

Incorporation of Benzothiophenes into Dibenzophosphole Oxide for Potential use in OLED

Displays

Joshua Kim, Conner Schell, Matthew P. Duffy

Southern Adventist University

Abstract:

This research concerns the synthesis of a two novel benzophosphole oxides with the intention for use in OLED displays. The first step, utilizing a Sonogashira reaction to join two benzothiophene molecules together, was successfully completed using 3-bromobenzothiophene. Analogous synthesis with 2-bromobenzothiophene is currently in progress. This allowed for work to begin on subsequent steps of creating the benzophosphole oxide.

Introduction:

Organic light emitting diodes (OLEDs) are a relatively new technology that most people use daily in their phones, smart watches, and other handheld devices. The advent of this display technology has allowed for reduced power consumption and the possibility of flexible displays while improving the quality of colors and contrast of whatever is being displayed. OLEDs work by using multiple thin layers of organic semiconductors which have emissive layers that emit light in the desired color spectra when their electrons are excited and allowed to drop back to the ground state.¹ The molecules used to emit light are constantly being improved on and this research seeks to synthesize a new benzophosphole oxide that could potentially be used as an emitter for OLED displays.

To make the desired benzophosphole oxide a series of reaction is required. The beginning step, a Sonogashira reaction, connects two benzothiophenes with an ethyne to make bisbenzothiophenyl ethyne. Next the product is extracted and reacted with diphenylphosphine oxide to make the benzophosphole oxide. Finally, a new C-C bond will be made between the benzothiophene rings, greatly increasing the conjugation of the aromatic system.

Conner Schell began research in Fall 2022 with 3-bromobenzothiophene. Joshua Kim began research at the same time with 2-bromobenzothiophene but the results revealed that the

Sonagashira product was too unstable to be used in further steps. Consequently, Kim is currently pursuing a similar line of research as Schell using the closely related 2-bromobenzothiophene.

Experimental:

The first step in the synthesis is a Sonogashira-Hagihara coupling reaction that joins the two benzothiophenes with a triple bond using trimethylsilylacetylene (TMSA), a Lewis base (DBU) and in the presence of the catalysts' $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and CuI . This reaction shown in Figure 1 is performed under a nitrogen atmosphere using a Schlenk flask. The first half of the reaction cannot have any water contamination because it will cause the TMSA to decompose into acetylene. The reactants and reagents are combined and dissolved in ~50mL of toluene before being heated in an oil bath to 80°C . The ratio of reactants and reagents used are found in Table 1. The second half of the reaction is started by adding the water (H_2O) to the Schlenk flask after checking that the intermediate was formed using TLC and drawing a vacuum to remove unused TMSA.²

A similar procedure was followed with 2-bromobenzothiophene. TLC at the halfway point clearly showed a new product being formed. However, following the hydrolysis and TMSA removal step, the final TLC did not show the desired product. The reaction was redone at room temperature with the same reactant ratios and amounts. The halfway point TLC appears promising, but the bisbenzothiophenyl ethyne creation has not been confirmed.

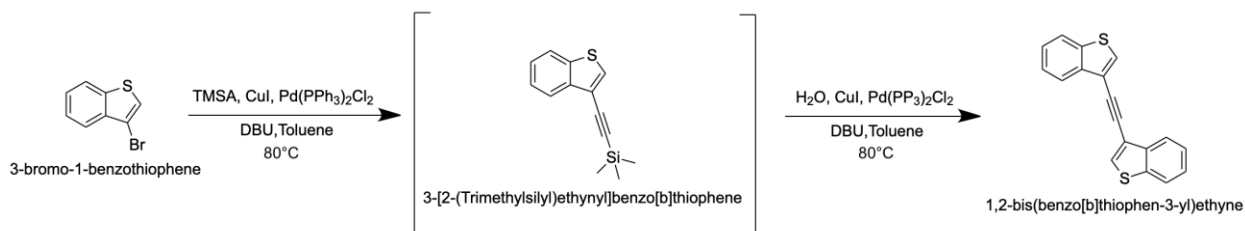


Figure 1: This is a drawing of the reaction being used to create the bisbenzothiophenyl ethyne from the 3-bromothiophene.

