Synthetic Study of para-Substituted 5,6-Fused Ring Pyridazines

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Synthetic Study of para-Substituted 5,6-Fused Ring Pyridazines

Presented in Fulfillment of the Requirements for Honors College Graduate Distinction at Western Kentucky University

By
Justin Mobley

*****

Western Kentucky University
2010

CE/T Committee:
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Approved by
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Department of Chemistry
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ABSTRACT

Much of the focus in organic chemistry today is in area of green chemistry. With such large amounts of attention being paid to how do we create a more sustainable world, the focus has been to come up with new ways to not only create energy but to conserve energy and use recyclable products. One possible solution is through the use of organic and organometallic semiconductors. Due to their structural nature, organic semiconductors show similar conducting potential to that of metals such as copper with the potential to be more durable and more efficient. This project focuses strictly on the synthesis and characterization of pyridazines and fulvenes that have shown promise in this field of organic conducting materials. Future applications could be in the electronics industry for components such as OLEDs, OTFTs, and RF-IDs. Due to the fact, that these molecules are air stable and can be synthesized at room temperature they also show the promise of low cost of production, making them well suited for commercial fabrication.

Keywords: Pyridazine, Fulvene, Green Chemistry, Organometallic Semiconductors, Organic Semiconductors
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PUBLICATIONS

   Phillips*, C. L.; Preston, A. Z.; Strain*, J. M.; Vanover*, E. S.; Starling*, M. P.;
   Sahl*, N. V.; Bunnell*, K. R. Synthesis of new substituted 5,6-fused ring
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FIELD OF STUDY

Major Field: Chemistry
Minor Field: Spanish
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Semiconductors are used everywhere in the modern world. From computers to wrist watches and everywhere in between, semiconductors are what make the world run. There is not a day that goes by that they are not used to perform some task, whether menial or complex. We use them to balance our checkbook and to play the radio in our car. The problem with today’s semiconductors is that they are comprised of metals, mainly copper and aluminum. These metals have a limited supply, and although cheap, are not very efficient in conducting electricity. One possible solution to these problems is to make semiconductors made of carbon. Carbon is an extremely abundant element found within the Earth’s crust. Carbon dioxide, a molecule comprised of carbon and oxygen, is the primary source of global warming. Carbon is also a cyclic element, meaning it can be recovered and reused. This would facilitate the making of semiconductors that are sustainable. My Thesis will demonstrate how carbon-based semiconductors work, what makes them better, and where they might be seen in the future.

How They Work

Carbon-based semiconductors, deemed organic semiconductors, rely on a conjugated pi electron cloud to transport electricity. This means that due to the fact
that electrons can flow freely through the molecule from one atom to another, the molecule can transport electrons from one molecule to the next. This is achieved via flat rings that contain the conjugated pi electron cloud called planar arene rings. When the molecule is polymerized (when consecutive molecules are bonded) the electrons can then flow from one molecule to the next. Polymers, most commonly associated with plastics, are often thought to be insulators, and in most cases this is true. However, due to the delocalization of electrons via the conjugated pi electron cloud, these polymers can be used as conductors. Interestingly, this class of molecule also absorbs color in the UV-Vis, or ultraviolet-visible, spectrum. Because of the optoelectronic properties of the compounds, some have illuminating properties, thus giving them the ability to be used in light emitting diodes also known as LEDs.

Organic semiconductors also rely on a process called doping. Carbon can covalently bond to up to four other atoms to form crystals, thus ensuring that no electrons can freely move throughout the system and therefore the molecule will have more insulator-like properties. In order to enhance carbon's electrical properties, one can simply add a small amount of impurity. This process has two forms. The first is called n-type doping, where “N” stands for negative. In this case
elements that form more than four bonds are added in small quantities in order to free electrons. These free electrons can move without limit through the molecule. The other form is called p-type doping, due to the positive charge located on the impurity once added to the carbon-based molecule. In this case the element can form only three bonds and thus attracts electrons from neighboring molecules. By mixing n-type and p-type doping a much more efficient electron flow is created and less energy is lost due to heat (1).

