselective stationary phase of chromatography.

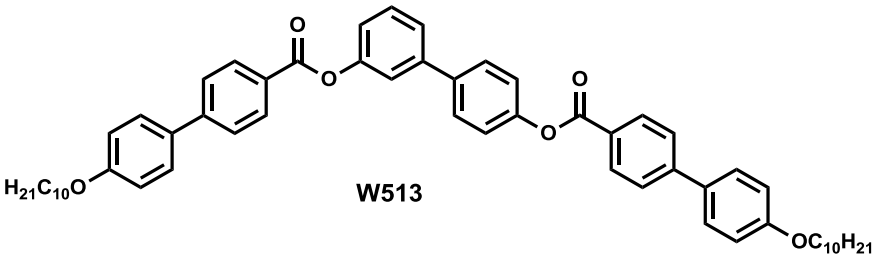



**Figure 10:** The proposed imine-free B4 phase.

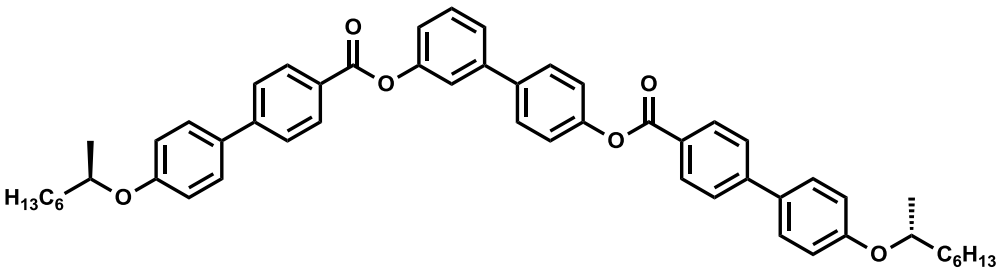
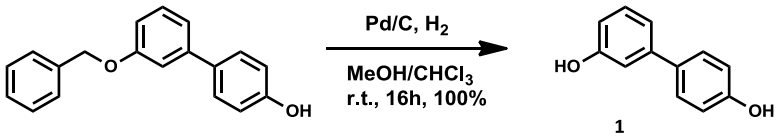