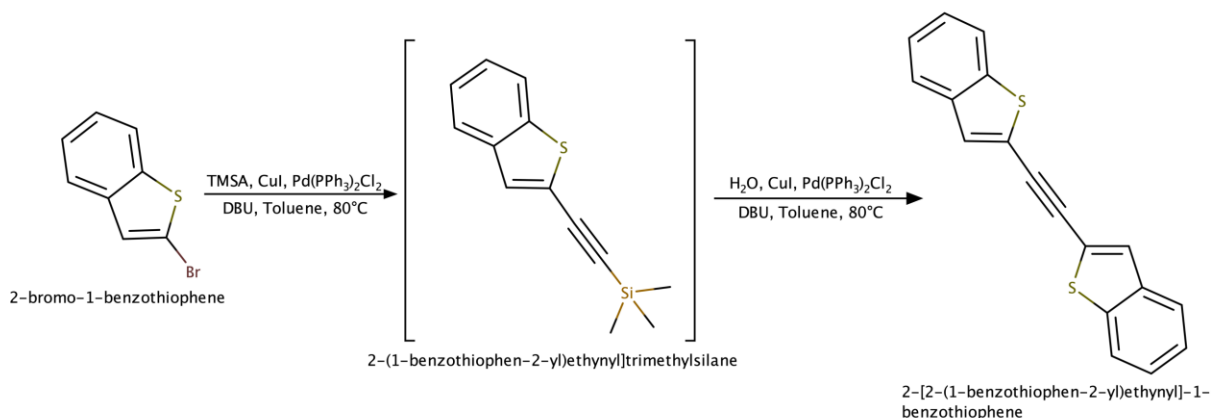


Figure 1: This is a drawing of the reaction being used to create the bisbenzothiophenyl ethyne from the 2-bromothiophene.

Table 1: This table shows the equivalences of reactant/reagent (Rt./Rg.) used and the theoretical amount of product (P.) that should be obtained for the Sonogashira-Hagihara coupling reaction.

Reactant/Reagent/Product (Rt./Rg./P.)	Equivalents (Eq.)
3-bromo-1-benzothiophene (Rt.)	1
TMSA (Rg./Rt.)	1.5
CuI (Rg.)	0.05
Pd(PPh ₃) ₂ Cl ₂ (Rg.)	0.03
DBU (Rg.)	6
1,2-bis(benzo[thiophen-3-yl)ethyne (P.)	0.5

The completion of the reaction is checked by using TLC. The product is then vacuum filtered to remove large particles before being put into a separatory funnel with ethyl acetate and water to wash the product and then gravity filtration is used to remove the rest of the solids. The product was then dry loaded into a silica gel column where it was eluted using increasing ratio DCM to Hexane 1:99, 2:98, 5:95, 10:90, 15:85). Test tubes collected where combined based on TLC's the

were run to determine where there was good separation, and the purest ones were combined and dried using rotary evaporation and then under high vacuum. The yield of the purest product was 43.2%. The less pure product will be rerun in another column to recover more of the product.

The second step of the synthesis starts with the bis-benzothiophenyl ethyne made in the previous step. This product is combined with diphenylphosphine oxide and silver oxide (Ag_2O) before being dissolved into dimethylformamide (DMF) (Figure 2, Table 2).³ This reaction is performed in a Schlenk flask under a dry nitrogen atmosphere. The reaction was run at 110°C for a week. TLC was used to check the reaction and there was still a significant amount of the bis-benzothiophenyl ethyne left. To help the reaction more diphenylphosphine oxide and silver oxide were added before leaving the reaction to run for another week.

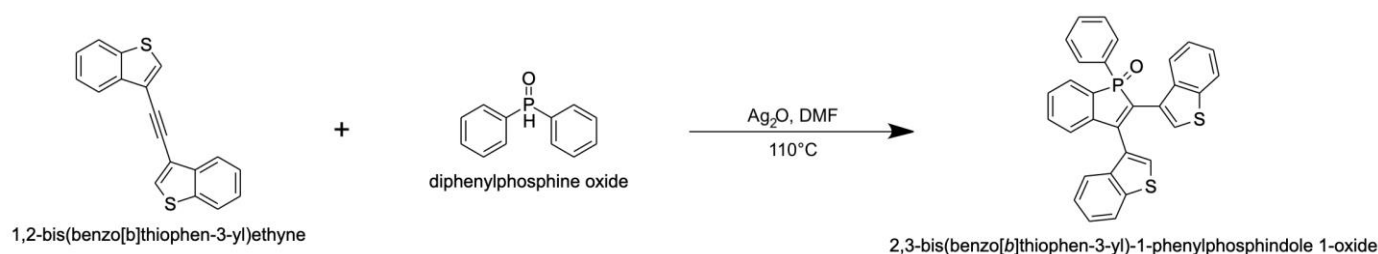


Figure 3: This figure shows the reaction for the second step of the synthesis.

Table 2: This table shows the equivalences of reactant/reagent (Rt./Rg.) used and the theoretical amount of product (P.) that should be obtained for benzophosphole synthesis. The

diphenylphosphine oxide and Ag₂O show a plus half and equivalence because that was added later.

Reactant/Reagent/Product (Rt./Rg./P.)	Equivalences (Eq.)
1,2-bis(benzo[thiophen-3-yl]ethyne (Rt.)	1
Diphenylphosphine oxide (Rt.)	2 + 0.5
Ag ₂ O (Rg.)	2 + 0.5
DMF (Rg.)	226
2,3-bis(benzo[b]thiophen-3-yl)-1-phenylphosphindole 1-oxide (P.)	1

The reaction was checked again using TLC; however, there was still a significant amount of starting material leftover. There was product formed so the reaction was stopped and the mixture was filtered and then washed with water and ethyl acetate to remove the DMF.

