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## Synthesis, Isolation, and Characterization of Novel Organic Electronic Architectures.

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**SYNTHESIS, ISOLATION, AND CHARACTERIZATION  
OF NOVEL ORGANIC ELECTRONIC ARCHITECTURES**

**A Dissertation**

**Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy**

**in**

**The Department of Chemistry**

**by**

**Taiya Sprull Fabre**

**B.S., Xavier University of Louisiana, 1995**

**May 2001**

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## **DEDICATION**

I dedicate this dissertation to my family. First and foremost, my loving husband Jason and my daughter Leah Nicole. My love for the both of you is my source of inspiration. Next, I would like to say **THANK YOU** to my father Jack for always pushing me to do my best. I would also like to express my gratitude to my mother and stepfather, Paulette and Freddie Solomon. I hope I make you proud. Of course, I cannot forget my siblings Lanisha, Matthew, and Justin. Finally, to the rest of my family, thank you for all of your support and love. I love all of you.



## **ACKNOWLEDGEMENTS**

I would like to thank GOD for allowing me to live, breathe, and succeed.

Next, I would like to thank my research advisor and mentor Dr. Robert M. Strongin. You have guided me through the good and the bad times with a never quit attitude that I appreciate deeply. I would especially like to thank the other members of "The Fab Four", my three brothers, Dr. Patrick Lewis, Dr. Douglas Willis, and Dr. Claude Davis. I love you guys and we will always be together. I also want to say thanks to all the members (past and present) of the Strongin Research Group especially Patti Beck, Jorge Escobedo, Dr. Mark Read, and my good friend Dr. Marcelo Saraiva. To all of the other members of the incoming class of 1995, I would like to say thanks for the memories, especially, Clinton "Doc" Hunt and Dr. Tracey Simmons. I would also like to acknowledge Dr. Tamara Nauman, Dr. Linda Allen, Dr. Dale Treleven, Dr. Tracey, McCarley, Dr. Rafeal Cueto, and Dr. Isiah Warner for their constant support and guidance.

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## ABSTRACT

Interest in the fullerenes is due, in large part, to the fact that they represent the third major form of carbon, following graphite and diamond. We have investigated synthetic methods towards the creation of new carbon molecules derived from the fullerenes. The sought-after dimeric carbon fullerene derivative,  $C_{122}$ , was successfully synthesized and isolated for the first time in modest yield from a complex reaction mixture. The all-carbon molecular allotrope was prepared via the new reaction of  $C_{60}$  with atomic carbon in solution. Atomic carbon was produced via the known thermolytic decomposition of diazotetrazole. Future work that could emanate from these studies includes the development of new fullerene chemistries toward the production of oligomeric and coalesced (cage-merged)  $C_{60}$  derivatives. Towards these ends, the first Suzuki coupling reaction of a methanofullerene was performed. Model reaction conditions, in keeping with strong literature precedent for other systems, were developed. Product characterization is ongoing. This work should lay the groundwork for future efforts in the area of methanofullerene coupling reactions.

Studies of the reaction of other azazole heterocycles (i.e., congeners of diazotetrazole) have begun in order to probe and broaden the scope of the reaction of these molecules with the fullerenes. The reaction of diazodicyanoimidazole with  $C_{60}$  is described along with detailed product isolation analysis. Apart from the analogy to our diazotetrazole reaction, these efforts appear to have led to the formation of new fullerene adducts which potentially embody more electron accepting character than the parent fullerenes. Fullerene derivatives with enhanced electron accepting character are

relatively rare. They help serve to create analogies between fullerene and benzene chemistries. They may find application in biology and materials science.

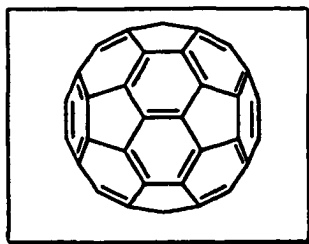
Studies of other relatively large benzenoid systems are described. The cyclic tetramers of resorcinol, the resorcinarenes were discovered by our research group to promote solution color changes in the presence of various sugars. This is a potentially highly practical result with possible applications in diagnostics and industrial product analysis. The resorcinarenes were discovered by von Bayer in 1872 and were shown to exhibit colorimetric effects at that time; however, no one has investigated the origin of these effects nor probed their utility. Herein initial studies towards HPLC chromatographic isolation of colored materials from resorcinarene solutions are described as well as the mass spectrometric analysis of the adducts of resorcinarenes with various analytes.

