SYNTHESIS OF A TRIPLE-DECKER \( \pi \)-CONJUGATED SYSTEM

TO STUDY CHARGE MIGRATION IN ORGANIC SEMICONDUCTORS

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ABSTRACT

Closely stacked π-systems exhibit physical properties that are a consequence of π- π interactions. The primary focus of this study is the production of a triple-decker π-conjugated system. Although many studies have investigated the use of para and meta-cyclophanes, research on ortho-cyclophanes in which arene rings are held in a stacked arrangement has been limited. This thesis describes a synthesis of the scaffold to hold conjugated units together. Ultimately, the stacked analog will be obtained by ketalization of a bicyclic ketone with ethylene glycol to lock the bicyclic core into a chair-chair conformation in which oligo(phenylene ethynylene)s are stacked atop one another. The optical properties of the stacked compound will be studied using UV-Vis and fluorescence spectroscopy. The electrochemical properties of the stacked compounds will be characterized using cyclic voltametry (CV) and differential pulse voltammetry (DPV).
CHAPTER 1

INTRODUCTION

Until the 1970s, polymer materials were believed to be suitable mostly as insulators. Since the discovery of semiconducting polymers in 1977, there has been interest in developing these types of materials for their electronic properties. Modification of the structure of conducting polymers presents the possibility of preparing novel materials for applications such as LEDs, solar cells, and molecular wires. Conductivity of these polymers is a result of conjugation arising from the overlap of p orbitals along the chain. The electrons in delocalized molecular orbitals are mobile. Neutral polymers are often semiconducting, and oxidation or reduction may lead to the formation of conducting materials.

There is a great deal of interest in the properties of closely stacked π-systems. These systems exhibit different chemical and physical properties compared to their unstacked analog due to their π-π through-space interactions. The movement of charge carriers along a linear conjugated chain does not fully describe conduction in the solid state and stacked oligomers may be viewed as well-defined molecular analogues of segments of closely packed conjugated chains.

Connection of conjugated oligomeric units to a scaffold may allow for the control of the proximity and orientation of these systems. The ability to tailor the structure would allow for examination of the interaction of conjugated chains on their properties. This would provide insights into the nature of charge transport in conjugated organic materials.
Most molecules in which arenes are stacked on top of one another are composed of cyclophane units. Meta- and paracyclophanes generally adopt a face-to-face arrangement in which the rings are held in short distance from each other. Orthocyclophanes generally offer more flexibility and usually adopt an unstacked conformation. However, an appropriate bridging scaffold may be prepared to provide a stacked π-system. This approach is a relatively simple way to prepare multilayered orthocyclophanes, which may allow for the examination of through-space π-π interactions.

Although benzene itself undergoes oxidation at a fairly high potential and forms poorly defined polymers (Dietrich 1986), previously synthesized stacked analogues undergo oxidation to the radical cation and dication at relatively low potentials (Knoblock 2006). The through-space interactions of stacked π-systems may be studied by UV-Vis spectroscopy (Cram 1959). Examples of such compounds are oligothiophenes (Knoblock 2006), thieno[3.3]orthocyclophanes (Thiemann 1999), and benzo-annelated bicyclo[4.4.1]undecanes (Mataka 1998).
CHAPTER 2

PROJECT GOALS

This study focuses on the synthesis and characterization of a triple-decker compound similar to one synthesized by Mataka in 1996. Mataka developed a triple-stacked analogue of anti-benzo[1,2-h;4,5-h’]bis(benzo[1,2-c]bicyclo[4.4.1]undeca-3,8-diene-11one, which has three benzeno rings held on top of each other. Here, we propose to extend this system by adding conjugated substituents to the top and bottom aromatic rings, as shown in Figure 2.

![Figure 1: Triple-decker conjugated system characterized by Mataka (1996)](image1.png)

![Figure 2: Target compound](image2.png)
The development and characterization of this model will require techniques from synthetic chemistry, electrochemistry, and spectroscopy. The synthetic pathway is similar to that of Mataka, and involves 9 steps.
CHAPTER 3
SYNTHESIS