Conclusions and Future Work:

Based on the research on other Sonogashira-Hagihara coupling reactions there is likely more product left over in a less pure mixture that will need to be run through a column again to extract more of it. This is because of the yields found in the research articles claim to be significantly higher than the numbers here in this experiment.² The TLC of the first reaction's products showed a secondary product that was formed in small amounts and was fluorescent. In the future this compound could be extracted and characterized. In future research, an effort to increase the yield of the reaction making the benzophosphole could be made by varying the amount of the diphenylphosphine oxide and the silver oxide. Lastly, the final step of making the desired compound will need to be completed Figure 3. This step is the closing of the ring between the two thiophenes to increase the compounds conjugation and thus the wavelength it

fluoresces at. This final molecule is the one that is hoped to be useful in OLED displays.

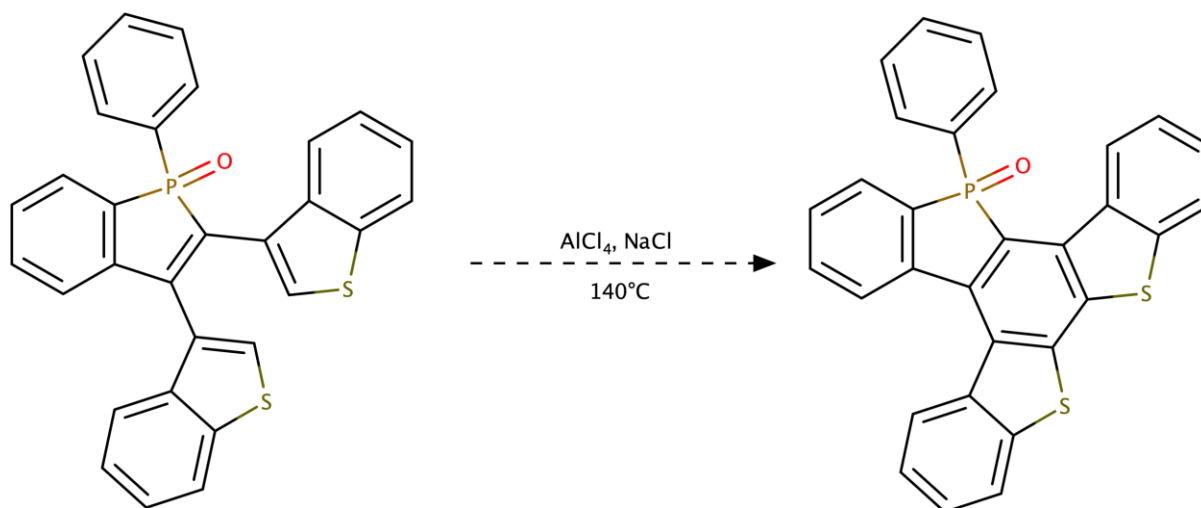


Figure 4: This figure shows the reaction that will close the benzophosphole oxide ring forming the final product for the 3-bromo starting material.

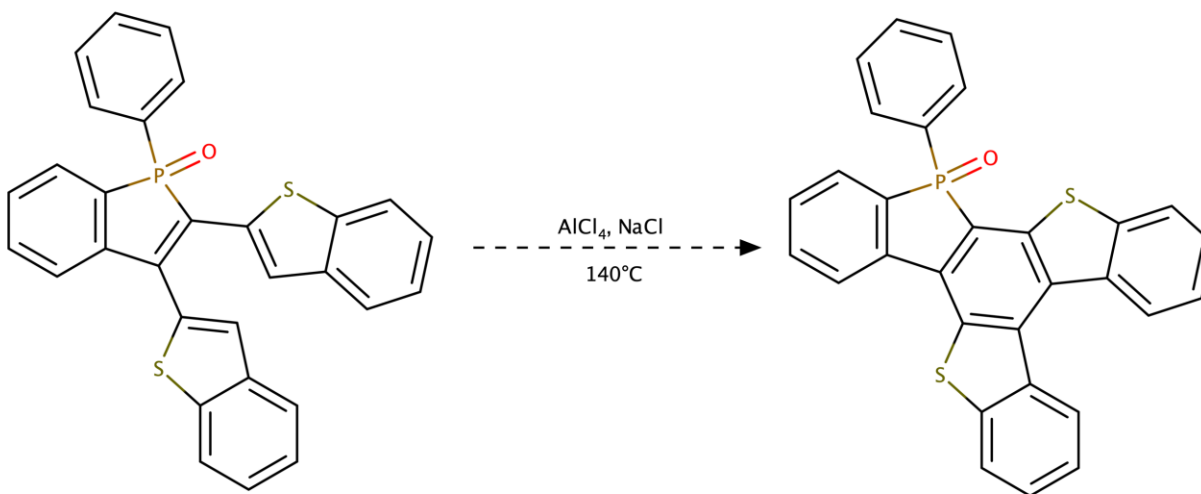


Figure 5: This figure shows the reaction that will close the benzophosphole oxide ring forming the final product for the 2-bromo starting material.

References:

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