# **CHAPTER 1.**

## **INTRODUCTION**

### **1.1 Background on the Fullerenes**

The fullerenes (i.e.  $C_{60}$ , (Figure 1.1) and higher molecular allotropes of carbon) were discovered by Kroto, Smalley, and Curl in 1985.<sup>1.1</sup> These molecules represent the third major form of carbon following graphite and diamond. In 1990, the fullerenes were isolated in macroscopic amounts by Kratschmer and Huffman via arc vaporization of graphite.<sup>1.2</sup> The fullerenes are the first monomeric form of which allows them to be soluble in organic solvents.



**Figure 1.1.** Structure of  $C_{60}$ .

As a result of the enhanced solubility in organic solvents, the physical properties of the fullerenes are improved. These strengthened physical properties result in fullerene applications in such areas as HIV protease inhibition, superconductivity, site specific DNA cleavage, and catalysis.<sup>1.3</sup> The synthesis of new all-carbon molecules from  $C_{60}$  is of interest to chemists. These efforts can lead to the formation of gas-phase

clusters<sup>1,4</sup>, solution phase production of methanofullerene-acetylene hybrids<sup>1,5</sup>, and all-carbon dimers.<sup>1,6,1,7</sup>

## **1.2 Background on Fullerene Dimers**

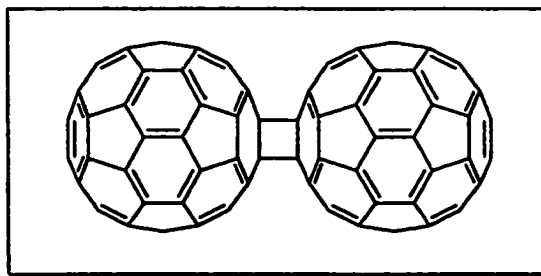
The synthesis of fullerene dimers has been of tremendous importance starting with the detection of coalesced fullerenes formed from laser irradiation of C<sub>60</sub> films.<sup>1,8</sup> There are three main types of fullerene dimers which include all carbon fullerene dimers, carbon allotropes containing two fullerene units, and fullerene dimers that are bridged through electroactive spacers. The synthesis of these dimers can be described in two main categories which are the dimerization of C<sub>60</sub> itself or some derivative of C<sub>60</sub> and cycloaddition reactions to C<sub>60</sub>.<sup>1,9</sup>

Although the observation of coalesced fullerenes (which result in stable, higher fullerenes which are multiples of the initial masses) is of importance, the structures of the products from these reactions are not known. It has also been very difficult to characterize the simple addition polymers. These products can be formed as large clusters (C<sub>60</sub>)<sub>n</sub> or as dumbbell shaped n=2 dimers.<sup>1,8</sup> Since fullerene dimers can embody subunits of all-carbon fullerene polymers, it is of importance to elucidate their structure, physical properties, and chemical properties, to aid in understanding fullerene polymers.<sup>1,6</sup>

## **1.3 Dimerization of C<sub>60</sub> and Derivatives**

Mass spectrometry indicates that C<sub>120</sub> (Figure 1.2) is the most abundant product of the coalescence experiments and polymerizations. Therefore, it has been of interest to determine the ground-state configuration of C<sub>120</sub>. The most probable bonding between two C<sub>60</sub> molecules in the neutral state has been reported to be via a [2+2]

cycloaddition. In the cycloaddition, a four membered ring is formed via the cleavage of (6,6) short bonds between two hexagons on adjacent  $C_{60}$  molecules.<sup>1.10</sup> Evidence for the cycloaddition is determined via the similarity of the FT-IR spectrum of  $C_{120}$  and other all carbon poly[60] fullerenes.