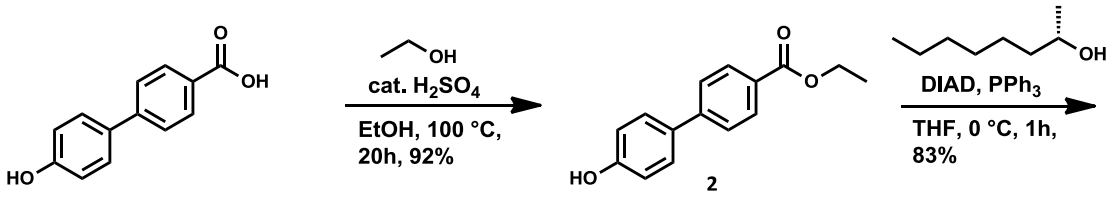

**Figure 11:** Chiral version of the W513. It is has high potential to give high enantiomer resolution.

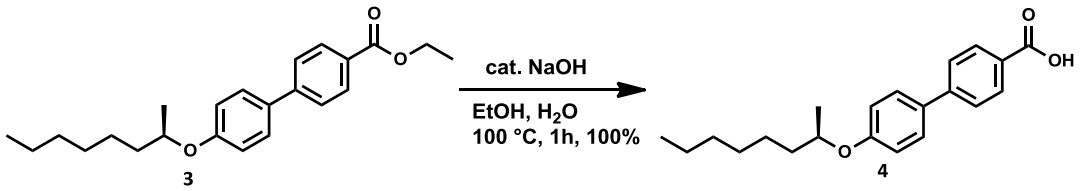
## Experimental Procedure

Bent unit

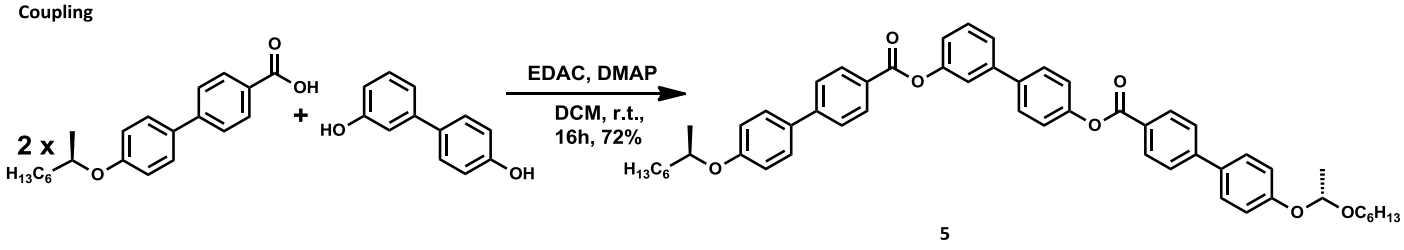



Side arms




Coupling




### [1,1'-biphenyl]-3,4'-diol (1):

3-benzoxy-4'-hydroxybiphenyl (6 mmol, 1.65g) was dissolved in MeOH/$CHC1l_3$ (100mL, 2:1) with Pd/C (150mg). The solution was stirred at room temperature for 16 hours under hydrogen atmosphere. After a full conversion (TLC check), the solution was filtered over celite. After filtration, the solution was recrystallized from $CHCl_3$ (150mL) and addition of EtOH until complete solution. No further purification was performed. Yield: 100%

### Ethyl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate (2):

4-(4-hydroxyphenyl) benzoic acid (20 mmol, 4.284g) was dissolved in EtOH (100mL) and a catalytic amount of $H_2SO_4$. The solution was allowed to reflux for 20 hours. The solution was neutralized with $NaHCO_3$ and a precipitate formed. The precipitate was filtered, collected, and recrystallized from EtOH (70mL). Yield: 92%

**(R)-ethyl 4'-(octan-2-yloxy)-[1,1'-biphenyl]-4-carboxylate (3):**

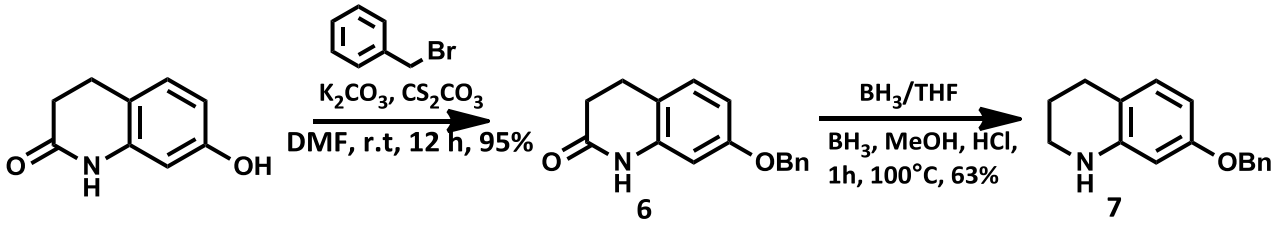
**2** (1 mmol, 242mg) and (S)-2-octanol (1.12 mmol, 145mg, 0.19mL) was dissolved in THF, and a stirred suspension of DIAD (1.25 mmol, 252mg, 0.25mL) and $PPh_3$ (1.13 mmol, 341mg) in THF was added to the solution under argon atmosphere and ice-cooling. Upon addition of the DIAD/ $PPh_3$ mixture, the solution turned yellow, then decolorized. The solution was stirred for 1 hour. After a full conversion (TLC check), the organic was extracted with ethyl acetate, and washed with brine (3x). The organic was dried over $MgSO_4$. Further purification was performed chromatographically with hexanes/DCM (1:2). Yield: 83%

**(R)-4'-(octan-2-yloxy)-[1,1'-biphenyl]-4-carboxylic acid (4):**

**3** (0.722 mmol, 256mg) and a catalytic amount of NaOH were dissolved in EtOH (30mL). The solution was refluxed for 1 hour. A catalytic amount of water was later added to the solution to form a precipitate. The precipitate was filtered and collected. No further purification methods were used. Yield: 100%

**4'-((4'-((R)-1-(hexyloxy)ethoxy)-[1,1'-biphenyl]-4-carbonyl)oxy)-[1,1'-biphenyl]-3-yl 4'-((R)-octan-2-yloxy)-[1,1'-biphenyl]-4-carboxylate (5):**

**1** (0.3mmol, 56mg), **4** (0.6mmol, 196mg), EDAC (1.2mmol, 230mg), and DMAP (0.1mmol, 12.2mg) were dissolved in dichloromethane (7mL) under argon atmosphere. The solution was stirred for 12 hours at room temperature. The organic was washed with water (1x), $NaHCO_3$ (1x), and brine (1x). The solution was dried over $MgSO_4$. Further purification was performed chromatographically with $CHCl_3$. Yield: 72%



