

Running head: THIOPHENEANTHRONE-1-THIOGLYCOLICCARBOXYLIC ACID

SYNTHESIS OF A SOLUBLE THIOPHENEANTHRONE ORGANIC
SEMICONDUCTOR: THIOPHENEANTHRONE-1-THIOGLYCOLICCARBOXYLIC
ACID

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Acceptance of Senior Honors Thesis

This Senior Honors Thesis is accepted in partial fulfillment of the requirements for graduation from the Honors Program of Liberty University.

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Abstract

Organic semiconductors are currently being researched for various uses, both electronic and biologic. They are less expensive than current inorganic semiconductors and do not require doping. They are useful in many areas including thin film transistors, photovoltaic cells, and Light Emitting Diodes (LED). However, synthesizing soluble organic semiconductors has been difficult. As a result, this study undertakes the synthesis of a specific organic semiconductor aiming at increased solubility following an adapted literature protocol. Tests for solubility, fluorescence, and conductivity potential will be used to assess the potential of this molecule as a semiconductor. Synthesis of anthraquinone-1,8-bisthioglycoliccarboxylic acid as an intermediate to thiopheneanthrone-1-thioglycoliccarboxylic acid was successful; however, results for the target molecule, thiopheneanthrone-1-thioglycoliccarboxylic acid, were inconclusive.

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INTRODUCTION

Semiconductors

Semiconductors are devices that are able to conduct electricity, but not as extensively as conductors, due to insulating properties. Restricted conductivity allows for applications in various electrical devices.(1-3) Computers for example use silicon, an inorganic semiconductor, in transistors and diodes. Semiconductors are beneficial in the field of electronics because they conduct electricity in a manner entirely different from metals. As a result, semiconductors do not burn out as quickly as metal conductors.

There are two different types of semiconductors: inorganic and organic. Inorganic semiconductors transfer charge due to free electrons, while organic semiconductors transfer charge by the electrons transitioning from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) resulting from π -bonds.(4) The smaller the energy gap between the HOMO and LUMO is, the better the semiconductor functions because the electrons are able to move faster between orbitals. The speed that electrons are able to move between orbitals, due to similar energy gaps, is an aspect of electron mobility (or carrier mobility). Electron mobility is a quantifiable measurement that characterizes the speed by which an electron can travel through a metal or semiconductor when pulled by an electric field. (4) The equation $V_d = \mu E$ is used to calculate electron mobility (μ). (4) The drift velocity (V_d) of the electrons is the result of

an applied electric field (E). Electron mobility is usually specified by units of $\text{cm}^2/(\text{V}\cdot\text{s})$.

(4) Unlike electron mobility, the energy gap between HOMO and LUMO is a computational value and cannot be measured directly.

The number of π -bonds associated with a molecule increase electron mobility by lowering the band gap energy (E_g).^(3, 5, 6) Thus, organic semiconductors are typically designed with the most conjugated π -bonds (alternating single and double bonds) possible so that the electrons can transition between HOMO and LUMO uninterrupted. Increased electron mobility is achieved by using fused, conjugated rings to create a more rigid and planar molecule.^(5, 7)

Semiconductors can increase their efficiency by undergoing a process called doping.^(8, 9) Doping is a method by which an impurity is introduced to the chemical. For inorganic semiconductors the impurity changes the electron conformations of the molecule and leaves electrons free to move and conduct a current. In organic semiconductors, doping acts like a stepping stone between the HOMO and LUMO, increasing conductivity.^(8, 9) However, doping is not necessary in organic semiconductors, and studies such as this Honors thesis are being conducted on organic semiconductors that do not include doping.

Increased interest in this field of study is a result of the discovery that building organic semiconductors is less expensive than making the inorganic counterparts.^(1, 10) Organic semiconductors also anneal at much lower temperatures than inorganic ones such as silicon. This would allow them to be applied to heat sensitive materials like plastic.

Applications for Organic Semiconductors

Additional applications organic semiconductors include light-emitting diodes (LED), photovoltaic cells, and field-effect transistors.^(1, 3, 9, 10) Photovoltaic cells have the ability to be used in carrier mobility, the ability to sensitize titania, LED devices, and luminescence.⁽¹⁰⁾ Thus, many semiconducting molecules are also being investigated for advances in these areas.⁽¹⁰⁾ These types of molecules show signs of being promising solar cell materials.

An ideal photovoltaic solar cell contains a panchromatic absorption band. This is directly related to the π conjugation within the system. Absorption range can be expanded by also expanding the conjugation. One method to accomplish this is by adding electron donating and electron withdrawing groups to the molecule.^(3, 10) Cyano groups are good electron-withdrawing groups that are effective in lowering the LUMO levels of certain molecules, and they also enhance the stability of the molecule. Nitro groups are electron acceptors that are also effective in enhancing electron currents in photovoltaic cells.⁽¹⁰⁾ Polymeric compounds are generally more commonly used in photovoltaic cells; however some studies on anthracene-containing compounds have been completed.

Thiophene-based aromatic molecules increase highly ordered, compressed packing due to the intermolecular sulfur-sulfur interactions.⁽¹¹⁾ The ordering of these molecules can produce nanoribbons of increased charge mobility which make them an appealing topic of study for electronic application.⁽¹¹⁾ The π - π interactions of aromatic, highly conjugated systems contributes to both the formation and packing of the nanoribbons.⁽¹¹⁾ While these molecules are promising for electrical applications, they

are difficult to study. One key factor is the lack of solubility. In that particular study, lack of solubility made solution electrochemistry impossible.(11) Solution electrochemistry would have made it possible to corroborate the HUMO values.

Aside from functioning as a semiconductor, conjugated systems can be useful in areas of biology as well. Current organic semiconductors have shown fluorescence capabilities enhancing the potential uses for new molecules beyond semiconducting(12).