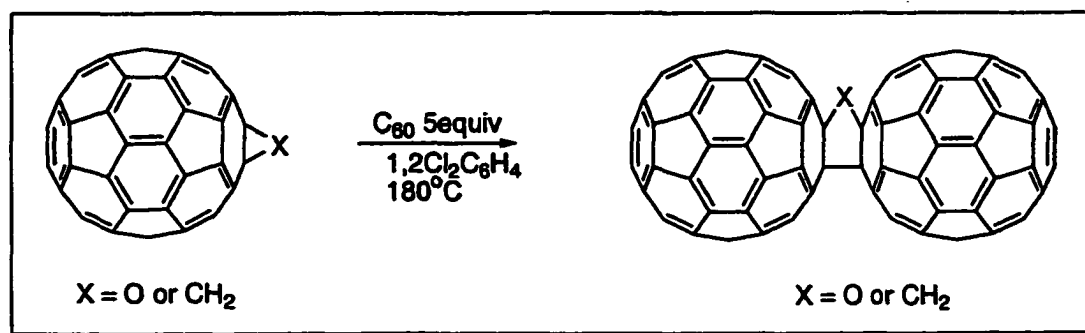


**Figure 1.2.** Structure of  $C_{120}$ .

Although there have been many studies carried out on  $C_{120}$ , only a few efficient syntheses have been reported.<sup>1.6</sup> An efficient synthesis of  $C_{120}$  can be achieved via a solid state reaction of  $C_{60}$  with potassium cyanide employing the technique of high speed vibration milling (HSVM). Using HSVM, dimerization of  $C_{120}$  can proceed through nucleophilic addition or coupling via an electron transfer step.<sup>1.10</sup> Very pure samples of  $C_{120}$  exhibit poor solubility in organic solvents. Cyclic voltammetric studies show that  $C_{120}$  dissociates into  $C_{60}$  after gaining extra negative charge.

Another extensively studied fullerene dimer is  $C_{120}O$ . The thermolysis of  $C_{60}O$  (a [6,6] epoxide structure) in the presence of  $C_{60}$  affords the formation of  $C_{120}O$ .<sup>1.11,1.12</sup> The corresponding methylene bridged  $C_{60}$  dimer can also be formed using the same experimental conditions (Scheme 1.1). Taylor and co-workers discovered that  $C_{120}O$  can be formed from the degradation of  $C_{60}$  in the solid state at ambient temperatures.<sup>1.13</sup>

The monomer  $C_{60}$  is also believed to oxidize to  $C_{60}O$  on exposure to air, and this monoxide is then capped by another  $C_{60}$  molecule to yield  $C_{120}O$ . The  $C_{120}O$  dimer is formed via the connection of two  $C_{60}$  molecules by a tetrahydrofuran ring instead of a cyclobutane ring as in the case of  $C_{120}$ . Electrochemical studies of  $C_{120}O$  indicate that the two fullerene cages are not reduced simultaneously and, therefore, are communicating with each other. Also, the thermolysis of  $C_{120}O$  in the presence of sulfur produces the sulfur analog  $C_{120}OS$ .<sup>1,14</sup> The production of this sulfur analog is the first synthesis and characterization by spectroscopic processes of a dimeric fullerene-containing sulfur.

