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Preparation, Analysis and Derivatization of Benzotris(thiazole) Triamine

Jonathan Patrick Peter Alessi

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Honors Thesis

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Abstract

Multiple fields are areas of active research where organic materials hold considerable promise, such as thermoelectrics or photovoltaics. In an effort to design and prepare a new system which would exhibit a set of promising features such as high thermal stability, high degree of planarity, rigid skeleton and strong electron accepting properties, we have undertaken the preparation and characterization of benzotrithiazole and its derivatives. Our work has led to a reproducible and scalable protocol for the generation of one particular structure: benzo[1,2-d:3,4-d':5,6-d"]tris(thiazole)-2,5,8-triamine. We have also conducted further attempts to functionalize this structure, leading to other derivatives of the target compound.

Dedication or Acknowledgements

I would like to acknowledge Dr. Benin for his support and guidance. Not only could this project never have been realized without him, but also his mentorship extended beyond the lab and classroom, forming my character and person. I would like to thank the Department of Chemistry for my formation as a chemist and its material support for the project. I would also like to acknowledge the Honors Program for their support with the resources and materials for this project. Finally, I would like to thank all my professors, friends and family for their formation and support before and through this project.

UNIVERSITY of DAYTON

Table of Contents

Introduction

There has been a push in recent years toward the use and further development of alternate forms of energy production. Fossil fuels are already seen by many as the way of the past while solar, wind, and nuclear energy are seen as the emerging energy sources of the future. However, in 2015, 81.3% of the total U.S. primary energy consumption came from fossil fuels, showing that fossil fuels are not quite yet the way of the past, like it may appear[1]. Much work and many years remain before fossil fuels are completely phased out of energy production and alternate energy sources take over.

Although wind and solar energy are the first two alternate energy sources that most people think of when they hear alternate energy, both these sources of energy are imperfect in energy delivery. Neither solar nor wind can provide energy continually like the fossil fuels to which we have become accustomed because unlike fossil fuels, the wind and the sun are often fleeting. This is an issue if we plan to power things like emergency rooms through the night during calm weather without the use of fossil fuels. However, it can be solved with the expansion of the pool of alternate forms of energy. With more options for energy than just wind or solar, the problem of non-consistent energy in one source could be solved by simply switching to a second or a third available energy source.

One form of energy production that shows promise is thermoelectric energy production. Thermoelectric energy is produced by taking advantage of the energy stored in temperature differences; when one side of a thermoelectric generator is hot and the other side is cold, current is produced. This is made possible using two different types of

material that are sandwiched between the hot and the cold sides of the generator. One type must have an excess of loosely held electrons while the other type must have an excess of electron holes. These are called, respectively, n-type and p-type materials. This is shown graphically in Figure **1**. We will focus almost exclusively on p-type materials.

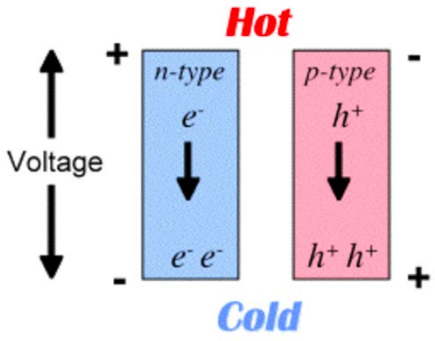


Figure 1: A general visualization of a thermoelectric generator where e^- represents electron movement and h^+ "movement" of electron holes. [2]

The market for p-type materials has been dominated for years by bismuth telluride (Bi_2Te_3, Figure **2**) and other inorganic compounds, but little research has been done on the development and use of organic compounds as p-type materials in thermoelectric cells. It is in order to bolster research into this topic that we have engaged ourselves in an attempt to create benzo[1,2-d:3,4-d':5,6-d"]tris(thiazole) (Compound **2**, Figure **4**), is a good candidate due to its planarity and ability to stack and arrange itself in a way that facilitates the transmission of π-electrons in all directions. This stacking of benzotris(thiazole) molecules, as shown in Figure **3a**, mimics the structure of bismuth telluride (Figure **2**).

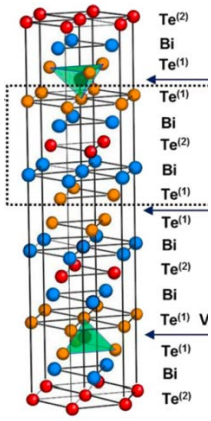
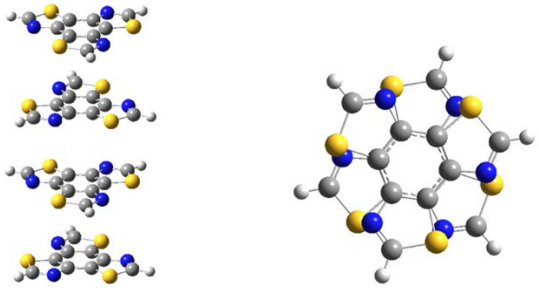


Figure 2: A depiction of the columnar structure of bismuth telluride.[3]



(a) **(b)**

Figure 3: Theoretical calculations done via Gaussian depicting stacking of Benzotris(thiazole) molecules.

This stacking removes the need to align molecules in a certain way that supports the transport of π-electrons across the various molecules, usually done by costly vacuum deposit techniques. This can be achieved using the property of chalcogen-nitrogen heterocycles that allows them to link via sulfur-nitrogen intermolecular contacts (Figure **3b**) at distances significantly shorter than those of the sum of the van der Waals radii.[4]

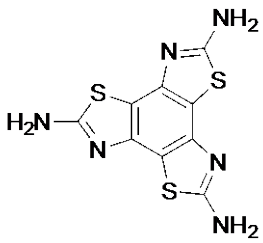
Further, the molecule has been shown to be very well suited to a wide range of applications above and beyond p-type thermoelectric materials. These include plastic

electronics and medicine. It has been shown suited for plastic electronic applications due to the need for electron-deficient π-conjugated semiconducting materials.[4] Many of the current semiconducting π-conjugated materials are electron rich and are not useful in electron transporting. It has been noted that benzobisthiazoles would be good starting materials for these applications due to their high fluorescence, thermal stability, electron affinity, and non-linear optical properties.[5] A benzotris(thiazole) would maintain these properties, and have an even greater ability for electron accepting and electron transporting through the use of an extra, identical substituent on the benzene skeleton.