Fluorescence is the result of photons being absorbed at one wavelength and then being emitted at a slightly longer wavelength.(12) If the organic molecule is able to fluoresce or if it has color, it can be tested as a biological dye or marker.(13) For example, DNA has partially localized negative charges on the oxygen in the phosphate groups that make up part of the backbone. As a result, cationic species are able to interact with this negative charge; however, this is typically a weak interaction under physiological conditions.(14) Other interactions with dyes can happen via intercalation, insertion in the major groove, or insertion in the minor groove.(14) The shape, size, and charge of the molecule dictate which area of the DNA it is able to interact with.(14) Intercalation usually occurs with cationic species with planar aromatic rings. Ideally, a fluorescent dye would show a different color when attached than when free, so that staining can be confirmed. Developing new stains can provide new opportunities for research particularly in the area of sensitivity. The more sensitive the stain is, the less DNA, or other molecule, is needed in order to observe results.

A particular color is the result of reflection (or absorption) of a particular wavelength in the range of about 390-700 nm of electromagnetic radiation within a conjugated system that corresponds to the HOMO/LUMO gap.(15, 16) Therefore, the

amount of conjugation in a molecule can alter its color. The band gap energies of molecules that are highly conjugated shift into the visible spectrum and produce the colors that are visually observed. The absorbance of the other wavelengths of light results in the reflection of the complement wavelengths pertaining to the observed color.

Importance of Solubility

Solubility is an essential characteristic of organic semiconductors because it allows for application in solution, such as printing. Due to the current insolubility of many of the organic semiconductors, they have to be applied using vacuum deposition. Thus, solubility allows for easier application and experimentation.^(17, 18) The development of small organic molecules that could overcome these limitations would provide many advantages in the production of photovoltaic cells. Small molecules tend to have higher charge mobility and are easier to synthesize than complex polymers. They also have more efficient charge transport capabilities because of their ability to facilitate charge electron delocalization.⁽¹⁰⁾

Optimal Characteristics of Organic Semiconductors

There are several categories of molecules that possess optimal characteristics necessary for good organic semiconductors.

Acenes. Molecules that demonstrate good semiconductor characteristics include those with a substructure of anthracene or pentacene (Figure 1).⁽¹⁹⁾ Anthracene and pentacene are good foundational molecules because they are planar, conjugated systems; however, symmetry within these molecules can reduce dipole moments, making the molecules as a whole less polar and thus less soluble in water. The biggest problem with

acenes, however, is that they are relatively unstable. The carbons on the central ring are easily degraded to form a transannular peroxide or undergo a Diels-Alder reaction.(2)

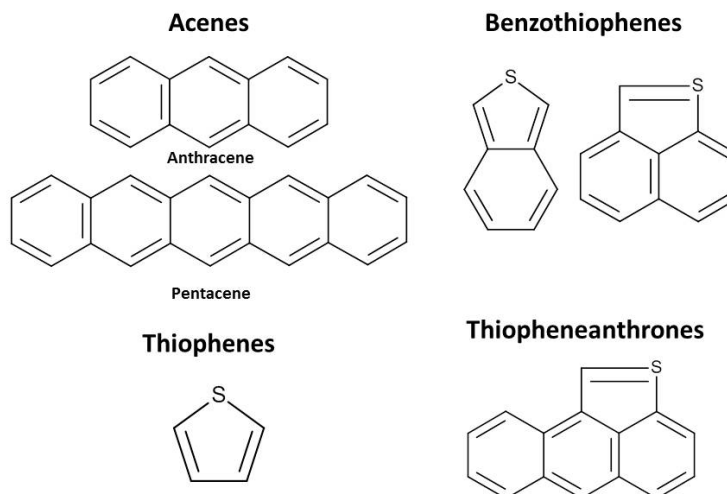


Figure 1. Categories of Molecules. Several examples of the discussed categories of molecules are shown. Each category contains additional molecules to those shown.

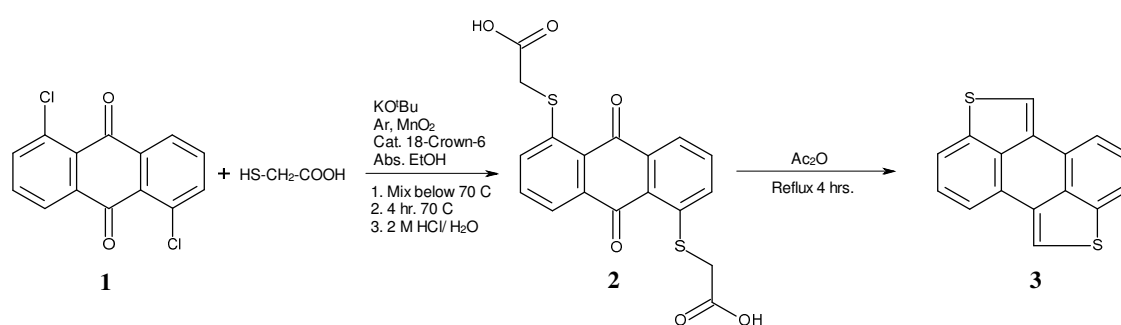
Thiophenes. To reduce the oxidative degradation of these aromatic cores, sulfur groups have been added in the form of thiophene units.(2) Thiophenes have been shown to lower HOMO-LUMO band gaps due to conjugation and the stability of the sulfur group.(2, 20) Theoretically, the implementation of thiophenes into an aromatic core such as pentacene or anthracene would help to lower band gap energies, creating a better organic semiconductor. This was the approach used for the molecule 3,4:3',4'-bis[*b*]benzothiophene (BBT, 3).

Benzothiophenes. Benzothiophenes are a group of molecules that contain a mixture of benzene rings and thiophene rings. BBT contains an anthracene as its aromatic core and has two thiophene groups. It is a symmetrical molecule which may reduce

solubility. BBT was first reported by *Wudl et al.* in 1979 (Scheme 1).(21) They showed that BBT presented electrical conductivity after being doped with iodine. The thiophenes in BBT increase the level of conjugation which is why it has a lower band gap (3.61 eV) than anthracene alone (approximately 5.65 eV).(22) However, there are several problems with the structure of BBT that prevent it from being an ideal organic semiconductor.