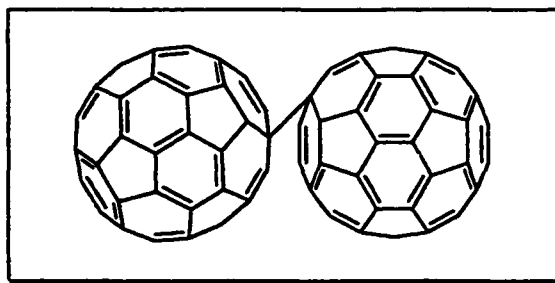


**Scheme 1.1.** Syntheses of  $C_{120}O$  and the methylene bridged  $C_{60}$  dimer.

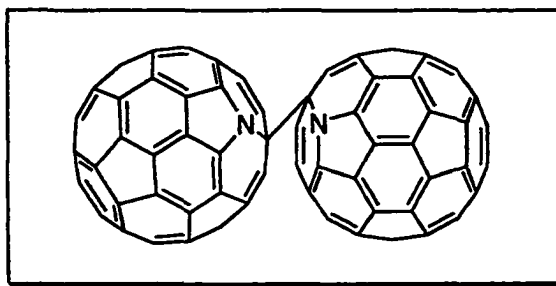
Mass spectroscopic studies have shown that fullerene epoxides can form odd dimeric species with an odd number of carbons (hereafter referred to as odd numbered dimers).<sup>1,15</sup> The discovery of the odd numbered fullerenes is a variation from the classical fullerenes which contain an even number of quasi- $sp^2$  carbons that are contained in a closed cage structure in which hexagons completely surround pentagons. The presence of odd numbered dimers such as  $C_{119}$ ,  $C_{129}$ , and  $C_{139}$  was discovered by McElvany and co-workers.<sup>1,4</sup> These clusters of dimers were seen in the thermal

desorption mass spectra of a toluene extract of commercial soot and in the spectra of products of ozone fullerene reactions. The thermal decomposition of  $C_{120}O_x$  ( $x < 3$ ) is responsible for the formation of these dimers. Even though the  $C_{119}$  dimer is stable when stored in the refrigerator under argon, it is oxygen sensitive and decomposes at room temperature after a couple of hours. The  $C_{119}$  dimer is proposed to consist of two partially opened cages that are connected by three  $sp^3$  carbons and two seven-membered rings.<sup>1,10</sup>

As mentioned earlier, a [2+2] cycloaddition is the most stable bonding conformation between two  $C_{60}$  molecules in the neutral state. Therefore, a single bonded isomer (Figure 1.3) which is formed by the covalent bonding between two  $C_{60}$  molecules has a higher energy than  $C_{120}$ . If an electron is added to each  $C_{60}$  unit, the single bonded isomer is proposed to be more stable than an isomer formed via a [2+2] cycloaddition.<sup>1,10</sup> These newly formed fulleride structures are isoelectronic with the azafullerene dimer (Figure 1.4) which is formed via a single C-C intermolecular bond.<sup>1,16</sup>



**Figure 1.3.** *trans* Conformation of single bonded  $(C_{60})_2^{2-}$  dimer.



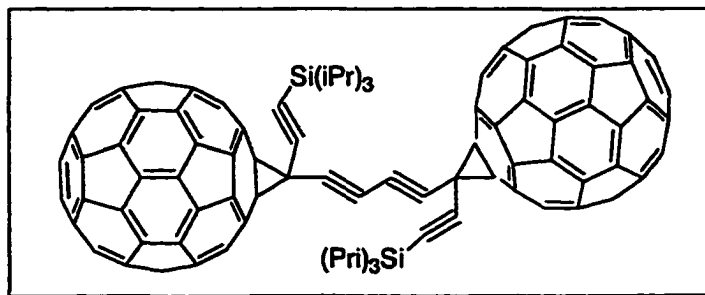
**Figure 1.4.** Structure of  $(C_{59}N)_2$ .

Fullerene radicals that are formed in situ by addition of  $R^\cdot$  to  $C_{60}$  fullerene dumbbell shaped dimers.<sup>1.17,1.18</sup> These dimers have the general structure  $RC_{60}C_{60}R$ . Radicals add quickly to  $C_{60}$  to give products  $R_nC_{60}$ . The intensity of the EPR spectrum of these species increases with an increase in temperature. This indicates the possibility of an existing equilibrium between the radical and its corresponding dimer which eludes to the fact that the dimer bond strength is dependent upon the size of the radical group.<sup>1.17</sup> Osawa and co-workers have discovered that dimers with R groups close too each (gauche) other are more stable than those with separated R groups (trans). The stability of this gauche-like conformation has been explained as a lever effect consistent with the dumbbell shape of the molecule.<sup>1.18</sup>

A different approach which leads to the formation of all carbon allotropes involves the combination of fullerene and acetylene units. In this process, methanofullerenes are used to end-cap macrocyclic polyynes.<sup>1.19</sup> Diederich and co-workers have prepared dimeric fullerenes (Figure 1.5) via symmetrically and unsymmetrically substituted diethynylmethanofullerenes. Dimeric fullerenes in which the acetylene spacers are directly attached to the fullerene core via homocoupling have been synthesized. Diederich and co-workers reported the homocoupling is done with