Benzothiazoles have also been shown to be well suited for the synthesis of medicines. Thiazolidinones have been shown to have antitubercular, anticancer, antibacterial, anticonvulsant, antifungal, antithyroid, and amoebicidal properties. Azetidinones are a class of β-lactam antibiotics that have also been tested as antidepressants, sedatives, and anticancer drugs. Both of these classes of compounds have been synthesized via a pathway containing 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole. Benzotris(thiazole) would most likely exhibit the same properties as its bis(thiazole) brother and create similar compound to the thiazolidinones and azetidinones that might be useful in the same kinds of applications.[6] In order for these to be viable applications of benzotris(thiazole), it is important to show that benzotris(thiazole) can be easily derivatized, especially through important coupling reactions. Many of these coupling reactions require halogenated forms of the compounds, and it has been shown that the corresponding aromatic iodide can be synthesized from 1,3-benzothiazol-2-amine with ~80 percent yield.[7-9] So, it was important that we attempt to create 2,5,8-triiodobenzo[1,2-d:3,4-d':5,6-d"]tris(thiazole) (Compound **3**, Figure **4**). The creation of

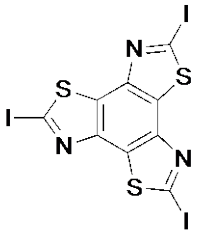
this form would give evidence that our compound would be able to undergo coupling reactions for the creation of anything from medicinal compounds to enhanced benzotris(thiazole) derived thermoelectric materials.

In summary, our research revolves around three basic goals. The first being to synthesize benzo[1,2-d:3,4-d':5,6-d'']tris(thiazole)-2,5,8-triamine (compound **1**, Figure **4**), a benzothiazole compound with potential uses in many different fields. The second is to carry out further functionalization of 1 to the corresponding halogenated derivatives or defunctionalization to the parent benzo[1,2-d:3,4-d':5,6-d'']tris(thiazole) (compound **2**, Figure **4**). Such derivatives, and further structures based on them, are expected to have a range of interesting properties, from anticancer drugs to thermoelectric materials. The third goal is to try to optimize the synthesis, in order to make it more efficient for possible scale-up.



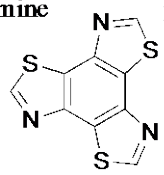
benzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole)-2,5,8-triamine

Compound 1



2,5,8-triiodobenzo[1,2-d:3,4-d':5,6-d'']tris(thiazole)

Compound 3



benzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole)

Compound 2

Figure 4: Structures and names of the three main target compounds of our project.

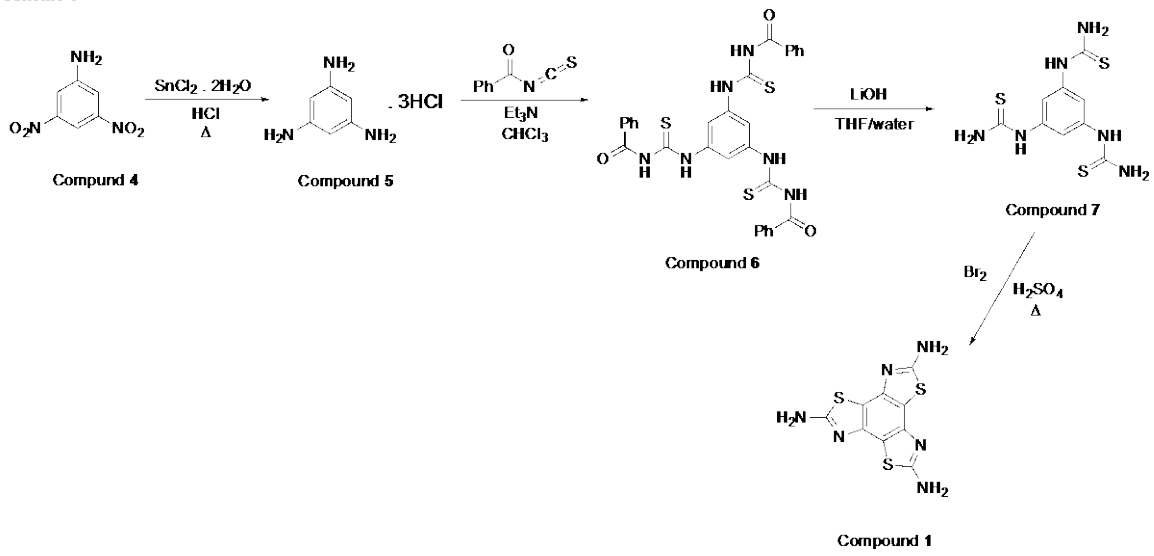
Results and Discussion

This project was split into two parts: 1) The synthesis of benzotris(thiazole) triamine and 2) The derivitizations of benzotris(thiazole) triamine.

Synthesis of Benzotris(thiazole) Triamine

The preparation of Compound **1** requires a multi-step synthesis from simple precursors. The overall synthesis is outlined in Scheme **1**.

Scheme 1



In step 1, 3,5-dinitroaniline, the starting material, is reduced by tin (II) chloride under acidic conditions. This reaction is well-documented and extremely common. However, the product's NMR was done in D_2O and its spectrum is interesting. The spectrum is shown below in Figure **5**.