First, it is symmetrical which reduces solubility by negating the dipole moments.

Secondly, the thiophenes limit the types and locations on the molecule for additional chemistry compared to the proposed molecule **17** that still maintains a double bonded oxygen.



Scheme 1. BBT Synthesis. 1,5-Dichloroanthraquinone (**1**) is treated with thioglycolic acid to create a diacid (**2**). The acid groups form a ring with the anthraquinone to yield molecule **3** upon treatment with acetic anhydride.

Products that have used BBT as the backbone have been of important use in fluorescence regarding the detection of caffeine. Recently, a bisbenzothiophene derivative (3,4:3',4' bisbenzo[*b*]thiophene-2,2'-disulfonate) was chosen based on its ability to meet three specific criteria: contains more polarizable atoms, a large π -stacking

surface, and the ability to delocalize the π -density.(12) The study was successful in producing a fluorescent indicator for caffeine using the BBT derivative, and the success was attributed to the π -stacking ability of the BBT core. (12)

Thiopheneanthrones. Some benzothiophenes also fit into the category of thiopheneanthrones. These molecules contain an anthracene core with additional thiophene rings for stability to prevent against oxidative degradation into peroxides.(2) This category of molecules combines the beneficial aspects of the acenes and thiophenes to create highly conjugated, stable species. BBT has good potential as an organic semiconductor; therefore, by utilizing the synthetic scheme of BBT to create an anthracene based molecule that possesses the conjugation of the thiophene, the aromatic core, and contains sites for additional chemistry to increase solubility could lead to a good semiconductor. Little has been done to investigate this area of chemistry until recently.

A literature search on molecule **25** and **17** did not produce any results, indicating that these are new molecules that have never been reported in the available published literature before. The closest published molecule was molecule **6**. The majority of the reported literature was used in the formation of dyes and dye intermediates.(15, 16, 23) A variety of structures of these molecules are similar to **16** (Figure 2). They appear in several foreign patents published in the 1930s. The vast time gap between then and now reveals just how little additional research has been done on these aromatic molecules.

The molecules shown in Figure 2 are grouped into three distinct categories based on the level and type of substitution. Molecules **6** and **14** are the most similar to the molecule being synthesized in this study. Molecules **9** and **16** increase the conjugation of

the anthraquinone substructure.^(16, 24) As mentioned above, changing conjugation allows for dyes if the molecule absorbs in the visible spectrum or for potential fluorescence. Molecule **16** was in fact synthesized for use as a dye.⁽¹⁶⁾ It produces a yellow-brown shade in water and is used to dye wool. While the molecules listed in Figure 2 have been studied as dyes and dye intermediates, there has been little study of their electrical properties.

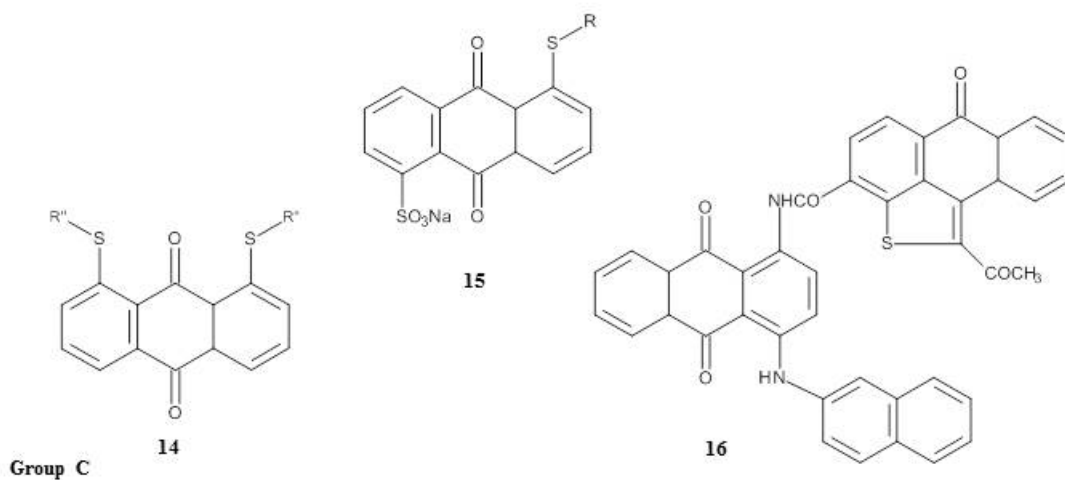
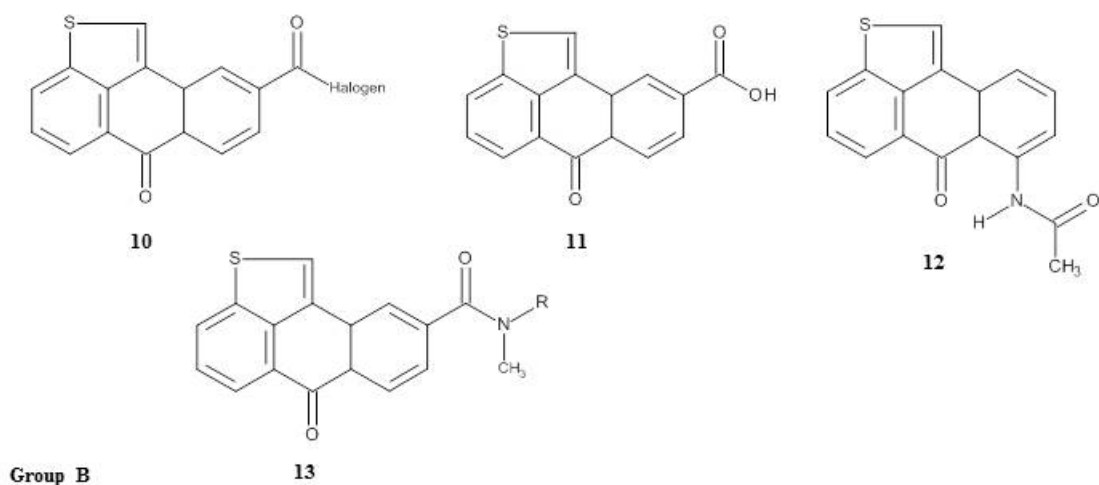
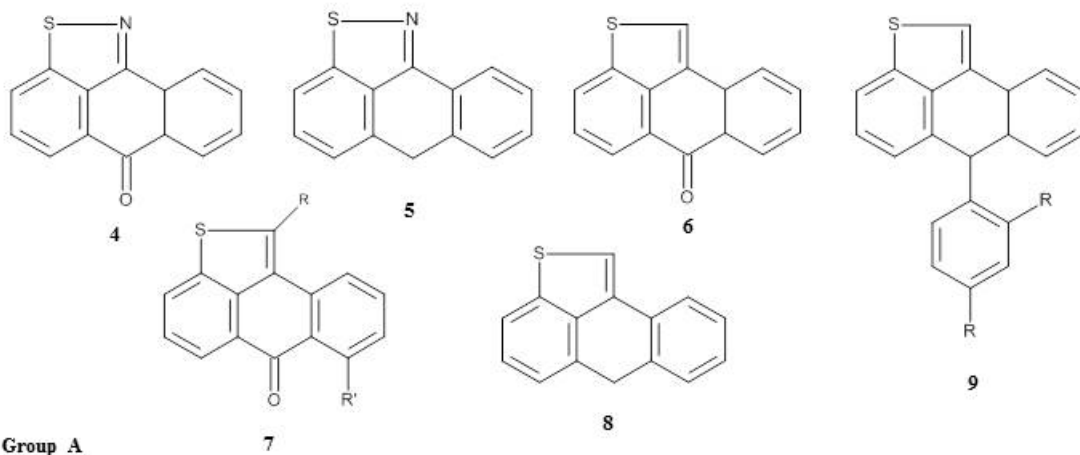