DIETHYL 4,5-DIMETHYLCYCLOHEXA-1,4-DIENE-1,2-DICARBOXYLATE

Diethyl acetylenedicarboxylate (147 mmol, 25.0 g) was combined with 2,3-dimethyl-1,2-butadiene (176 mmol, 14.8 g) in ethanol (150 mL). The mixture was heated at reflux for 24 h. The solution was cooled and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography (10% ethyl acetate / 90% hexane as solvent) to yield the product as a yellow, oily liquid. $^1$H NMR (300 Hz, CDCl$_3$): $\delta$ 4.1 (q, $J$ = 7 Hz, 4H, ester CH$_2$), 2.78 (s, 4H, cyclic-CH$_2$), 1.53 (s, 6H, cyclic-CH$_3$), 1.18 (t, $J$ = 6 Hz, 6H, ester CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.5 (carbonyl), 132.2, 121.2 (cyclic alkene), 60.6 (ester CH$_2$), 33.8 (cyclic-CH$_2$), 17.5 (cyclic-CH$_3$), 13.6 (ester CH$_3$). IR (KBr): 2980, 2934, 2905, 2864, 1716, 1661, 1219, 1067, 1025, 765 cm$^{-1}$. MS (EI), m/z (%) = 252.1 (M$^+$, 4), 206.1 (75), 191.1 (50), 163.0 (100), 133.1 (25).
A solution of 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylic acid diethyl ester (36.6 g, 142 mmol) in benzene (500 mL) was stirred for 10 minutes. DDQ (36.4 g, 156 mmol) was added slowly to the mixture. The mixture was then stirred for 24 h at room temperature, diluted with ethyl acetate (200 mL), and washed with 10% aqueous NaOH solution (100 mL). The solvent was removed under reduced pressure and the organic residue was subjected to flash column chromatography to yield the title compound as a clear yellow colored oil (34.0 g, 93%). $^1$H NMR (300 Hz, CDCl$_3$): $\delta$ 7.44 (s, 2H, Ar-H), 4.30 (q, $J$ = 9 Hz, 4H, ester CH$_2$), 2.26 (s, 6H, Ar-CH$_3$), 1.31 (t, $J$ = 6 Hz, 6H, ester CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 167.5 (carbonyl), 139.8, 129.8, 129.6 (Ar-C), 61.1 (ester CH$_2$), 19.3 (Ar-CH$_3$), 13.9 (ester CH$_3$). IR (KBr): 2977, 2360, 2338, 1721, 1368, 1294, 1131, 1035, 1027 cm$^{-1}$. MS (EI), m/z (%) = 250.0 (M$^+$, 16), 205.1 (42), 177.01 (100), 133.0 (5). HRMS calculated for C$_{14}$H$_{18}$O$_4$, 250.12051; Found, 250.12064, $\Delta$ = -0.5 ppm.
(4,5-DIMETHYL-1,2-PHENYLENE)DIMETHANOL

