

Bottom-Up synthesis of n-doped Polycyclic Aromatic Hydrocarbons

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ABSTRACT: *Polycyclic Aromatic Hydrocarbons, an important class of nanographenes, have been extensively investigated as possible components in organic electronics. As part of a collaboration with the Green Research Group, the synthesis of n-doped polycyclic aromatic hydrocarbons were investigated to quantify the effect of heteroatom doping. Many syntheses were investigated and several n-doped Polycyclic aromatic hydrocarbons were formed, and the synthesis of a new polycyclic aromatic hydrocarbon was investigated.*

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a type of nanographene molecule that have significant applications in OLEDs (organic light-emitting diodes) and OFETs (organic field effect transistors). Unlike graphene nanoribbons, another type of nanographene, bottom-up approaches to synthesizing PAHs are common. Bottom-up syntheses are convenient for PAHs since they allow for modifications to the size, shape, and even the atomic composition of the molecule. Heteroatom doping can easily modify the electronic properties of a PAH, making it a particularly attractive modification technique¹. Nitrogen, for instance, can be used to raise the highest occupied molecular orbital (HOMO) energy level without seriously affecting the lowest unoccupied molecular orbital (LUMO) energy level, providing an easy means of decreasing the HOMO-LUMO energy gap.² This means that these compounds are particularly effective as semiconductors, where a lower HOMO-LUMO energy gap is preferable.³ This warrants further investigation. To test the impact of heteroatom doping on the electronics of PAHs, several PAHs were prepared. Several attempts were also made to form novel PAH structures.

2. Synthesis of Nitrogen-doped PAHs

The following *n*-doped PAHs were targeted: tetrabenzophenazine and tetrapyridophenazine. These were targeted because of a collaboration with the Green Research Group in synthesizing and characterizing these molecules due to the possible greater conductivity and lower band gaps of nitrogen-doped PAHs. *N,N'*-diaryldipyridodihydrophenazines were targeted as a new polycyclic aromatic hydrocarbons.

Scheme 1 depicts the reaction developed by Miyake and coworkers⁴ and was performed to find suitable conditions for *N,N'*-diaryldipyridodihydrophenazines since *N,N'*-diaryldihydrophenazines are very similar due to the phenazine core. Unfortunately, initial attempts to replicate the procedure were unsuccessful. Dihydrophenazine was prepared according to the procedure reported by Miyake and coworkers⁴ and is shown in scheme 2. Scheme 5 and Scheme 6 were designed to produce other potential precursors to *N,N'*-diaryldipyridodihydrophenazines utilizing an alternative methodology. However, the condensation between aniline and 1,10-phenanthroline-5,6-dione

(phenidione) yielded no observed product. We hypothesize the ketone positions of phenidione are not electrophilic enough in character for aniline, which is already a weak nucleophile. Scheme 5 produced trace yield on one of the reactions tested, and Scheme 6 produced trace yield on both of the reactions tested. Scheme 3 and 4 were used to prepare precursors to the formation of tetrabenzophenazine and tetrapyridophenazine, specifically phenanthrene dioxime and phenanthroline dioxime. Through methodology utilized by our lab, these compounds are then reduced to the diamine species before being reacted with the dione analogues to form the target compounds.

3. Experimental Procedure Section

Below are listed the experiments conducted and their procedures.

3.1. Scheme 1 Reaction Procedure and Results

First, the dihydrophenazine (0.27 mmol) was loaded into the glove box. Tri-*tert*-butylphosphine (0.011 mmol) and potassium *tert*-butoxide (1.1 mmol) were added to the vial containing dihydrophenazine. 4-iodosole (1.1 mmol) and palladium (II) acetate (0.011 mmol) were added to an oven-dried 1mL reaction tube. The reaction tube underwent 3 vacuum-nitrogen cycles to purge oxygen from the tube. Anhydrous 1,4-dioxane (1 mL) was added to the vial containing dihydrophenazine and potassium *tert*-butoxide, creating a brown solution. The reaction tube was then placed in a 110 °C oil bath. After 24 hours, the reaction was cooled to room temperature and diluted with 10mL dichloromethane, washed three times with 10mL water and the organic layer was dried with MgSO₄ and concentrated under reduced pressure. Column chromatography was used to purify the compound. Solvent system was 20% CH₂Cl₂ in hexane. A dark green band was observed after polarity was increased to 30% dichloromethane, and a yellow band was observed after the polarity was increased to 100% dichloromethane. All bands were collected. The column was purged with 10% MeOH in CH₂Cl₂. 4-iodosole was found in the initial clear fractions. After checking all of the fractions, only phenazine was found, with no fractions containing the desired product.