Doping Schemes

These molecules can also be used in combination with transition metals such as rhenium and manganese to exploit other optoelectronic properties. For example, rhenium has oxidation states of +1, +3, +5, and +7 that can be used to limit or increase the electron flow depending on the desired application. Transition metals also tend to influence absorption in the UV-Vis spectrum and can create a wide variety of different colors. This can be very advantageous in the fields of LEDs and thin-film transistors.

Advantages

Organic semiconductors are comprised mainly of carbon, which can be harvested from a wide variety of places. Since every organism is made of carbon and
carbon dioxide is an ever increasing greenhouse gas, the sources for carbon are nearly endless. A novel idea would be to sequester the carbon dioxide created in coal burning power plants in order to synthesize these new molecules. This could significantly decrease the rate of global climate change due to greenhouse gas emissions.

Today's semiconductors are made of metals like copper, which are natural resources that are not renewable. Since many compounds are considered to be toxic they can create problems with disposal and development. An example of this is mercury, which is found in fluorescent light bulbs. As listed in the safety information for mercury on the Sigma-Aldrich website, mercury is “very toxic to aquatic organisms,” “may cause long-term adverse effects in the aquatic environment,” “toxic by inhalation,” and has the “danger of cumulative effects” (2). Organic semiconductors, on the other hand, have a very low level of risk to the environment and to humans in most cases. They can be readily synthesized in a laboratory and disposed equally as easily. The end result is semiconducting material that is a sustainable resource.

Another advantage is the fact that many of these new molecules are more efficient, or could potentially be more efficient, than their metal-based analogues. Dadvand et al. (2008) discuss the fact that many organic semiconductors already rival the charge translation of amorphous silicon and that there is the possibility that these news organic semiconductors will surpass the carrying capacity of silicon (3).
Longevity is one of the greatest advantages of organic semiconductors. Organic semiconductors may be used in products such as LEDs, which last up to 10 times longer than most incandescent bulbs. In a paper by Jean Bouffard, Robert F. Eaton, Peter Muller, and Timothy M. Swager it is suggested that compounds with electron deficient properties innately have “a resistance to photooxidation ... which can translate to devices operating at lower voltages and with extended lifetimes” (4). Therefore, because the device will not need as much energy to operate and will last longer, the product would pay for itself.

Applications

Organic semiconductors can be used in a wide variety of devices including light emitting diodes (LEDs), thin-film transistors (TFTs), radio-frequency identification tags (RF-IDs), and photovoltaic cells (5).

LEDs

Since these molecules show absorbance throughout the UV-Vis spectrum, the LEDs could come in a variety of colors and be used in everything from street lights to cell phones to Christmas lights. The color property may be taken advantage of to a further extent if the organic semiconductors are coordinated to a metal which give an even greater variety of color. These organic LEDs, denoted OLEDs, have already been used in products such as Nikon’s...
COOLPIX S70 camera, which has an OLED display. The OLED display reduces the effect of afterimages, or the essence of the image after the display has been changed or turned off (6).

**OTFTs**

Organic thin-film transistors (OTFTs) work in a similar fashion to the OLEDs. Both OLEDs and OTFTs are made of organic semiconductors but they differ in their direct application. OLEDs are typically used for the backlight in electronic devices such as televisions and digital cameras. OTFTs are what actually produce the picture on the screen. The main difference between OTFTs and TFTs is the substrate they are printed on. TFTs are typically made of amorphous silicon, which inherently must be attached to a glass substrate. Unfortunately glass is a very rigid, fragile material. OTFTs, on the other hand, benefit from being able to be attached to a plastic substrate. This allows for flexible displays (7). The Anthony research group at the University of Kentucky envisions a television made of organic semiconductors that will be able to be rolled up and put into a poster tube (8). OTFTs also offer “lower temperature manufacturing (60-120° C),” “lower-cost deposition processes such as spin-coating, printing, evaporation,” and “less need to worry about dangling bonds makes for simpler processing” (7).