Figure 2. Previously reported thiopheneanthrone derivatives. These molecules have been previously synthesized and reported in several patents and papers. Variations can occur at different sites: 1) the C=O (Compound **9**), 2) the thiophene ring (**Group A**), and 3) the benzene ring. Compound **16** was synthesized for use as a dye, while many of the other compounds were synthesized for electrochemical purposes. R=CO₂Me, NO₂, PH, H; R'=H, NHMe, NMe₂; R''=methyl, ethyl, butyl, iso-butyl, iso-amyl.

Molecular Modeling Using Density Functional Theory

Density Functional Theory (DFT) uses a series of complex formulas based on electron density to determine the properties of many-electron systems. It can be used to determine the HOMO/LUMO band gap energy (in electron volts, eV) and polarity, as in this study. The band gap energies for BBT, thiopheneanthrone, and thiophene-1-thioglycoliccarboxylic acid were calculated to be 3.61, 3.80, and 3.82 eV respectively.

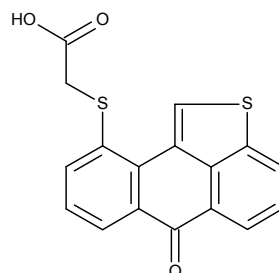
Summary of Optimal Characteristics for Organic Semiconductors

Based on the above properties of organic molecules and electron flow, good organic semiconductors are molecules that have the following characteristics:

1. They are planar.
2. They possess a small bang gap between HUMO and LUMO due to increased π -conjugation.
3. They have increased solubility in either water or organic solvents.(2, 25, 26)

GOALS AND OBJECTIVES

The goal of this project is to synthesize thiopheneanthrone-1-thioglycoliccarboxylic acid.



17

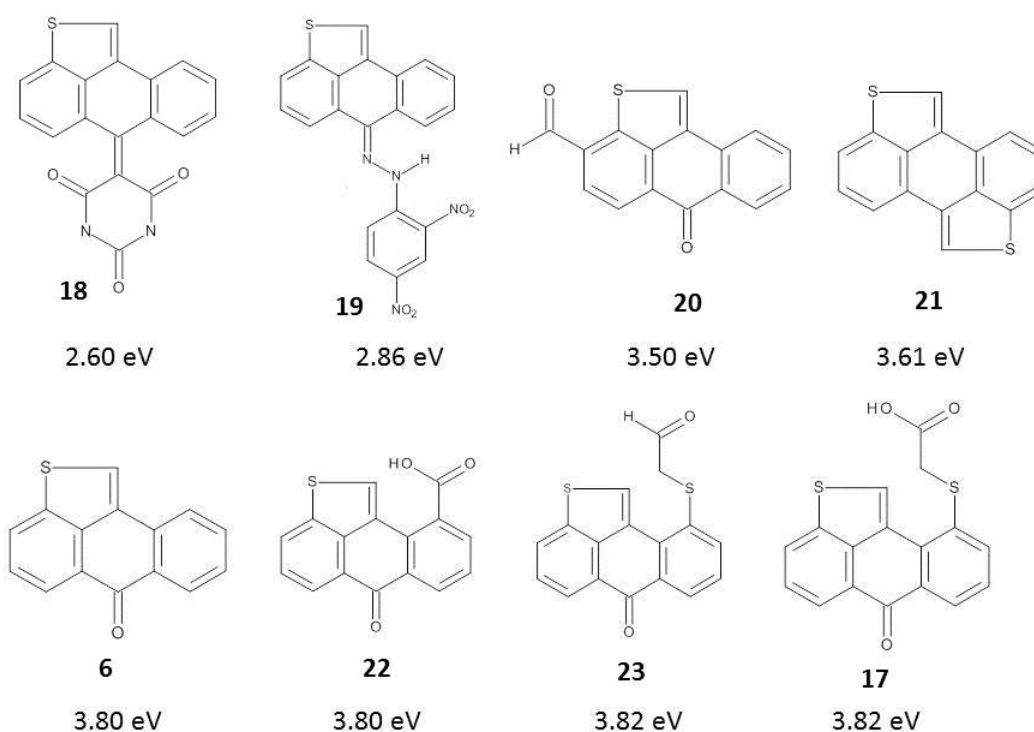
The specific substructure studied in this thesis is an anthraquinone. This molecule expresses conjugation throughout the molecule, and it is planar in structure. The quinone provides a means for extended modification.