NaBH$_4$ (20.0 g, 0.529 mol) was added to a solution of diethyl 4,5-dimethyl phthalate (10.0 g, 40.0 mmol) in dry THF (150 mL) and the mixture was heated at reflux for 24 h. Methanol (150 mL) was then added dropwise over 15 min. After 18 h of stirring at room temperature, the reaction was cooled to 0 °C and saturated NH$_4$Cl solution (100 mL) was added dropwise over 45 min. The organic layer was separated and the aqueous portion was extracted with CH$_2$Cl$_2$ (3 x 50 mL). The combined organic layers were washed with H$_2$O (100 mL), and the solvent was removed under reduced pressure to afford the title compound as a white solid (18.5 g, 92%) $^1$H NMR (300 Hz, CDCl$_3$): $\delta$ 7.08 (s, 2H, Ar-H), 4.60 (s, 4H, benzylic), 2.23 (s, 6H, Ar-CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 136.8, 134.2, 131.3 (Ar-C), 63.9 (benzylic), 19.3 (Ar-CH$_3$). IR (KBr): 2977, 2971, 1466, 1366, 1268, 1260, 1098, 1031, 1014, 901, 766, 745 cm$^{-1}$. 
Phosphorus tribromide (4.20 mL, 44.4 mmol) was added dropwise to the solution of 1,2-bis(hydroxymethyl)-4,5-dimethylbenzene (4.80 g, 29.6 mmol) in Et$_2$O (150 mL). After complete dissolution of all the solids, the solution was heated to reflux for 24 h. The resulting mixture was poured onto crushed ice (200 g). The organic layer was extracted with Et$_2$O (2 x 100 mL). The combined organic layers were dried over MgSO$_4$, the solvent was removed under reduced pressure to afford 1,2-bis(bromomethyl)-4,5-dimethylbenzene as a white crystalline solid (6.5 g, 76%). $^1$H NMR (300 Hz, CDCl$_3$): $\delta$ 7.10-7.15 (s, 2H, Ar-H), 4.60-4.65 (s, 4H, benzylic), 2.20-2.30 (s, 6H, Ar-CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 138.1, 133.7, 132.3 (Ar-C), 30.3 (benzylic), 19.3 (Ar-CH$_3$). IR (KBr): 3050, 3046, 2759, 2652, 1520, 1261, 1111, 1084, 947, 778 cm$^{-1}$. MS (EI), m/z (%) = 289.9 (M$^+$, 9), 211.1 (M$^+$-Br, 75), 132.1 (M$^+$-2Br, 100). HRMS (EI), m/z = Calcd. For C$_{10}$H$_{12}$Br$_2$, 289.93057; Found, 289.93327, $\Delta = 9.3$ ppm.
Compound 4 (6.00 g, 120 mmol) and dimethyl acetone-1,3-dicarboxylate (7.00 g, 41.1 mmol) in CH₂Cl₂ (28.0 mL) were added dropwise to a mixture of tetrabutylammonium bromide (4.00 g, 12.24 mmol) and sodium bicarbonate (5% aqueous solution, 170 mL) in CH₂Cl₂ (60.0 mL). The mixture was stirred at room temperature for 30 h under argon. CH₂Cl₂ (200 mL) and H₂O (200 mL) were added and the organic layer was separated and dried with MgSO₄. The solvent was removed under reduced pressure, and a white powder was obtained. The product was recrystallized from methanol to yield the title compound as a white, free-flowing powder (4.81 g, 80.8%). ¹H NMR (300 Hz, CDCl₃): δ 7.10 (s, 2H, Ar-H), 3.72 (doublet, J = 15 Hz, 6H, O-CH₃), 3.51 (doublet, J = 4.5 Hz, 2H, C-H), 3.12 (t, J = 4 Hz, 4H, Ar-CH₂), 2.12 (d, 6H, Ar-CH₃).
A solution of Bu₄NBr (1.14 g, 3.53 mmol), NaOH (23% wt/vol, 48.5 mL), and CH₂Cl₂ (48.5 mL) was stirred vigorously. To this mixture, a solution of diester 5 (4.81 g, 18.3 mmol) and 1,2,4,5-tetrakis(bromomethyl)benzene (3.56 g, 7.91 mmol) in CH₂Cl₂ (100 mL) was added dropwise over 30 min. The solution was stirred vigorously for 24 h. Additional CH₂Cl₂ (100 mL) and H₂O (100 mL) were added, and the organic layer was separated and dried with MgSO₄. The solvent was removed under reduced pressure to yield a white powder. Methanol was added to the product, and a free flowing powder containing syn and anti diketones was precipitated and filtered from the solution. The two diastereomers were separated by column chromatography (5% EtOAc / 95% CH₂Cl₂), and the title compound was obtained as a white solid (6.55 g, 54%). ¹H NMR (300 Hz, CDCl₃): δ 7.10 (s, 2H, central ring Ar-H), 7.05 (s, 4H, flanking rings Ar-H), 3.46 (s, 12H, O-CH₃), 6.81 (s, 4H, Ar-H), 2.78 (m, 6H, Ar-CH₂), 2.27 (s, 12H, Ar-CH₃)
A solution of tetraester 6 (2.00 g, 2.72 mmol), potassium hydroxide (3.00 g, 53.5 mmol), ethanol (100 mL), and H₂O (100 mL) was heated at reflux for 24 h. The solution was acidified with 1:1 H₂O/HCl to pH ~3.5 and stirred for an additional 24 h. The product was then gravity filtered and washed with acetone (1.00 g, 5.42%). ¹H NMR (300 Hz, acetone-d₆): δ 6.98 (s, 2H, Ar-H), 6.81 (s, 4H, Ar-H), 2.78 (m, 6H, Ar-CH₂), 2.29 (s, 12H, Ar-CH₃)
DIKETONE 8