**RF-IDs**

Radio Frequency Identification Tags are a way of storing and transmitting data across short distances and consist “of a microchip, antenna, and, in the case of active and semi-passive tags, a battery” (9). Essentially every part of the RF-ID could at least be partly made of organic semiconductors. As stated by Bonsor & Keener,
RF-IDs could one day be used in grocery stores to replace the barcode. This would be accomplished by putting the items in a cart, and once the cart was pushed past a receptor at the exits the cost of the items would be recorded and automatically deducted from the shopper's bank account (9). Similarly, many credit card and cell phone companies have been working with technology to allow payment by phone to be as simple as passing a credit card over an antenna on a cell phone. Organic Radio Frequency Identification Tags, ORF-IDs, would have exactly the same applications as inorganic RF-IDs, however they would be cheaper to produce and would be able to be printed on plastic, meaning the end product would be flexible (10).

**Photovoltaic Cells**

Photovoltaic cells are an area where I have done some personal research. Dr. Jack Selegue, Dr. John Anthony and I collaborated on a molecule that could be used in photovoltaic cells, better known as solar cells, which are used to collect energy. Dr. Anthony has used organic semiconductors to produce solar cells that can be sprayed on a rock or printed off on an inkjet printer. His spray on solar cell could be particularly useful in providing energy for emergency first response personnel and the military (11).

**Pyridazines and Fulvenes**

Fulvenes can be obtained in many different ways. By cracking dicyclopentadiene and mixing it with chilled "BuLi and an acid chloride in a dry diethyl ether solution substituted fulvenes can be created. Currently our associate Dr. Nathan Tice from Eastern Kentucky University has been working on a process to obtain fulvenes from plant based derivatives, further adding to the sustainability of
these molecules. Through a simple reaction involving hydrazine these fulvenes can be converted into 5,6-fused ring pyridazines (Scheme 2). In this project, the typical six member pyridazine containing two adjacent nitrogen atoms has been integrated into the iptycene skeleton. This allows them to have a wide variety of possible applications including gas absorption storage (12) and polymer sensors (13).

The focus of this project was the synthesis of pyridazines that could play a potential role in the electronics market. The synthesized pyridazines share many structurally similar traits to the previously mentioned organic semi-conductors. This is most easily exemplified in conjugated pi electron cloud. These molecule lack planarization, and therefore a conjugated pi electron cloud, by a sp³ hybridized nitrogen atom in the six membered pyridazine ring. This can be easily overcome in two fashions. First, the molecule can be complexed to metal, allowing for fluctuations in oxidation states and giving the molecule tunability. Second, the molecule can be converted into a polypyrrole through a process described by Boger and associates (14). This may again be complexed giving the organic portion of the molecule planarization and allowing for a conjugated π-electron system. The ability of these molecules to polymerize and leads to the inherent possibility in a wide variety of electronic devices such as Organic Light Emitting diodes (OLEDs), Organic Thin Film Transistors (OTFTs), Radio Frequency Identification Tags (RF-IDs), and Organic Photo-Voltaic Cells (OPVs) (15). These molecules also show the advantages of being air stable and having a relatively low cost of production.

In addition to many of the electronic applications mentioned above, pyridazines also show a great amount of pharmaceutical drugs and herbicides. Thus
the ability to synthesize these molecules with the desired substituents in a two step reaction is of great interest not only in electronics, but also the agricultural, and pharmaceutical industries.

The purpose of this project was to create new molecules that could either be directly used in an optoelectronic field or was an easily converted precursor to a molecule that could be used in the field. In addition to synthesizing these molecules our hope was to create them in such a method that would be both cost effective and efficient under ambient conditions. Efficiency was a key theme in this project, because the goal was to synthesize the molecules in as few steps as possible while still observing relatively high yields and with short reaction times.
For ease of reference all molecules, tables, and figures are labeled according to their appearance in our recent publication in *Synthetic Communication* (16). This paper was published online on the 30th of March 2011. Figures, Schemes, Tables, and Synthesis come from directly from this publication which I was the lead undergraduate contributor.