This study is focused on the solubility and molecular structure of thiopheneanthrone derivative **17**. Producing a new molecule with increased water solubility would allow for simplified application of semiconductors to various applications such as the above mentioned photovoltaic cells and thin film transistors. Thus, this study will attempt to synthesize molecule **17** (Scheme 2). The free acid group of this molecule should add to the solubility aspects while the thiophene ring will add to the conjugation and stability of the anthraquinone substructure. If this is accomplished, additional functional groups such as carboxyl groups (-COOH) will be explored in order to enhance solubility around the molecule. The carbonyl group (-C=O) will allow for additional chemistry, as well as additional polarity around the molecule. Since the molecule is asymmetrical there is no cancelation of the dipoles, which should help to increase the solubility around the molecule.

Predictions for several different compounds were computed with SPARTAN 10 software using the hybrid DFT functional and basis set combination designated the B3LYP/6-31G* level. The B3LYP stands for Becke, 3-parameter, Lee-Yang-Parr, which is the most commonly used version of hybrid functionals. Hybrid functionals are approximations to the exchange-correlation energy functional in DFT calculations.(27) The 6-31G aspect of the parameters refers to the basis set, which creates molecular orbitals by combining a set of functions in linear combinations.(27) This particular basis set is known as a split-valence basis set, which has a subgroup called Pople basis sets. John Pople was the person who developed many of the calculations necessary for these functions.(27) In the case of 6-31G, the 6 refers to the number of primitive Gaussians comprising each core atomic orbital basis function.(27) The 3 and 1 are indicative of the two basic functions of the valence orbitals which are a linear combination of the listed number of primitive Gaussian functions.(27) The HOMO and LUMO energies and band gap energies (eV) were determined. The planar and rotational aspects of the molecule were also predicted. Changes in band gap (ΔE_g) indicate that molecule **17** does not produce a significant change from the reported experimental values for BBT.(21) Molecular modeling shows that compound **17** does not decrease the band gap between the HOMO and LUMO as expressed in Table 1; however the band gap energy is not much higher than BBT which has been shown to be a decent organic semiconductor.(21) Thus, the thioglycoliccarboxylic acid being added will not negatively affect the band gap. However, by freeing the carbonyl group for additional chemistry, such as Wittig reactions, can decrease the band gap by nearly 70% from that of **17**. Other molecules whose properties were predicted with this program show lower band gaps and could

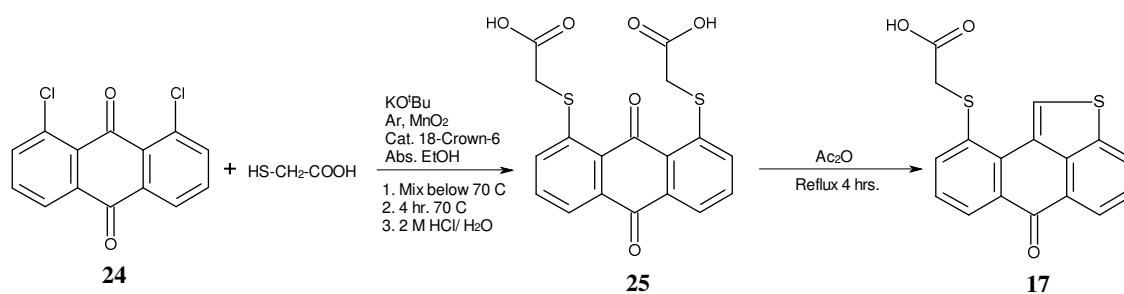
potentially be more promising semiconductors. Several molecules, including a mono-thiopheneanthrone with the carboxylic acid (**22**) will be synthesized for comparison to molecule **17**.

Table 1. Molecular Modeling Band Gaps. The presented molecules were modeled on SPARTAN 10 software using the B3LYP/6-31G* level. The change in energies (eV) between the HOMO and LUMO represents the band gap. The smaller this gap is, the more apt the molecule is to function as a semiconductor.



Through the synthesis of molecule **17**, this current study will attempt to increase the solubility through the free thioglycoliccarboxylic acid group, increase conjugation via the thiophene group, and conduct additional chemistry to increase solubility at the free

carbonyl group on the anthracene backbone, the thiophene group, and the thioglycoliccarboxylic acid group. If each of these aspects can be achieved, a suitable organic semiconductor will be produced. Additionally, tests for fluorescence will be performed to see if the proposed molecule could have any other properties indicating other uses in addition to being an organic semiconductor, such as molecular dyes or photovoltaic cells.



Scheme 2. Proposed Modification of 1,8-Dichloroanthraquinone. 1,8-dichloroanthraquinone was treated with thioglycolic acid following the same reaction stipulations from the BBT synthesis. Only one ring closure is expected because the thioglycoliccarboxylic acid group can only interact with one of the carbonyl groups of the anthraquinone.

To synthesize this molecule, 1,8-dichloroanthraquinone (**24**) will be treated according to the same basic procedure that resulted in BBT.(21) The closest known reported molecules to the one being synthesized here are monothiophene derivatives of the anthraquinone core, all shown in Figure 2.