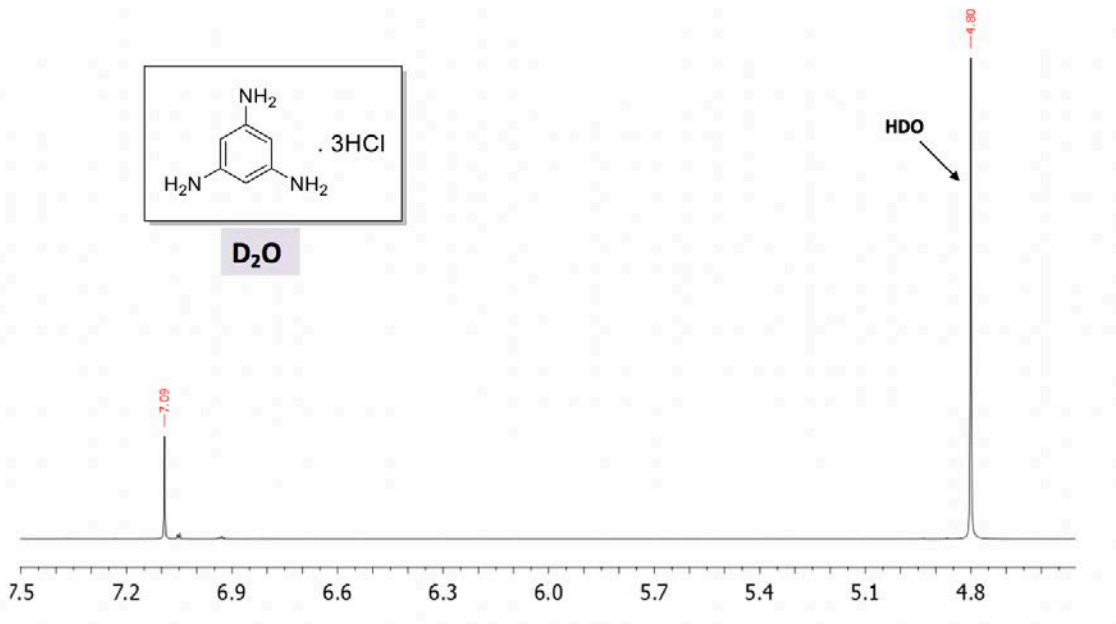
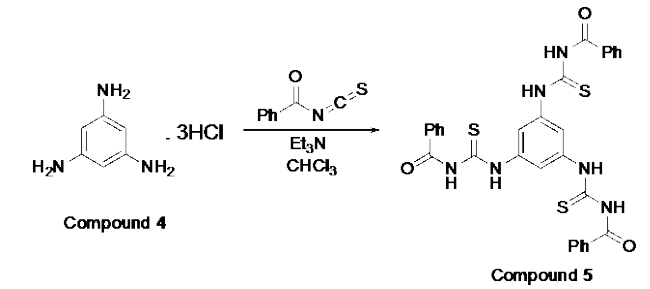


Figure 5: ^{1}H NMR spectrum of the product of Step 1 in the synthesis scheme.

In this NMR, we very clearly see two signals, one representing partially deuterated water, and the other aromatic protons. We do not see any signal for the amine protons. One would normally take this as evidence that what we got in the reaction is not what we wanted, but in this case, the absence of the amine hydrogen signal in D_2O proves that we have what we want. This is because the amines in this compound are in the form of ammonium ions, and each has a positive formal charge, making it acidic. Because of this acidity, the protons in question can exchange with deuterium in the D_2O. It is due to this exchange that the HDO signal in our NMR is large while the amine proton signal is non-existent.

Scheme 2



In the second step of the preparation, the product from the first reaction is reacted with benzoyl isothiocyanate as shown in Scheme **2**. The detailed mechanism for this reaction is reflected in Figure **6**.

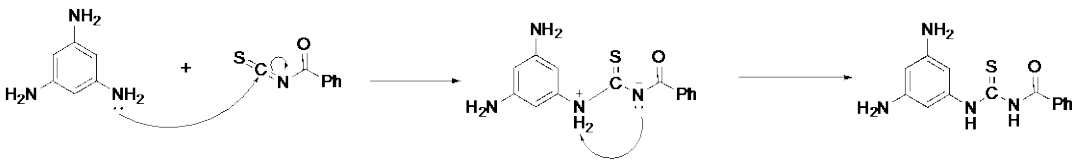


Figure 6: Reaction mechanism for the addition of benzoyl isothiocyante to benzene-1,3,5-triamine.

In this reaction, the isothiocyanate carbon of the benzoyl isothiocyanate undergoes nucleophilic attack by the amine nitrogen of the benzene-1,3,5-triamine. A protonation-deprotonation follows, and the desired structure is formed. The mechanism shown is, of course, only for one of the amino groups and must take place three total times for each molecule of benzene-1,3,5-triamine. Both the proton and the carbon NMR spectra of the product support the conclusion that the reaction occurred as planned. These NMR spectra are shown in Figures **7** & **8**, respectively.