All reactions were performed in atmospheric conditions using standard Schlenking techniques. All reactants were obtained from Sigma-Aldrich and required no further purification. CDCl$_3$ and DMSO-d$_6$ were the NMR solvents used and were obtained from Sigma-Aldrich as well. C$_5$H$_3$(COC$_8$H$_5$S)(COHC$_8$H$_5$S) (1d) was prepared by methods developed by Selegue, Snyder, and Tice (17) (18) (19) (20) (21). Sodium benzophenone ketyl was used to dry the ethyl ether.

A JOEL-500 MHz NMR spectrometer was used to obtain $^1$H and $^{13}$C NMR spectra using residual solvent peaks at 22 °C. Spectra from $^{13}$C NMR are listed as decoupled. Melting points were obtained using a Mel-Temp apparatus. A Spectrum One FT-IR and a Varian Saturn GC/MS was used to record infrared spectra and electron ionization (EI) mass spectra (at 70 eV) respectively. The advanced
materials institute at Western Kentucky University performed elementary analysis. A Nonius KappaCCD diffractometer from the University of Kentucky X-ray Crystallography Laboratories was used to obtain X-ray data at 90K.

**Synthesis of 1,2-C₅H₃(COC₄H₃O)(COHC₄H₃O) (1d)**

Freshly cracked cyclopentadiene (3.14 mL, 2.51 g, 38.1 mmol) was added dropwise to a cooled solution (0 °C) of n-butyllithium (16.2 mL of 2.50 M, 23.4 g, 40.5 mmol) in ethyl ether (120 mL). A white precipitate of cyclopentadienyllithium was formed immediately. The suspension was stirred for 10 minutes and 2-furoyl chloride (2.48 mL, 3.29 g, 25.2 mmol) was added dropwise. A bright orange color formed immediately. The solution was stirred for 45 minutes at room temperature. The reaction mixture was hydrolyzed with dilute (3%) acetic acid (100 mL). The organic layer was separated, and the aqueous layer was extracted twice more with ethyl ether (2 x 10 mL). The combined ethyl ether extracts were dried (MgSO₄) and removed under reduced pressure to leave a red oil. The oil was eluted through a silica plug (50:50 dichloromethane:hexane) to give an orange solution. The organic solution was removed under reduced pressure to leave an orange semi-solid. The solid was trituated with hexane (2 x 10 mL) to leave a bright orange solid (337 mg, 1.33 mmol, 10.5%). **Mp:** 109–110 °C. **¹H NMR (500 MHz, CDCl₃, ppm):** δ 6.07 (t, 1H, 3J = 4 Hz, CHCHCH), 6.62 (dd, 1H, 3J_AB = 3.5 Hz, 3J_AC = 1.7 Hz CHCHCHO), 7.40 (d, 1H, 3J_BC = 3.5 Hz, CHCHCH), 7.72 (d, 1H, 3J_AB = 1.7 Hz, CHCHCHO), 8.15 (d, 1H, 3J = 4 Hz, CHCHCH). **¹³C NMR (125 MHz, CDCl₃, ppm):** δ 83.8 (CHCCO), 112.5 (CHCHCH), 119.8 (CHCHCH), 123.5 (CCO), 124.1, 139.3, 146.9 (Fr), 152.0 (OCCO), 169.3 (CO). **IR (KBr, cm⁻¹):** 1530, 1565 (COC₄H₃O), 3076, 3115,
3134, 3143 (C–H). **MS:** \( m/z \) 254 (M\(^+\)), 186 (M\(^+\) – C\(_4\)H\(_4\)O), 119 (M\(^+\) – 2C\(_4\)H\(_4\)O). Anal. Calcd. for C\(_{15}\)H\(_{10}\)O\(_2\): C, 70.86; H, 3.96. Found: C, 67.56; H, 3.56.