Several of the molecules currently being investigated by our research group are based on chloroanthraquinones as precursors. Nucleophilic aromatic substitution is the process by which chlorides on the anthraquinone are replaced with other, larger groups.

One such group is thioglycolic acid forming the thioglycoliccarboxylic acid substituent. This group can be closed into a ring by reacting with the double-bonded oxygen on the quinone upon treatment with acetic anhydride.⁽²¹⁾ This method has been shown with the molecule BBT which begins as a 1,5-dichloroanthraquinone and becomes BBT after two symmetrical ring closures (see Scheme 1) as outlined in the US patent US2009/0292130.⁽²¹⁾

MATERIAL AND METHODS

Reagents

The following reagents were used: 1,8-dichloroanthraquinone (Lot # MKBG0020V) from Aldrich Chemistry, thioglycolic acid (Lot # MKBHO417V) from Sigma Aldrich, 200 proof ethanol from Quantum Chemical Corporation, potassium butoxide (KO^tBu) (Lot # A0313286) from Acrōs Organics, manganese dioxide (Lot # 723291), acetic anhydride (Lot # 113625) and HCl (Lot # 096570) from Fisher.

Synthesis of Anthraquinone-1,8-bisthioglycoliccarboxylic Acid (25)

To construct the proposed molecule in Scheme 2, 8.32g (30.0 mmol) of 1,8-dichloroanthraquinone **24** was dissolved in approximately 50 mL of ethanol in a round bottom flask. The mixture was immediately stirred with a magnetic stirrer and remained stirring throughout the experiment. The color of the beginning mixture was soft yellow. Thioglycolic acid was added to the solution via a syringe in intervals until approximately 5 mL (70 mmol) were added. An additional 20 mL of ethanol was added. The mixture remained a soft yellow. Next, 442mg (5.09 mmol) of MnO₂ was added followed by two separate additions of KO^tBu at 11.06g and 8.01g, respectively, for a total addition of 19.07g (170.0 mmol). Upon the first addition of KO^tBu the solution turned dark red; after

the second addition the color was darker reddish-brown and was becoming warm to the touch. Approximately 90 mL of Ethanol was used to rinse the KOtBu divided between the two additions. The mixture appeared to thicken. A balloon filled with Argon gas was attached to the stop-cock.

The mixture was left to react at room temperature for three days. After three days, a reflux condenser was attached, and the balloon was refilled with Argon. The reaction was heated at around 76°C for approximately 5.5 hours. There was no additional color change, the mixture remained dark red-brown.

Once cooled, the extremely viscous, red-brown product was dissolved in approximately 500 mL of water. Vacuum filtration was performed twice to remove any particles. Solids from both filtrations were dried and saved for later analysis.

To the clear, orange filtrate, 60 mL of 2M HCl was added to bring the pH to 2. After the addition of the first 25 mL, the mixture became yellow and settled into an orange. The second addition of 25 mL produced a vibrant orange of pH 3. The final addition of 10 mL produced no additional color change and lowered to pH 2.

Vacuum filtration was performed to isolate the product (solid). The solids were washed with water until the pH was approximately 5. The solids were then washed with 20 mL of cold ethanol. The liquid filtrate was observed for fluorescence, with a Ultra Violet black light at 254nm and 365nm, once in the middle of the washing step and again after the pH reached 5. The product (DMP-1c) was left to dry completely giving 5.215g (55.7% yield).

A second batch of **25** was synthesized with similar ratios of reactants. The solution was put on an ice bath before the addition of KOtBu. Ethanol was increased

from 160 mL to 300 mL to help reduce some of the viscosity of the resulting solution. Instead of reacting the solution at room temperature for several days prior to the addition of heat, the mixture was immediately put into a water bath and heated at 76°C for four hours. The initial color was milky-orange-brown. The mixture was less viscous than the previous reaction. The final color was deep red.

The mixture was dissolved in 600 mL H₂O, filtered, washed with HCl, filtered a second time and brought to pH 5 as indicated above. The product (DMP-3b) was dried overnight and weighed giving 8.235g (87.9% yield).

Synthesis of Thiopheneanthrone-1-thioglycoliccarboxylic Acid (17)

To perform the ring closure, 5.82 g (15.0 mmol) of DMP-1c (**25**) was added to approximately 200 mL of acetic anhydride in a round bottom flask. The solution was somewhat cloudy and yellow. The solution refluxed for two hours. After five minutes a color change took place, switching from yellow to a dark brown-orange/black; however, the actual liquid appeared to remain orange/yellow. At the end of the reflux, the color of the mixture was black with no apparent particles. The solution was transferred to the refrigerator to cool and allow for crystal formation.

Several days later the solution was removed from the refrigerator. The crystals were isolated by vacuum filtration. The solids (DMP-2a) were allowed to dry over the weekend giving 1.256g. The liquid from the filtration was reduced to about half of its volume by distilling off the solvent. The solution was returned to the refrigerator to allow a second crop of crystals to form. The crystals were filtered, dried, and weighed giving 2.132g. The second crop (DMP-2b) appeared flattened and larger than DMP-2a.

Ring closure was repeated using 9.70g (25.0 mmol) DMP-3b in approximately 333 mL of acetic anhydride. The solution was refluxed as above for two hours instead of four. The product, a black liquid, was stored in the refrigerator for crystal formation. The resulting crystals were filtered, dried, and weighed giving 1.352g (DMP-4a). The remaining solution was reduced as above to yield a second crop giving 2.173g (DMP-4b). The remaining filtrate from the first ring closure was added to the remaining solution from the second ring closure and the solvent was distilled off to yield a final crop of crystals weighing 2.241g (DMP-4c).

Sublimation, Charcoal Decolorization, and Thin Layer Chromatography (TLC) for purification

A portion (0.71g) of DMP-2a was sublimed for purification with little success. A second apparatus was used on a second sample also with little success. A very thin film of yellow could be on top of the black crystals, but isolation was impossible. A third apparatus yielded better results when subliming DMP-4b, producing enough yellow crystals for analysis. Sublimation of the obtained product (DMP-3c) proved difficult even with the use of several sublimation apparatuses. Small amounts were able to be collected to test, however, most samples were too small to weigh or were just enough to be collected using a solvent such as acetone.