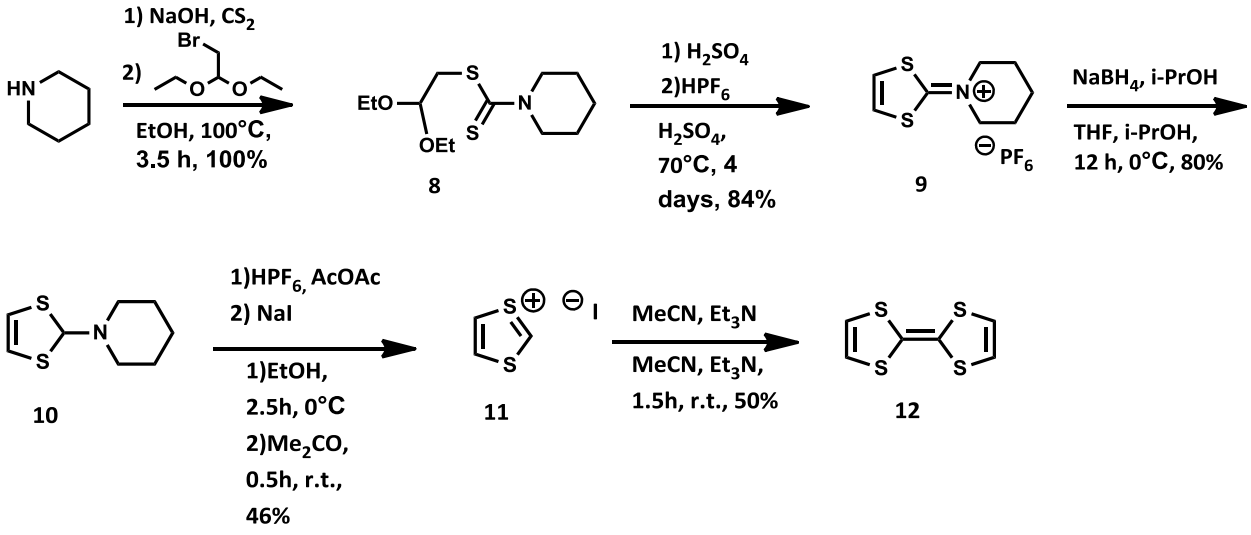

**7-(benzyloxy)-3,4-dihydroquinolin-2(1H)-one (6):**

3,4-dihydro-7-hydroxy-2(1H)-quinolinone (50mmol, 8.158g), benzyl bromide (60mmol, 10.262g, 7.136mL), $K_2CO_3$ (100mmol, 13.820g), and $Cs_2CO_3$ (100mmol, 3.258g) was dissolved in DMF

(70mL) under argon atmosphere. The solution was allowed to stir for 12 hours at room temperature. The organic was extracted from ethyl acetate and dichloromethane. The organic was washed with water (3x), and brine (1x). The organic was dried over $Na_2SO_4$ and recrystallized from EtOH (300mL). Yield: 95%

**7-(benzyloxy)-1,2,3,4-tetrahydroquinoline (7):**

**6** (2mmol, 0.506g), was dissolved in THF under argon atmosphere. While ice-cooling, $BH_3$·THF (1 M, 12.5mmol, 1.07g, 12.5mL) was slowly added. The solution was refluxed for 12 hours. The solution was placed under ice-cooling, was quenched with MeOH (8mL), and acidified with HCl (3mL). The solution was refluxed for 1 hour. After refluxing, the solution was placed under ice-cooling and NaOH was added until the solution was neutralized. The organic was extracted with ethyl acetate (3x) and washed with brine (1x). The organic was dried over $Na_2SO_4$. Further purification was performed chromatographically with dichloromethane. Yield: 63%




**2,2-diethoxyethyl piperidine-1-carbodithioate (8):**

Piperidine (1mol, 85.15g, 98.78mL) was dissolved in EtOH (375mL) and NaOH pellets (1mol, 40.0g) were slowly added to the solution. $CS_2$ (1mol, 76.13g, 60.42mL) was added dropwise for 1 hour to the solution under ice-cooling and stirring. The solution was stirred continuously for 1 hour under ice-cooling until a white precipitate formed. After the precipitate formed, the solution was refluxed for 3 hours. While refluxing, the solution became yellow and the precipitate dissolved. Bromoacetaldehyde diethyl acetal (1mol, 197.07g, 150.43mL) was added dropwise to the solution for 30 minutess while refluxing. The solution refluxed for 24 hours. After cooling the solution, water (500mL) was added and the organic was extracted with dichloromethane (4x), and washed with water (3x). The organic was dried with $Na_2SO_4$. The solution was recrystallized from hexane. Yield: 100%