3.2. Scheme 2 Reaction Procedure and Results

The ethanol (6 mL) was first purged with an argon balloon for 30 minutes and added to a Schlenk line flask containing $\text{Na}_2\text{S}_2\text{O}_4$ (3.3 mmol) and phenazine (0.28 mmol) under nitrogen. After the reaction was placed in an oil bath for 3 hours and cooled to room temperature, it was filtered using canula filtration under nitrogen. Light green flecks were observed after washing excess $\text{Na}_2\text{S}_2\text{O}_4$ with degassed water. The resulting solid (0.14 mmol, 50%) was dried overnight under vacuum.

3.3. Scheme 3 Reaction Procedure and Results

To a 100mL reaction flask, the 9,10-Phenanthrenequinone (2.4 mmol), NH_3OHCl (18.5 mmol), and a stir bar were added (9,10-Phenanthrenequinone is a fine powder, so care should be taken when transferring). Ethanol (25 mL) was added to dissolve the solids in the flask, yielding an orange solution (To dissolve the solids, the flask was heated with a heat gun while stirring, and was equipped with a waterless condenser). 1.5mL of pyridine (12 mmol) was added, causing the solution to turn green. The flask was then stirred while heated in an oil bath for 30 minutes. A TLC was taken, showing bands at $\text{RF}=0.5$ and $\text{RF}=0.9$. After another 90 minutes, the reaction was cooled to room temperature, and the ethanol was removed under reduced pressure, leaving a green oil. This was poured into a water-methanol bath where a yellow-green solid precipitated. This solid was filtered using a frit funnel and dried under vacuum, affording a yellow solid (357 mg, or 63%).

3.4. Scheme 4 Reaction Procedure and Results

To a three-necked round-bottomed flask, 1,10-Phenanthroline-5,6-Dione (2.38 mmol) was dissolved in 15mL ethanol. The solution was yellow. Na_2CO_3 (3.92 mmol) and a stir bar were added and the solution was stirred at 90 degrees Celsius. During the stirring, a solution of 35mL ethanol with NH_3OHCl (9.12 mmol) was slowly added, yielding a green solution with black flecks. After 5 hours, the reaction was cooled to room temperature. Yellow precipitate and solution were decanted into a 250mL round-bottomed flask to prevent the desired product from mixing with a grainy, black solid that had formed at the bottom of the flask. The ethanol was removed under reduced pressure to produce a yellow solid. The solid was removed from the flask by sonicating it with 20mL of water and was then filtered with a frit funnel. Further washing with THF yielded a pale, yellow solid that was transferred to a tared vial and placed in a vacuum oven at 50 degrees Celsius overnight (328 mg, 58%).

Cotton and MgSO_4 were added to two Pasteur pipettes. 33 μL Octyl aniline (0.141 mmol) and 22 μL tert-butyl aniline (0.141 mmol) were added to the tops of the two pipettes to be dehydrated and were added to reaction tubes. They were then transferred to two more flame-dried reaction tubes containing 1,10-phenanthroline 5,6-dione (0.047 mmol). 59 μL anhydrous Et_3N (0.423 mmol) was added to each tube after 1 mL anhydrous toluene was also added to each tube. 3 freeze-pump-thaw cycles were used to remove oxygen. Reactions were stirred for 24 hours at room temperature. A brown solid filtered out of both reactions, and the liquid layer and solvent were removed under reduced pressure. The reaction using the tert-butyl group as R had a trace

yield, and using the octyl group as R showed no observed product.