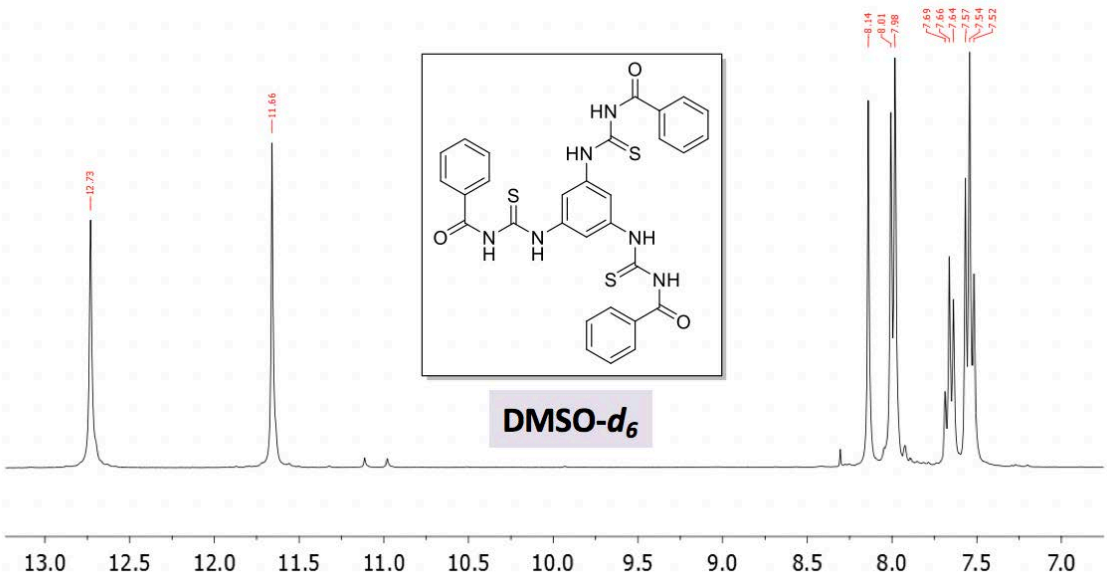


Figure 7: ^{1}H NMR spectrum of the product of Step 2 in the synthesis of benzotris(thiazole) triamine.

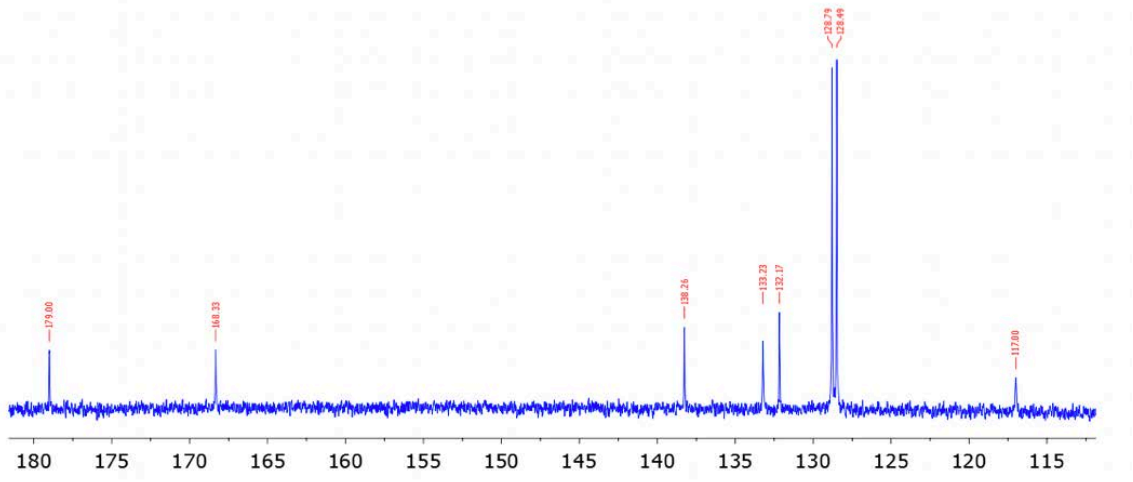
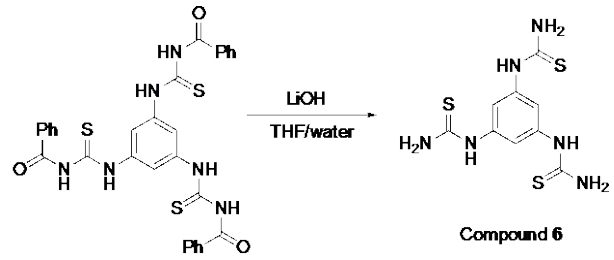


Figure 8: ^{13}C NMR spectrum of the product of Step 2 in the synthesis of benzotris(thiazole) triamine.

Scheme 3



Compound 5

Compound 6

In the third step of the synthesis, shown in Scheme **3**, LiOH is used to hydrolyze the amide C-N bonds. There are two amide-like C-N bonds to which this process could happen in the starting compound. However, because the carbonyl carbon is more electron deficient than the thioamide carbon, the reaction with the carbonyl carbon is favored and the desired thiourea product is attained instead of the reactant in Step 2.

The NMR spectra for the product of this reaction do agree with our expected structure. The carbon NMR is shown in Figure **9** while the proton NMR is shown in Figure **10**. Interestingly though, the NMR shows only two obvious peaks when three would be expected, based on the desired structure. The reason for this has to do with a well-documented feature of amide, and thioamide, C-N bonds. The C-N bond, while formally single bonds, have partial double bond nature. When the partial double-bond nature partially restricts rotation around that bond, the two protons attached to the nitrogen experience different environments, become chemically different, and show in NMR spectra as two separate peaks. This is what would occur at low temperatures. However, at high temperatures, when the rotation barrier around that bond is negligible in relation to the kinetic energy of the molecule, the protons at that position would experience the same environment and would show in NMR spectra as one single peak somewhere in between where the two peaks appeared at lower temperatures.