**2-Piperidino-1,3-dithiolium Dexafluorophosphate (9):**

**8** (1mol, 277.0g) was added portionwise to $H_2SO_4$ (233mL) for 6 hours while ice-cooling. The solution was heated at 70°C while stirring for 96 hours. The mixture was poured slowly into ice water (1L) and $HPF_6$ (146mL) solution while stirring. Upon addition, a white precipitate formed. The precipitate was collected via filtration and washed with water. After collecting the solid, it was dissolved in dichloromethane (2L) and washed with water, $NaHCO_3$, and water (respectively). The organic was dried with $MgSO_4$ and was recrystallized from diethyl ether. Yield: 84%

**1-(1,3-dithiol-2-yl)piperidine (10):**

**9** (840mmols, 278.88g) was dissolved in THF/i-PrOH (2.2L, 1:1). $NaBH_4$ was added to the solution for 6 hours under argon atmosphere, ice-cooling, and mechanical stirring. The solution was allowed to stir for 12 hours in an ice bath. The solvent was evaporated and added water (1L). The organic was extracted with ether (4x) and washed with water (3x) and brine (1x). The organic was dried with $MgSO_4$. No further purification methods were employed. Yield: 80%

**1,3-Dithiolium Iodide (11):**

$HPF_{6\backslash}$ (1.722mols, 420.0g, 254mL) was added to a mechanically stirred solution of $Ac_2O$ (1L) for 2 hours, under argon atmosphere while ice-cooling. **10** (840mmols, 127.0g) dissolved in anhydrous diethyl ether (1L) was added to the $HPF_6/Ac_2O$ solution for 1 hour. Upon addition of **10**, a precipitate formed. The mixture was diluted with diethyl ether (500mL) and stirred for 1 hour. The precipitate was collected via filtration and washed with diethyl ether. For further purification, an anion exchange was performed. The precipitate was dissolved in anhydrous acetone (500mL) while stirring mechanically under argon atmosphere at room temperature. Sodium iodide (792mmol, 119.0g) dissolved in anhydrous acetone (200mL) was added to the solution. Upon addition of the sodium iodide, a precipitate formed. The precipitate was collected via filtration, and was washed with anhydrous acetone and diethyl ether. Yield: 46%

**Tetrathiofulvalene (12):**

**11** (385mmols, 89.40g) was dissolved in anhydrous acetonitrile (1.1L), and anhydrous triethyl amine (421mmols, 60.4mL) was added dropwise to the mechanically stirred solution for 1.5 hours under argon atmosphere at room temperature. The solution was stirred for 1 hour. After stirring, water (2L) was added to the solution, and a precipitate was formed. The precipitate was collected via filtration and washed with water. The precipitate was dissolved in dichloromethane and the organic was washed with water (2x). The solution was dried over $MgSO_4$. The solvent was evaporated, and the remaining solid was dissolved in hot cyclohexane. The solution was treated with decolorizing charcoal and filtered while hot, and the filtrate was

immediately diluted with hexane to recrystallize. The product from recrystallization were long, orange needles. Yield: 50%

**Results**

The complete synthesis of the B4 mesogen (**4**) was successful, and appeared to be homochiral under the polarized microscope. However, the phase is yet to be determined, officially.

The complete synthesis of tetrathiofulvalene (**12**) was successful, but was not fully synthesized into the bent unit for the NLOphore. The complete synthesis of the NLOphore has not yet been completed.

The complete synthesis of 7-(benzyloxy)-1,2,3,4-tetrahydroquinoline (**7**) was successful, but the complete synthesis of the NLOphore has not yet been completed.

**Conclusions**

The goal of the conducted research was to synthesize the target structures of a $SmAP_F$ phase for electro-optic translators and a B4 phase that has potential to separate enantiomers by acting as the stationary phase in chromatography. The $SmAP_F$ phase would be able to translate electronic signal to optical signal, and vice versa. The bent core of one of the target structures of the $SmAP_F$ phase was completed successfully, however, the other bent units and the whole mesogen have not yet been completed. The B4 phase was designed to be imine-free and homo-chiral in order to be able to work under water-conditions and to give high enantiomer resolution, respectively. The chiral version of the W513 was successfully synthesized, and appeared homo-chiral under the polarized microscope, however, the phase has yet to be officially determined. In the future, all target structures would be synthesized and the materials would be applied to what they were designed for to see if they are effective candidates for each application.

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