Acetone was used to isolate the yellow crystals from the sublimation and left to evaporate off. Small, oblong yellow crystals were formed. The remaining DMP-4b was boiled in methanol, producing a clear, amber liquid, with small black particulates that were vacuum filtered. The filtrate was then decolorized using charcoal, producing a clear,

yellow liquid. Small yellow crystals formed in the filtrate immediately after vacuum filtration.

Thin layer chromatography (TLC) was performed on the sublimed DMP-2a using dichloromethane, methanol, petroleum ether, and acetone. Samples of the sublimed material were taken from the condenser and a partially melted sample pellet in the bottom of the flask and run against each other.

RESULTS AND DISCUSSION

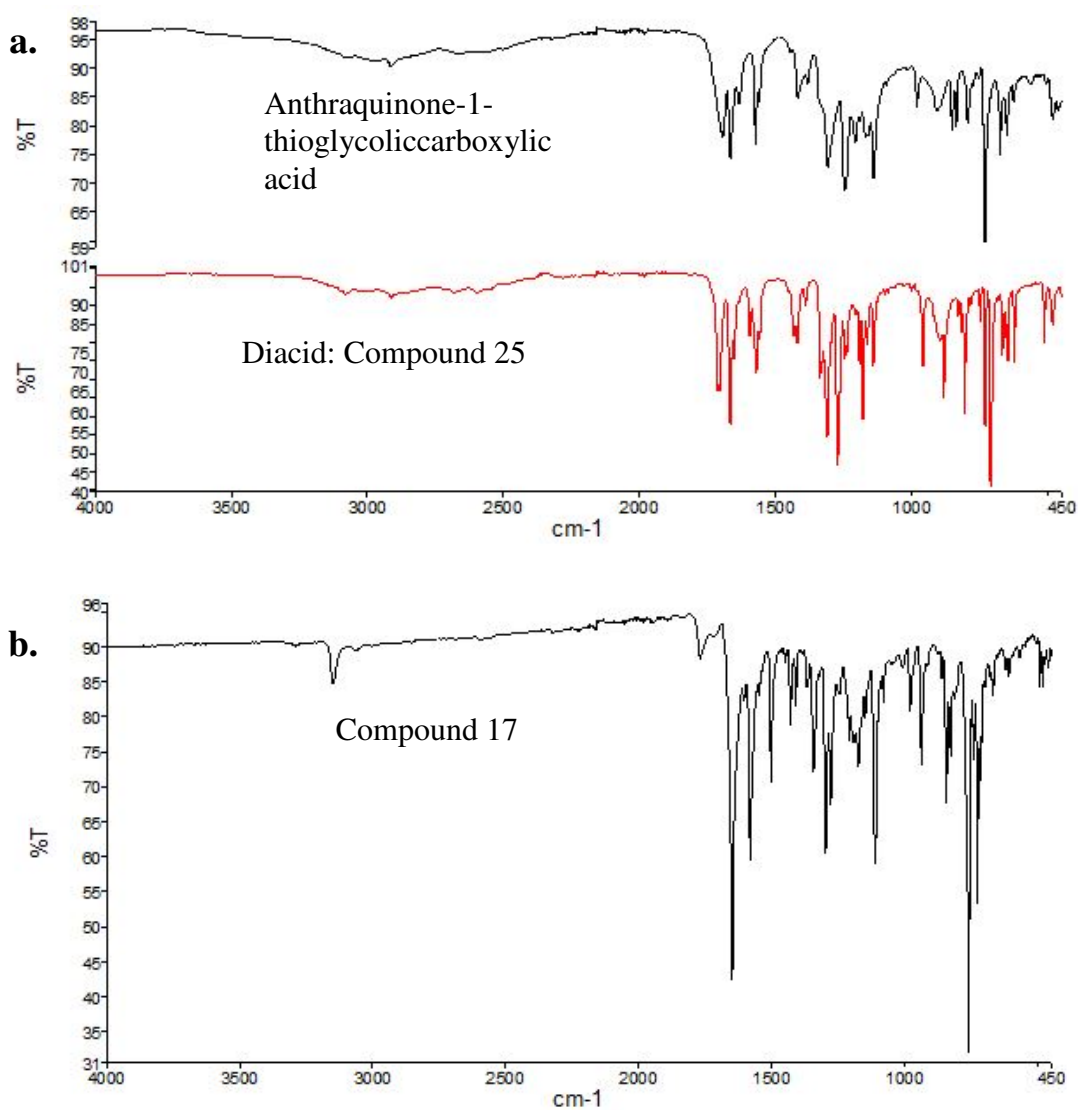


Figure 3. FT-IR Spectrum analysis. Peaks present in the 3000-2500 cm^{-1} range indicate the presence of a carboxylic acid group. Peaks in the 1780 - 1680 cm^{-1} range represent carbonyl functional groups. **a)** FT-IR spectrum data shows the comparison of **25** with a previously synthesized monoacid of the same basic structure. The acid group is confirmed due to the peak in the 3000-2500 cm^{-1} region. **b)** This spectrum of **17** shows no sign of a carboxylic acid group, and has one peak for a carbonyl group in the 1780 - 1680 cm^{-1} range.

The synthesis of compound **25** appeared to be successful based on the data obtained from the Fourier Transform Infra-red Spectroscopy (FT-IR), see (Figure 3 above and refer to FT-IR section below for further explanation). Solubility tests also show that the compound is soluble in various solvents, consistent with the presence of an acid group.

The results for molecules **25** and **17** are as of yet inconclusive. The proposed molecule **17** appears to not be the expected structure, and more investigation with better equipment is necessary to confirm this.