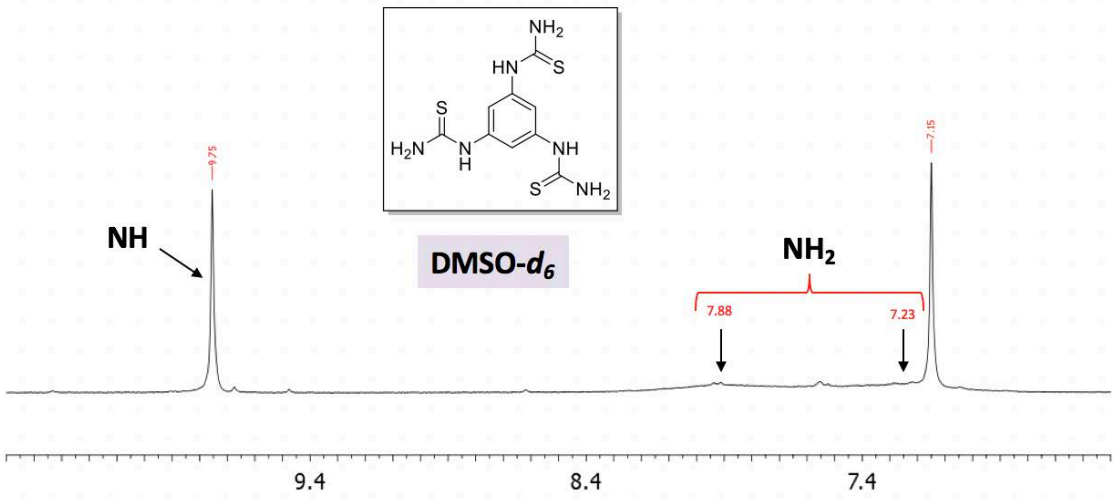


Figure 9: ^{1}H NMR spectrum of the product of Step 3 in the synthesis of benzotris(thiazole) triamine.

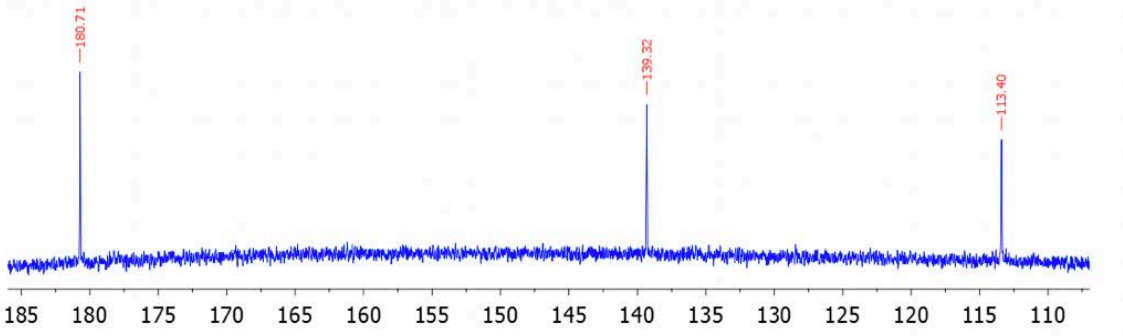
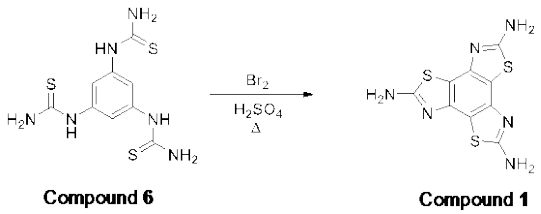


Figure 10: ^{13}C NMR spectrum of the product of Step 3 in the synthesis of benzotris(thiazole) triamine.

Scheme 4



Compound 6 **Compound 1**

In the fourth and last step of the synthesis of Compound **1**, elemental bromine is used to form a bond between the sulfur of the thiourea groups and the adjacent benzene carbon as shown above in Scheme **4**. A proposed mechanism for this reaction is shown

below in Figure **11**.

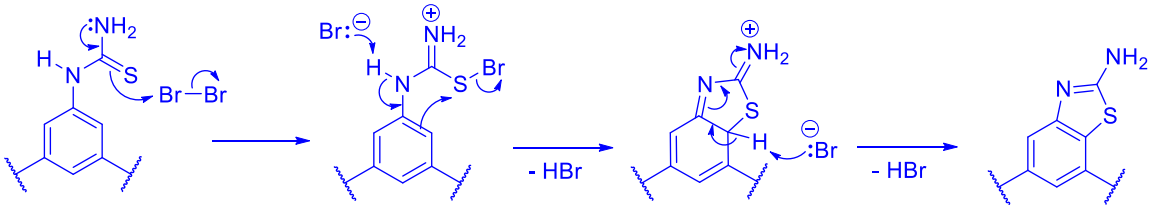


Figure 11: Proposed reaction mechanism for Step 4 in the synthesis of Compound **1**

In this reaction, the elemental bromine first acts as an electrophile, accepting electrons from the thiourea functional group. This is followed by a nucleophilic attack by bromide on the proton of the secondary amide nitrogen, ring closure and the first bromine atom leaving as bromide. Following this, a second bromide atom removes the extra proton on the benzene, and the resulting product is the desired thiazole functional group.

The NMR spectra are shown below. The carbon is shown in Figure **13** and the proton is shown in Figure **12**. Both these spectra align with the proposed structure for the product of this reaction. Based on the proposed structure, there should be three signals in the carbon NMR and only one signal in the proton NMR. That is what is seen in the below spectra.

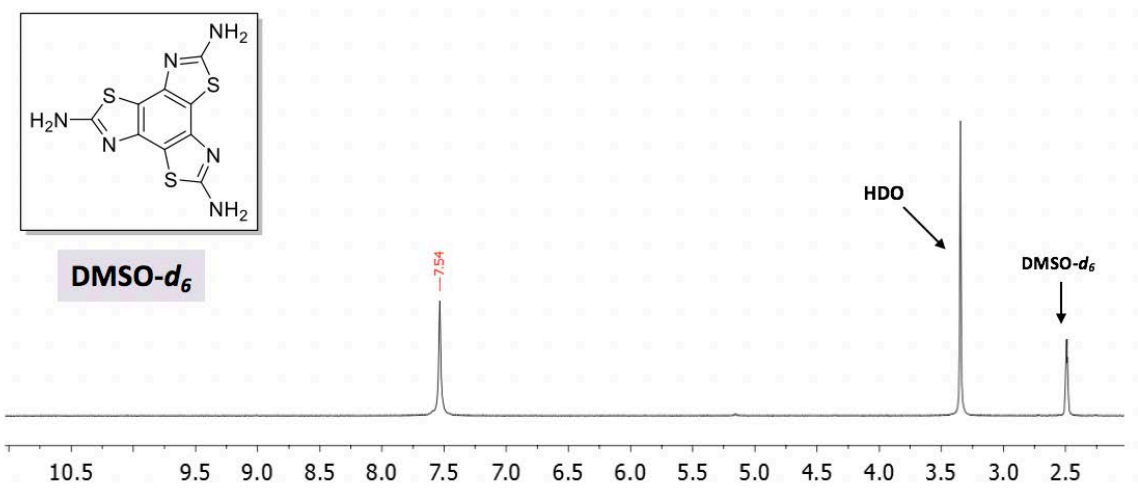


Figure 12: ^{1}H NMR spectrum of Compound **1**.