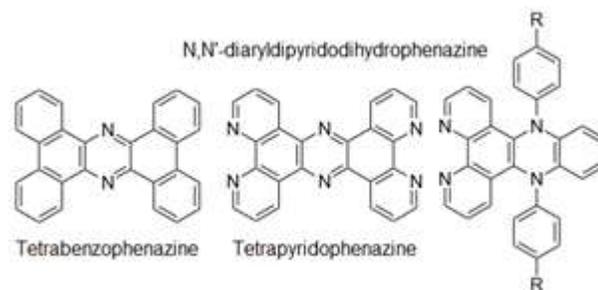
3.6. Scheme 6 Reaction Procedure and Results

1,10-Phenanthroline-5,6-Dione (0.75 mmol) was added to two tubes, followed by 0.34 mL of octyl aniline (1.5 mmol), and 0.05 mL H_2SO_4 was added to one of the tubes. $\text{Si}(\text{OEt})_4$ (2.25 mmol) was added to a 25 mL round-bottomed flask which was then then filled with argon gas and sonicated. The two tubes were filled with N_2 gas and 0.5 mL $\text{Si}(\text{OMe})_4$ was added to each one, then stirred for 24 hours at 150 °C. The reaction was then cooled to room temperature, diluted with ether, and washed with water twice. Trace yield was found on both reactions.

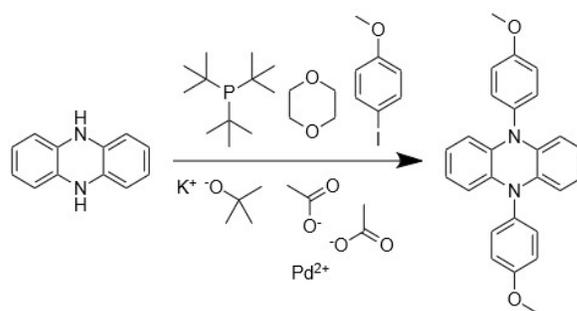
4. Conclusion

While reasonable yields were only attained on the immediate precursors to tetrabenzophenazine and tetrapyrrophenazine, these compounds can now be characterized. Several precursors to form N,N'-diaryldipyridodihydrophenazines were also made, but future work is needed to refine the techniques used to synthesize the precursors and synthesize N,N'-diaryldipyridodihydrophenazines.

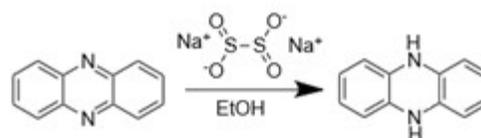
Figure 1. Target Molecules



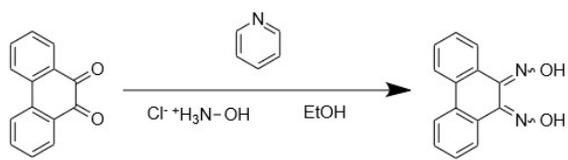
Scheme 1



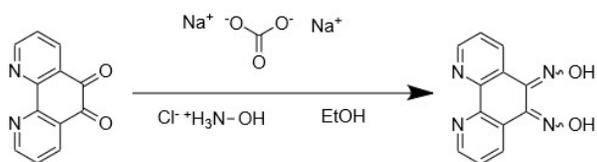
Scheme 2



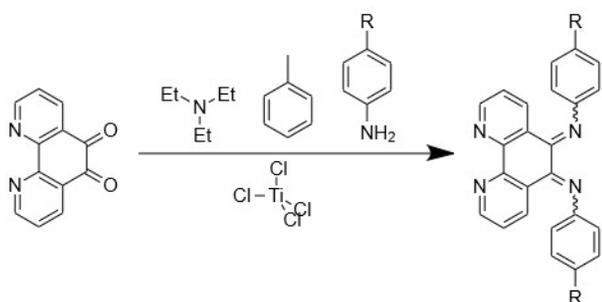
Scheme 3



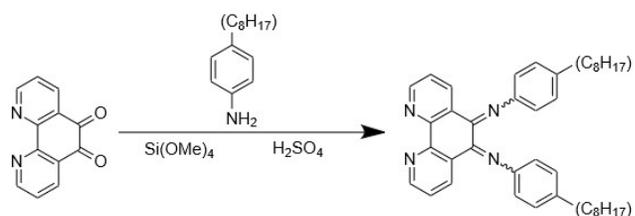
Scheme 4



Scheme 5



Scheme 6



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- ⁴ Theriot, C.; Lim, C.; Yang, H.; Ryan, M.; Musgrave, C.; Miyake, G. *Science* **2016**, *352*, 1082-1086