**Synthesis of 1,2-C\(_5\)H\(_3\)(CC\(_4\)H\(_3\)ONH)(CC\(_4\)H\(_3\)ON) (2e)**

1,2-C\(_5\)H\(_3\)(COC\(_4\)H\(_3\)O)(COHC\(_4\)H\(_3\)O) (1e, 100 mg, 0.394 mmol) was dissolved in 50 mL of methanol in a 200 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 hours. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and the organic layers were collected, dried (MgSO\(_4\)), and filtered. The volatiles were removed *in vacuo* and the crude product was triturated with cold hexane to give 1,2-C\(_5\)H\(_3\)(CC\(_4\)H\(_3\)ONH)(CC\(_4\)H\(_3\)ON) (2e, 40.0 mg, 0.160 mmol, 40.6%) as a red powder. **Mp:** 146–148 \(^\circ\text{C}.** **1H NMR (500 MHz, CDCl\(_3\), ppm):** \( \delta \) 6.66 (dd, 1H, \( ^3J_{AB} = 3.5 \text{ Hz}, ^3J_{AC} = 1.7 \text{ Hz} \) CHCHCHO), 7.25 (d, 1H, \( ^3J = 4.0 \text{ Hz}, \text{ CHCHCH} \)), 7.33 (d, 1H, \( ^3J = 3.5 \text{ Hz}, \text{ CHCHCHO} \)), 7.53 (t, 1H, \( ^3J = 4.0 \text{ Hz}, \text{ CHCHCH} \)), 7.66 (m, 2H, Fr), 11.2 (br s, 1H, NH). **13C NMR (125 MHz, CDCl\(_3\), ppm):** \( \delta \) 108.5 (CHCHCH), 112.4 (CHCHCH), 112.7 (NCCCH), 112.6, 118.0, 133.2 (Fr) 144.3 (CHCHCN). **IR (KBr, cm\(^{-1}\)):** 1612 (CN), 2958 (C–H), 3120 (N–H). **MS:** \( m/z \) 250 (M\(^+\)), 221 (M\(^+\) – CHO), 193 (M\(^+\) – C\(_2\)H\(_2\)O\(_2\)). Anal. Calcd. for C\(_{15}\)H\(_{10}\)N\(_2\)O\(_2\): C, 71.99; H, 4.03. Found: C, 74.32; H, 6.30.
Synthesis of 1,2-C₅H₃(CC₆H₄ClNH)(CC₆H₄ClN) (2f)

1,2-C₅H₃(COC₆H₄Cl)(COHC₆H₄Cl) (1f, 256 mg, 0.766 mmol) was dissolved in 50 mL of methanol in a 200 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and the organic layers were collected, dried (MgSO₄), and filtered. The volatiles were removed in vacuo and the crude product was triturated with cold hexane to give 1,2-C₅H₃(CC₆H₄ClNH)(CC₆H₄ClN) (2f, 186 mg, 0.548 mmol, 74.0%) as a yellow-orange powder. Mp: 218–222 °C. ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.05 (d, 1H, 3J = 3.45 Hz, CHCH₂CH₂), 7.46 (d, 1H, 3J = 8.55 Hz, CHCH₂CCl), 7.54 (t, 1H, 3J = 3.45 Hz, CHCH₂CH), 7.81 (d, 1H, 3J = 8.55 Hz, CHCH₂CCl), 11.8 (br s, 1H, NH). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 109.2 (CHCH₂CH₂), 120.3 (CHCH₂CH₂), 129.4, 128.9, 133.4 (Ph) 136.5 (CHCH₂CN). IR (KBr, cm⁻¹): 1598 (CN), 3047 (C–H), 2931, 2965 (CH₃), 3192 (N–H). MS: m/z 338 (M⁺), 302 (M⁺ – Cl). Anal. Calcd. for C₁₉H₁₂N₂Cl₂: C, 67.27; H, 3.57. Found: C, 67.56; H, 3.56.