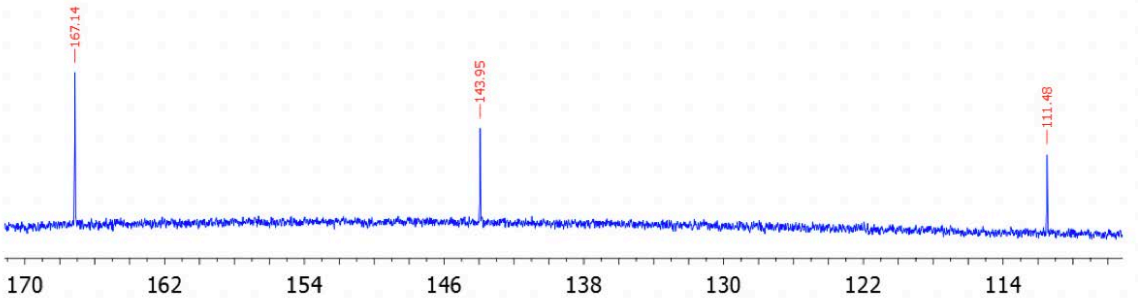


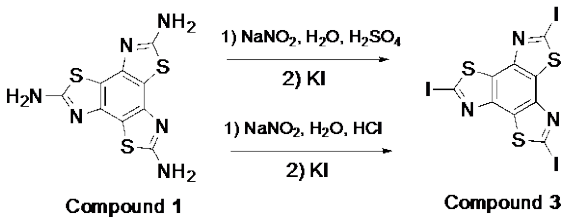
Figure 13: ^{13}C NMR spectrum of Compound **1**.

Reactions of Benzotris(thiazole) Triamine

Three main types of derivatization reactions were attempted: halogenation reactions, Schiff base formation reactions, and acylation reactions. While we believe two of these three types were successful, only one type has been shown to form desired product.

Halogenation

Scheme 5

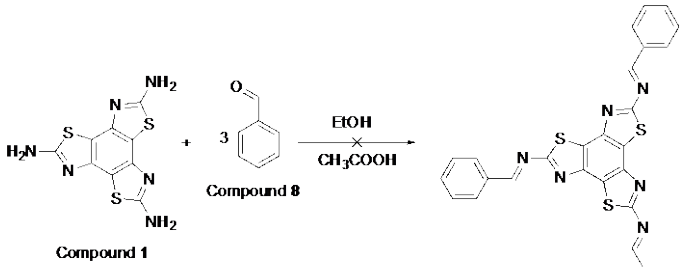


Compound 1 Compound 3

The first derivatization done of benzotris(thiazole) triamine was an attempt at iodination. Any form of halogenation would allow us to generate a structure that would be suitable for the creation of carbon-carbon single bonds, *via* coupling reactions. The reactions shown above in Scheme **5** were performed, but the extreme insolubility of the product made it impossible for us to characterize in the limited time. So, although we believe it is likely that the red solid we retrieved from the reactions is the halogenated derivative given the results of the experiments by Krasnokutskaya, E. A., *et. al.*, we have not been able to run any tests to support this hypothesis.

Schiff Base Formation

Scheme 6

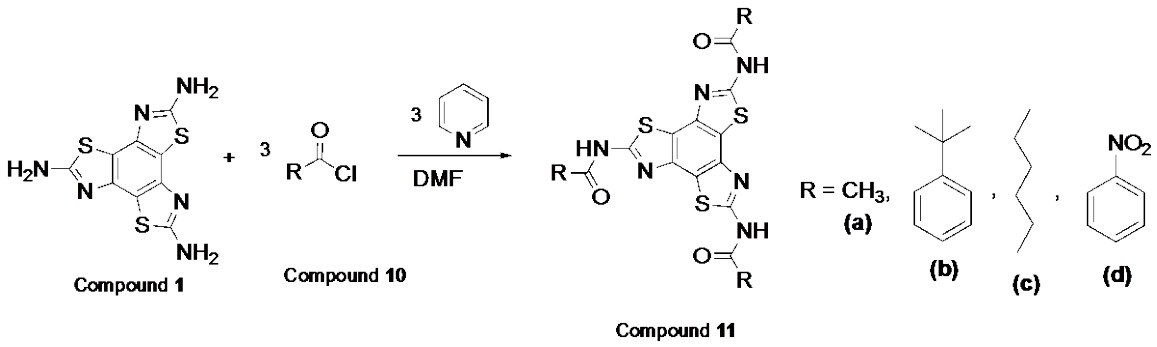


Compound 1 Compound 8 Compound 9

The only Schiff base formation reaction attempted was a reaction with benzaldehyde, shown above in Scheme **6**. The NMR spectrum obtained from the product of this reactant was that of benzotris(thiazole) triamine. We concluded that there was no reaction and that the material recovered was the starting materials.

Acylation

Scheme 7



The final type of derivatization reaction, acylation, was largely a success when done using pyridine as the base. A representative reaction of this type is shown above in Scheme **7**. This reaction occurs via the loss of hydrochloric acid and formation of an amide. Yields for this reaction were generally around 50% and NMR spectra all suggested that we did get the expected material. Reactions of this type were carried out in the hopes of increasing the solubility of the compound we are working with. Compound **1** and many of its derivatives are insoluble in everything but DMSO and DMF. For it to be easier to work with, it is important to make it more soluble in, hopefully, a variety of solvents.