Tetraacid 7 (100 mg, 0.147 mmol) was heated to 300 °C with a heat gun for 45 min to produce a needle-like product. The solids were then dissolved in ~25 mL of CH₂Cl₂ and the solution was passed through a silica plug. The solvent was removed under reduced pressure to obtained light yellow solids as the title compound (420 mg, 56.7%). ¹H NMR (300 Hz, CDCl₃): δ 7.25 (s, 2H, Ar-H), 6.81 (s, 4H, Ar-H), 3.00-3.15 (m, 4H, Ar-CH₂), 2.78 (m, 6H, Ar-CH₂), 2.10 (s, 12H, Ar-CH₃)
Diketone 8 (100 mg, 0.190 mmol) was combined with mercury(II) trifluoromethanesulfonate (0.690 g, 1.38 mmol) and iodine (0.349 g, 1.38 mmol) in chloroform (18.0 mL). The mixture was stirred at room temperature for 24 h. Additional chloroform (50.0 mL) was added, and the resulting solution was washed with sodium thiosulfate (5.00 g in 50 mL). The organic layer was dried with MgSO₄, and solvent was removed under reduced pressure. Additional exposures of the residue to iodine may be needed if iodination is not completed.
CHAPTER 4

RESULTS AND DISCUSSION

\[ \text{CHAPTER 4} \]

\[ \text{RESULTS AND DISCUSSION} \]

\[ \begin{align*}
\text{4} & \quad \text{PBr}_3, \text{Et}_2\text{O}, \text{heat, 24h} \\
\text{3} & \quad \text{NaBH}_4, \text{MeOH, THF, heat, 24h} \\
\text{2} & \quad \text{DDQ, benzene 24h} \\
\text{1} & \quad \text{EtOH, heat, 24h}
\end{align*} \]
A Diels-Alder reaction was performed between diethylacetylenedicarboxylate and 2,3-dimethyl-1,2-butadiene to yield diethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (1). This compound was then dehydrogenated with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) to produce diethyl 4,5-dimethylphthalate (2). Treatment of diester 2 with sodium borohydride resulted in a reduction to yield (4,5-dimethyl-1,2-phenylene)dimethanol (3). This compound was subjected to bromination with PBr₃ to yield 1,2-bis(bromomethyl)-4,5-dimethylbenzene (4). The brominated intermediate was alkylated using dimethyl acetone-1,3-dicarboxylate in the presence of tetrabutylammonium bromide to produce dimethyl 6,7,8,9-tetrahydro-5H-benzo[7]annulene-6,8-dicarboxylate (5). The dicarboxylate compound was then treated with 0.5 molar equivalents of 1,2,4,5-tetrakis(bromomethyl)benzene in the presence of tetrabutyl ammonium bromide to yield the polycyclic diketone 6. The esters of 6 underwent saponification with 10% potassium hydroxide to produce diacid 7. The compound was decarboxylated by heating to 300 °C, and then iodinated with mercury(II) trifluoromethanesulfonate and iodine. Complete iodination of this compound was not achieved, as is shown by the ¹H NMR spectrum found in Appendix A. A second exposure to the mercury triflate and iodine reagents was not successful, with the ¹H NMR spectrum suggesting a loss of product.
CHAPTER 5

FUTURE WORK

The last two steps of the synthesis are: (I) attachment of the phenylacetylene arms, and (II) ketalization with ethylene glycol.

These steps, which have yet to be completed, are the starting points for any future work. In addition, once the triple-decker compound is obtained, it must be characterized. Characterization of this compound includes $^1$H and $^{13}$C NMR, infrared spectroscopy, mass spectrometry, and voltammetric studies (DPV and LSV).
REFERENCES


APPENDIX

$	ext{EtO} - \text{O} - \text{OEt}$

$^1$HNMR spectrum of Compound 1 (300 Hz, CDCl$_3$) (NMR taken by Subodh Jagtap)
$^1$HNMR spectrum of Compound 2 (300 Hz, CDCl$_3$) (NMR taken by Subodh Jagtap)
$^1$H NMR spectrum of Compound 3 (300 Hz, CDCl$_3$)
$^1$H NMR spectrum of Compound 4 (300 Hz, CDCl$_3$)
$^1$H NMR spectrum of Compound 5 (300 Hz, CDCl$_3$) (NMR taken by Subodh Jagtap)
$^1$H NMR of Compound 6 taken at 60°C (CDCl$_3$, 300Hz)
$^1$H NMR of Compound 6 taken at room temperature (CDCl$_3$, 300Hz)
$^1$H NMR of Compound 7 (d-acetone, 300Hz) (NMR taken by Subodh Jagtap)
$^1$H NMR of Compound 8 (d-acetone, 300Hz)
$^1$H NMR of Compound 9 (CDCl$_3$, 300Hz)