Synthesis of 1,2-C₅H₃(CC₆H₄OCH₃NH)(CC₆H₄OCH₃N) (2g)

1,2-C₅H₃(COC₆H₄OCH₃)(COHC₆H₄OCH₃) (1g, 383 mg, 1.15 mmol) was dissolved in 50 mL of methanol in a 200 mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 hours. To the reaction, water (20 mL) was added and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3 x 10 mL) and
the organic layers were collected, dried (MgSO₄), and filtered. The volatiles were removed in vacuo and the crude product was triturated with cold hexane to give 1,2-C₅H₃(C₆H₄OCH₃NH)(C₆H₄OCH₃N) (2g, 262 mg, 0.793 mmol, 69.2%) as a yellow solid. **Mp**: 180-184 °C. **1H NMR (500 MHz, CDCl₃, ppm)**: δ 3.90 (s, 3H, CH₃), 6.96 (d, 1H, 3J = 8.6 Hz, OCHCH), 7.07 (d, 1H, 3J = 3.4 Hz, CHCHCH), 7.54 (t, 1H, 3J = 3.4 Hz, CHCHCH), 7.85 (d, 1H, 3J = 8.6 Hz, OCCHCH), 12.1 (br s, 1H, NH). **13C NMR (125 MHz, CDCl₃, ppm)**: δ 55.4 (OCH₃), 108.8 (CHCHCH), 114.3 (CHCHCH), 120.2 (CCN), 130.0, 131.9 (Ph) 161.0 (CHCHCN). **IR (KBr, cm⁻¹)**: 1573 (CN), 2934, 2963 (CH₃), 3057 (N-H). **MS**: m/z 298 (M⁺ – HOCH₃), 239 (M⁺ – C₆H₄OCH₃). Anal. Calcd. for C₂₁H₁₈N₂O₂: C, 76.34; H, 5.49. Found: C, 74.32; H, 6.30.
CHAPTER 3

RESULTS AND DISCUSSION

A technique developed by Linn and Sharkey (Scheme 1) was used to synthesize compound 1d from 1,2-diacylcyclopentadiene (17). A solution of two molar equivalents of nBuLi and dry ethyl ether was cooled in an ice bath to which three molar equivalents of freshly cracked cyclopentadiene was added. The mixture was stirred for circa 10 minutes in a relatively air free environment and 2-furoyl chloride was added dropwise producing a color change from white to a milky yellowish brown color. The solution was then stirred to approximately 45 minutes and brought to room temperature. This was followed a hydrolyzation with dilute acetic acid (3%). The contents of the reaction flask were then extracted using ethyl ether in a separatory funnel and dried using anhydrous magnesium sulfate.
Scheme 1: Synthetic route to fulvenes 1d.

$^1$H NMR, $^{13}$C NMR, and IR spectroscopy was used to describe the structure of 1d. The proton from the furoyl are observed as a doublet of doublets (6.62 ppm, $3J_{AB} = 3.5$ Hz, $3J_{AC} = 1.7$ Hz, CHCHCHO), a doublet (7.40 ppm, $3J_{BC} = 3.5$ Hz, CHCHCHO) and a doublet (7.72 ppm, $3J_{AB} = 1.7$ Hz, CHCHCHO). The protons from the cyclopentadiene ring are observed as a doublet (CHCHCH) and a triplet (CHCHCH) at 8.15 and 6.07 ppm respectively. $^{13}$C NMR shows a shifts corresponding to the cyclopentadiene ring at 112.5 ppm (CHCHCH) and 119.8 ppm (CHCHCH). Analysis via IR revealed carbonyl groups located at 1530 and 1565 cm$^{-1}$ which have been shifted downfield due to their delocalized structure.
Scheme 2: Synthetics route for pyridazines 2e-g.