Solubility was the major challenge in this project. DMSO freezes at 18° C and is very difficult to remove via evaporation. This makes it difficult to purify via recrystallization as well as to remove solvent following a reaction. It is increasing the solubility that will be the first challenge for those that continue with this project following my departure.

Experimental Methods

Synthesis of Benzotris(thiazole) Triamine

1,3,5-Triaminobenzene trihydrochloride (5). 3, 5- dinitroaniline (5.00 g, 27.30 mmol) in a 1:1 v/v (250 mL) mixture of ethanol and concentrated HCl was heated to 125° C. Tin (II) Chloride dehydrate (37.8 g, 167.69 mmol) was then added slowly and in portions using a solid addition funnel. This mixture was then allowed to reflux for four hours before being filtered and rinsed with methanol and ether to yield a light grey solid. 2.79 (83%) ^{1}H NMR (D_2O) δ 7.09 (s, 3H)

***N*,*N*',*N*''-((benzene-1,3,5-triyltris(azanediyl))tris(carbonothioyl))tribenzamide (6).**[10] A three-necked round bottom flask equipped with a pressure-equalizing addition funnel was charged with Compound **5** (7.11 g, 30.58 mmol), chloroform (30 mL), and a magnetic stir bar to form a suspension. Benzoyl isothiocyanate (15.00 g, 30.64 mmol) was added to the suspension with an additional 20 mL of chloroform. Then, triethylamine (12.8 mL) was placed in the addition funnel along with 30 mL of chloroform. Both the addition funnel and the flask were purged with nitrogen gas. This was followed by a slow (15-20 min) addition of the triethylamine-chloroform solution to the suspension. The resultant mixture formed a paste initially that then became less viscous as the reaction proceeded. Stirring continued overnight at ambient temperature. The resultant solid was vacuum filtered, suspended in water, stirred for ~15 min, and vacuum filtered again to yield a pale yellow solid. 13.25 g (71%) ^{1}H NMR (DMSO-d_6) δ 7.54 (t, J = 9 Hz, 6H), 7.66 (t, J = 9 Hz, 3H), 8.00 (d, J = 7.3 Hz, 6H), 8.15 (s, 3H), 11.67 (s, 3H), 12.76 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 48.6, 117.0, 128.5, 128.8, 132.2, 133.2, 138.3, 168.3, 179.0

1,1',1''-(benzene-1,3,5-triyl)tris(thiourea) (7)[10] A round bottom flask was charged with Compound **6** (13.15 g, 21.50 mmol) and a THF/water (1:1 v/v, 180 mL) mixture. LiOH (1.56 g, 65.1 mmol) was then added to this solution. Mixture was put under a gentle reflux for five hours. Following the reflux, the solvent was removed under low pressure, and the resulting mixture was cooled in an ice bath for ~10 min. The resultant solid was then vacuum filtered and dried to yield a yellow solid dotted with brown clumps. Recrystallization via water was then performed for further purification. 3.40 g (53%) 195° C ^{1}H NMR (DMSO-d_6) δ 7.15 (s, 3H), 7.23 (bs, 3H), 7.88 (bs, 3H) 9.76 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 113.4, 139.3, 180.7

benzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole)-2,5,8-triamine (1)[6] A round bottom flask, equipped with a stir bar, was charged with 30 mL neat sulfuric acid and heated to 50° C. Compound **(7)** (1.89 g, 6.29 mmol) was then added to the flask and stirred until its dissolution. Elemental bromine (0.945 mL, 0.0189 mol) was added dropwise and reflux and stirring was continued overnight at the same temperature. This solution was then poured over ice and NaOH (aq.) was added until a pH > 12 was reached. The resultant solid was vacuum filtered, suspended in methanol, stirred for ~15 minutes, then vacuum filtered again. Finally, the solid was suspended in water, stirred for ~15 minutes and again filtered. The grey solid was air dried. 1.59 g (86%) ^{1}H NMR (DMSO-d_6) δ 7.54 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 111.5, 143.9, 167.1.

Reactions of Benzotris(thiazole) Triamine

2,5,8-triiodobenzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole) (3) (HCl as medium)[11] A round bottom flask, equipped with a stir bar was charged with 20% HCl (20 mL) and Compound **1** (0.35 g, 11.89 mmol). This mixture was stirred until dissolution of the solid.

The mixture was then cooled in an ice bath to 0° C. Then Sodium nitrite (0.38 g, 55.1 mmol) dissolved in 2.5 mL water was added dropwise to the flask in the ice bath. Foaming was vigorous but was controlled with a few drops of diethyl ether and constant stirring. After the addition of the sodium nitrite, the solution was stirred for an additional 20 minutes before the addition of potassium iodide (0.63 g, 38.0 mmol) dissolved in 20 mL water. This was done at room temperature. The mixture was then heated to 70° C with continued stirring. This solution was then slowly added to a solution of sodium thiosulfate. Following this pH neutralization, the resulting precipitate was vacuum filtered and rinsed with methanol and ether to help with drying. Resultant of this reaction was completely insoluble; NMR could not be run. 1.09 g (141%)

2,5,8-triiodobenzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole) (3) (H_2SO_4 as medium)[7-9] Sodium nitrite (0.49 g, 71.0 mmol) was added to sulfuric acid (5 mL) and the mixture was stirred and heated to 70° C until dissolution of the sodium nitrite. This mixture was then cooled to below 40° C. Once cool, the Compound **1** (0.32 g, 10.9 mmol) was then slowly added to the mixture. The resulting mixture was stirred for two hours until dissolution of the triamine. This solution was then added to a solution of KI (1.056 g in 10mL water) and then heated to 70° C. It was then stirred at 70° C for 15 minutes before being poured into 100mL of water and vacuum filtered to yield a black solid with a dark red tinge. Resultant of this reaction was completely insoluble; NMR could not be run. 0.22 g (30%)