Solubility

Solubility attempts for compound **25** were more successful than for attempted compound **17**. Compound **25** has stronger dipole moments and would result in a more soluble compound. However the expected structure for compound **17** would have still allowed for some solubility because of the free acid group that should be present. However, **17** was not only insoluble in water it was only slightly soluble in acetone. If the acid group was present, the compound should have become soluble when reacted with a base, but the compound remained insoluble, suggesting that the acid group was not present.

Fluorescence

The fluorescence of the reaction was tested along varying intervals of the reaction synthesis. The first test resulted in green fluorescence at 365 nm during the synthesis of **25** after the addition of HCl. The repeated synthesis also produced fluorescence at this wavelength after the addition of HCl. However, after the ring closure was performed in acetic anhydride, no fluorescence occurred when dissolved in acetone.

Fluorescence was tested when **25** was dissolved in acetone. The resulting solution fluoresced a vibrant blue (Figure 3). The attempted ring closure product, **17**, did not show any fluorescence regardless of solvents. Solvents used include dichloromethane, methanol, petroleum ether, acetone, and NaOH.

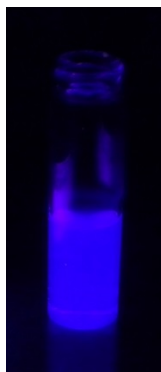


Figure 2. Fluorescence in acetone. The diacid, compound **25** was dissolved in acetone and fluoresced blue at 365nm. The original solution was colorless. The acetone solution was extremely dilute and differed in comparison with the green fluorescence of the same compound in an HCl or a water solvent.

Sublimation

In order to purify the attempted product **17**, several sublimations using various types of equipment were performed. The first sublimation yielded a thin yellow film. The total yield was extremely small and unable to be collected. In the next attempt, using a more complex apparatus as outlined above, more product was produced. Several colors were noted. Yellow powder ran along the surfaces of the glassware, while a small pellet had formed in the bottom of the round bottom flask. The pellet consisted of orange and yellow-green remains. In both cases un-sublimed material remained, and the yield was too small to process beyond FT-IR and TLC. After several weeks of sitting in a vial, a portion of the collected product from the second sublimation appears to have darkened in color. At the time of collection it was a soft yellow with some black un-sublimed material unable to be separated from it, and the entire collection appears to be a darker brown.

Thin Layer Chromatography

In order to isolate an appropriate solvent to purify the final product, a TLC was performed using dichloromethane, methanol, petroleum ether, and acetone as the solvent. The resulting retardation factors (R_f values) showed that acetone (R_f values of 0.85, 0.78, 0.85) and methanol (R_f values of 0.83, 0.82) were too good of solvents. Petroleum ether was not a good solvent as the samples did not migrate any distance from the application site (R_f values of 0.00). Dichloromethane was the best solvent for separation purposes. It produced an adequate migration from the application site, and there were two separate spots for each of the samples (sublimed DMP-3c) showing the presence of contaminants within the samples; however, the separation between the sample and contaminants was not large. The R_f values for the first sample were 0.46 and 0.55, and from the second sample were 0.38, 0.43, 0.49. These values show that there was better separation in

dichloromethane, and the spots only migrated about half way up the plate, showing that there

The samples from the sublimed DMP-3c dissolved in acetone were assessed for fluorescence before being run on the plates and neither fluoresced under the 365 or 254 nm wavelengths. Fluorescence was tested for again once the samples were run on the plates.

Fourier Transform Infra-Red Spectroscopy

Confirmation of the structure of the compounds was analyzed by the use of FT-IR. The peaks in the range of 3000-2500 cm^{-1} indicate the presence of the hydroxyl group (-OH) in a carboxylic acid group (-COOH). In Figure 3, this group is present in compound **25**; however, it is missing in the product from the ring closure reaction, attempted compound **17**. Both compounds showed peaks in the range of 1780 - 1680 cm^{-1} indicating carbonyl functional groups (-C=O) from the carboxylic acid and the central ring of the anthracene substructure. In compound **25**, three peaks formed, while for compound **17**, there was only one distinct peak present in this range. This is consistent with the presence of three unique carbonyl groups in compound **25**, while the single peak for compound **17** implies that the only remaining carbonyl group is possibly the one on the anthracene core. To confirm the presence of the thioglycoliccarboxylic acid group in compound **25**, FT-IR was run on the monoacid anthraquinone-1-thioglycoliccarboxylic acid. Both compounds showed the peaks in the range of carboxylic acid groups. Thus, it appears that during the reaction the acid was removed. One idea for this is decarboxylation. Future synthesis will alter the reaction parameters to try to correct for

the loss of acid, or explore the current parameters by analyzing samples taken at certain time intervals during the reaction.

FUTURE DIRECTION

The inability to make compound **17** shows that the reaction parameters need to be explored or altered in order to determine an effective synthesis. If the acid did decarboxylate during the reaction with acetic anhydride, then removing samples from the reaction at various time points could determine at which point in the reaction it leaves. Other modifications to the synthesis, such as reflux time and temperature, should be made to find the best reaction parameters for synthesizing this compound.

Purification of the product we did obtain was also a challenge. The small amount of product obtained from the sublimation attempts at least suggests that the compound in question is able to be sublimed. The vacuum pump used was not strong, which may explain the limited results. Future attempts will be made using a third sublimation apparatus as well as a more powerful pump.

If the proposed compound can be made by the alterations listed above, then additional chemistry can be done to further increase solubility and conjugation. The addition of electron donating or withdrawing groups such as nitro and cyano groups, respectively, could help to lower HOMO/LUMO levels and enhance electron currents.

Overall, the success of making anthraquinone-1,8-bisthioglycoliccarboxylic acid (**25**) and the failure to make thiopheneanthrone-1-thioglycoliccarboxylic acid (**17**) shows the difficulty and the variability of organic chemistry, while also providing additional areas for research.

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