The 5,6-fused ring pyridazines 2e-f were synthesized adding excess hydrazine hydrate in methanol at room temperature to the appropriate fulvene for approximate 24 hours (this is exemplified in scheme 2). The reaction was then quenched with water and extracted using ethyl ether. The pyridazines were then purified using a silica plug and hexane tituration. The percent yield varied from 40-74%.

Pyridazines 2e-f structures were described using $^1$H NMR, $^{13}$C NMR, and IR spectroscopy (tables 1 and 2). The cyclopentadiene ring showed proton stretches as a doublet found in the 7.05-7.84 ppm range (CHCHCH) and a triplet found in the 7.21-7.61 ppm range (CHCHCH). The coupling constant for CHCHCH and CHCHCH were found to be between $3J = 3.4-4.0$ Hz. The stretches for the amine protons were observed downfield in the 11.2-12.1 ppm range because they show delocalization characteristics in solution. Encouragingly $^{13}$C NMR showed no signs of carbonyl stretching which would have indicated a fulvenes product rather than a pyridazine. Pyridazines 2e-f did show C=N stretching in the 136.5-144.3 ppm region while the
cyclopentadiene ring carbons (CHCHCHH and CHCHCH) were found in the 108.5-114.3 ppm and 119.5-120.3 ppm ranges respectively. Likewise, analysis via IR spectroscopy show the disappearance of a carboxyl stretches in the pyridazines and formation C=N stretches in the 1573-1612 cm\(^{-1}\) as seen in Table 2. Secondary amine stretches were observed in the 3059-3192 cm\(^{-1}\) range. Correspondingly an analysis via GC/MS verifies the structures of 2e and 2f with a parent ion peak of 298 (M\(^+\) - HOCH\(_3\)).

![Diagram of molecule with labels](image)

**R = C\(_4\)H\(_2\)O (2e)**

**R = C\(_6\)H\(_4\)Cl (2f)**

**R = C\(_6\)H\(_4\)OCH\(_3\) (2g)**

**Table 1: Selected \(^1\)H and \(^13\)C NMR data for 2e-g.**

<table>
<thead>
<tr>
<th></th>
<th>2e</th>
<th>2f</th>
<th>2g</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_a)</td>
<td>11.2 (br s)</td>
<td>11.8 (br s)</td>
<td>12.1 (br s)</td>
</tr>
<tr>
<td>H(_b)</td>
<td>7.25 (d, (J = 4.0 \text{ Hz}))</td>
<td>7.05 (d, (J = 3.45 \text{ Hz}))</td>
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<td>7.53 (t, (J = 3.45 \text{ Hz}))</td>
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<td>114.3</td>
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<td>120.2</td>
</tr>
<tr>
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<td>136.5</td>
<td>146.9</td>
</tr>
<tr>
<td></td>
<td>2e</td>
<td>2f</td>
<td>2g</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>C=N</td>
<td>1612</td>
<td>1598</td>
<td>1573</td>
</tr>
<tr>
<td>N-H</td>
<td>3120</td>
<td>3192</td>
<td>3057</td>
</tr>
</tbody>
</table>