Attempted Preparation of (1*E*,1'*E*,1''*E*)-*N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris(thiazole)-2,5,8-triyl)tris(1-phenylmethanimine) (9) A round bottom flask was charged with Compound **1** (0.30 g, 10.19 mmol) and a 2:1 ethanol-acetic acid mixture

(44 mL). The resultant mixture was then stirred and heated to 80° C. Benzaldehyde (0.33 mL, 32.0 mmol) was then added to the mixture and this mixture was then refluxed at 85° C overnight. The solvent was then removed under low pressure. The resultant paste was then stirred in methylene chloride. This was decanted and stirred in water for 5 minutes, the vacuum filtered to yield a tan solid. ^{1}H NMR (DMSO-d_6) δ 7.54 (s, 6H).

Attempted Preparation of *N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tris(thiazole)-2,5,8-triyl)triacetamide (11a) (triethylyamine as medium) A hot, round bottom flask was charged with Compound **1** (0.30 g, 0.00102 mol), a stir bar, and purged with N_2. Following purging and using a hot syringe and needle, DMF (3 mL) was added to the flask. Then, triethylamine (0.2323 mL, 0.00316 mol) and acetyl chloride (0.274 mL, 0.00316 mol) were added to the mixture in that order. At addition of acetyl chloride, a gas evolved from the mixture. The mixture was stirred and allowed to react at room temperature for an hour before being heated to 50° C and stirred for another hour. It was then vacuum filtered. The material under NMR appeared to be triethylamine derivative.

***N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tris(thiazole)-2,5,8-triyl)triacetamide (11a) (pyridine as medium)** Compound **1** (0.30 g, 0.00102 mol) was added to a hot, round bottom flask that was then purged with N_2 gas. Following this, pyridine (0.26 mL, 0.00316 mol) and acetyl chloride (0.27 mL, 0.00316 mol) were added, in that order. This mixture was left to react at room temperature for an hour. At this point, the mixture had become so pasty and viscous that it arrested the stir bar. It was then heated to 50° C and stirred for another hour. Solvent was then removed under low pressure, and a pasty substance was left. This substance was dispersed in water and stirred overnight. It was

then vacuum filtered, and dried with the help of methanol and ether rinses. 0.18 g (42%) ^{1}H NMR (DMSO-d_6) δ 2.22 (s, 9H), 12.51 (s, 3H)

***N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tris(thiazole)-2,5,8-triyl)tris(4-nitrobenzamide) (11d)** A hot, round bottom flask, equipped with a stir bar, was charged with Compound **1** (0.30 g, .00102 mol) and purged with N_2 gas. Then, DMF (2 mL) was added via hot needle and syringe to the round bottom flask. This was followed by the addition of pyridine (0.26 mL, 0.00316 mol). The 4-nitrobenzoyl chloride (0.587 g, .00316 mol) was first dissolved in DMF (1 mL) and then added to the round bottom flask via hot syringe. The mixture was then left to stir for about an hour at room temperature before being heated to 50° C and stirred for another hour. Solvent was removed under low pressure and the remaining paste was dispersed in water and stirred overnight. This was then vacuum filtered, washed with methanol and ethyl ether, and allowed to dry. 0.37 g (50%) ^{1}H NMR (DMSO-d_6) δ 4.89 (s, 3H), 8.15 (d, J = 7.5 Hz, 2H), 8.33 (d, J = 8.1 Hz, 2H)

***N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tris(thiazole)-2,5,8-triyl)triheptanamide (11c)** A hot, round bottom flask, equipped with a stir bar, was charged with Compound **1** (0.30 g, 0.00102 mol) and purged with N_2 gas. DMF (3 mL) and pyridine (0.26 mL, 0.00316 mol) were then added to the round bottom flask with a hot syringe and needle, followed by heptanoyl chloride (0.49 mL, 0.00316 mol). This mixture was then left stirring at room temperature for an hour before being heated to 50° C and stirred for another hour. Solvent was removed under low pressure. The resultant pasty substance was dispersed in water and stirred overnight. It was then vacuum filtered and dried. 0.47 g (73%)

***N*,*N*',*N*''-(benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tris(thiazole)-2,5,8-triyl)tris(4-(*tert*-butyl)benzamide) (11b)** A hot, round bottom flask, equipped with a stir bar, was charged with Compound **1** (0.30 g, 0.00102 mol) and purged with N_2 gas. DMF (3 mL) and pyridine (0.26 mL, 0.00316 mol) were then added to the round bottom flask with a hot syringe and needle, followed by 4-t-butylbenzoyl chloride (0.62 mL, 0.00316 mol). This mixture was stirred at room temperature for 20 minutes before being heated to 50° C and stirred for an hour. Solvent was removed under low pressure. The resultant material was dispersed in water and left to stir for over 72 hours. It was then vacuum filtered, dried, and weighed. NMR was taken. Recrystallization in mixtures of varying amounts of DMF and 1-propanol was attempted but unsuccessful. 0.83 g (105%) ^{1}H NMR (DMSO-d_6) δ 1.28 (s, 27H), 7.50 (d, J = 8.4 Hz, 6H), 7.87 (d, J = 8.4 Hz, 6H)

Conclusions and Future Directions

- The target structure, benzotris(thiazole) triamine, was successfully prepared via a reproducible 4-step procedure
- Target and intermediate structures were fully characterized using NMR techniques
- Conversion to the iodo-derivative was attempted but the results are currently inconclusive
- N-acylated derivatives were prepared and characterized by ^{1}H NMR. However, solubility did not change dramatically

In the future, focus and emphasis should be on the following:

- Further attempts to enhance compound's solubility
- Characterize the structure through X-ray crystallography
- Produce halogenated derivatives
- Conduct coupling reactions on the halogenated derivatives

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