The crystal structure of 2f was established using X-ray crystallography. The crystals were cultivated at room temperature using slow evaporation from acetone. The crystals were then mounted with Paratone N oil on glass fibers. A Nonius KappaCCD diffractometer was used to collect the data at 90K. The programs used to obtain the cell parameters and data reduction, absorption correction, structure solution, and refinement were DENZO-SMN, SCALEPACK, SHELXS-86, and SHELXL-93 respectively. Geometrically calculated positions were used to place hydrogen atoms. Crystal data is located in Table 5.
Table 5: Crystal data and structure refinement for pyridazine 2f.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{22}\text{H}</em>{18}\text{Cl}<em>{2}\text{N}</em>{2}\text{O}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>397.28</td>
</tr>
<tr>
<td>Temperature</td>
<td>90.0(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, $P\bar{1}$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 8.6250(1) \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$b = 9.8027(2) \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$c = 11.4677(2) \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 97.9313(7)^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 93.0136(7)^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 95.8685(7)^{\circ}$</td>
</tr>
<tr>
<td>Volume</td>
<td>$953.08(3) \text{ Å}^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.384 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.355 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>412</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.15 x 0.15 mm</td>
</tr>
<tr>
<td>$\theta$ range for data collection</td>
<td>1.80 to 27.47$^{\circ}$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>21631/4346 [R(int) = 0.0195]</td>
</tr>
<tr>
<td>Completeness to $\theta = 27.47$</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.949 and 0.932</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4346/0/246</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.014</td>
</tr>
<tr>
<td>Final R indices [I&gt;2 $\sigma(I)$]</td>
<td>$R_1 = 0.0322$, $wR_2 = 0.0856$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0391$, $wR_2 = 0.0908$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.383 and -0.278 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
Figure 1: Molecular structure for pyridazine 2f.

2f was recrystallized from hot acetone yielding a yellow-orange block crystal (Figure 1) which crystallizes in a triclinic $P\bar{1}$ space group, having only molecule per unit cell. The average carbon-carbon bond length in the cyclopentadiene and aromatic rings were 1.4115(22) Å and 1.3927(10) Å respectively. The bond length for N$_1$-N$_2$ was found to be 1.3586(15) Å. The bond length of the carbon-chlorine bond in the 2f substituents was found to be 1.7437(13) Å and 1.7382(13) Å. As expected from Gaussian09 calculations the phenyl chloride rings twisted out of the molecular plane (22). Upon an initial run of the molecule Gaussian09 was unable to predict the exact torsion angles of 36.92° and -39.73° for [C$_{13}$-C$_8$-C$_7$-N$_2$] and [C$_{19}$-C$_{14}$-C$_1$-N$_1$] respectively; however it was relatively accurate at predicting most of the bond lengths. The inadequacy of the Gaussian09 calculations was most likely due to its desire to calculate to best local minimum potential energy for each atom rather than calculating the global minimum for the entire molecule. Also, hydrogen bonding was observed between N$_1$-H$_1$ from the pyridazine and O$_1$ from one acetone solvent molecule; this could have shifted the torsion angles of the molecule making
creating a larger error in the Gaussian09 calculations. The distance of said hydrogen bond was calculated to be 2.00Å.
CHAPTER 4

CONCLUSIONS

The fulvene 1d and the pyridazines 2e-g were synthesized in moderate percent yields and characterized using several commonly employed characterization techniques. The synthesis of these molecules were moderately good especially considering most of the reactions took place in ambient conditions and required little to no use of air-free chemistry. Most of the product loss can be attributed to workup conditions. This is best exemplified by the use of a silica plug to effectively purify some of the products from an oily residue to a powder or crystal. Effectively much of the product was still present in the silica plug and to avoid recontamination with the impurity the rest of the product was not sought after. Efforts are still being made to optimize this process. The reactions were relatively quick (20 mins-24hrs). The reaction conditions along with the percent yield and the reaction time lead to the conclusion that with some efforts to increase yield production of these molecules commercially would be well suited via this method.

Our hope as a group is that we will be able to optimize the process and integrate more “Green” techniques, allowing for a more sustainable environment. Other future plans include the complexation of the molecules with group seven
metals as well incorporating more computational techniques. These computational
calculations may allow us to create molecules with higher conduction potentials as
well as prevent efforts on creating molecules that may not be well suited for
optoelectronic applications.
REFERENCES


8 Nethery, J. Bowling Green, Kentucky, United States, November 20, 2009.


1 Ghanem, B. S.; Msayib, K. J.; McKeown, N. B.; Harris, K. D. M.; Pan, Z.; Budd, P. M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. A Triptycene-Based Polymer of Intrinsic Microposity that Displays Enhanced Surface Area and Hydrogen Adsorption. 


2 Frisch, M. J.; al., *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, CT, 2009.