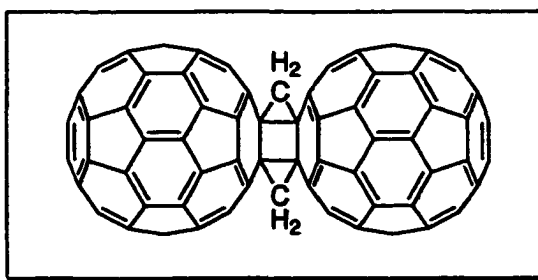


ethynylfullerenes. Electrochemical studies indicate that the  $C_{60}$  moieties behave independently in both cases.



**Figure 1.5.** Butadiynyl-linked dimeric methanofullerene.

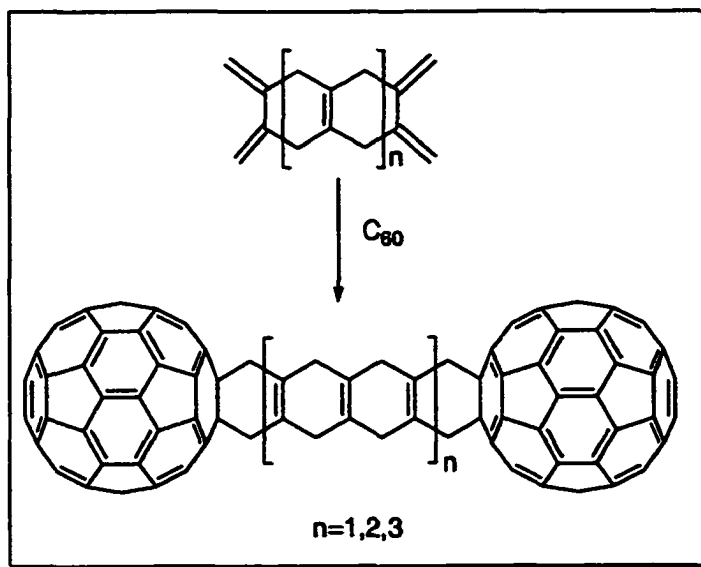
A study of the addition of the methanofullerene carbene  $C_{60}C:$  to  $C_{60}$  itself has led to the carbon allotropes  $C_{121}$  and  $C_{122}$ . These results will be discussed in detail later.<sup>1,20</sup> The isolation of the fullerene dimer  $C_{122}H_4$  (Figure 1.6) has recently been reported.<sup>1,21</sup> The resulting ring  $CH_2-CC-CH_2-CC$  has a rigid boat conformation. Electronic interactions have been observed between the fullerene cages and the effects of these interactions on the optical properties of the dimers are currently being studied.



**Figure 1.6.** Structure of  $C_{122}H_4$ .

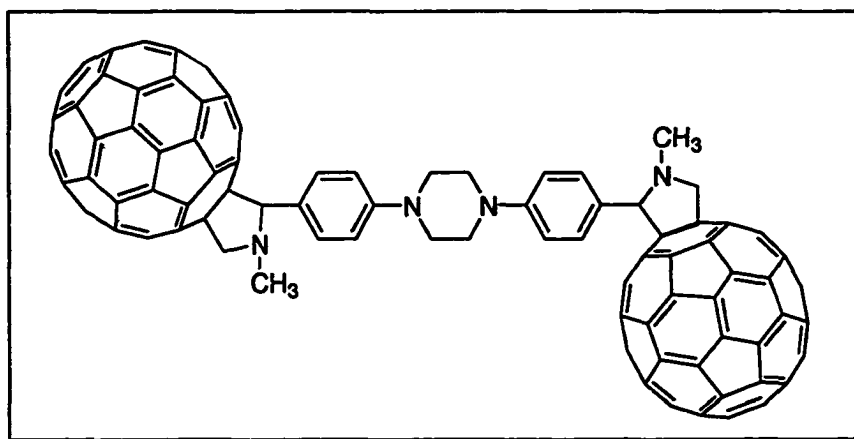
## 1.4 Cycloaddition Reactions to C<sub>60</sub>

In cycloaddition reactions, C<sub>60</sub> is a good dienophile and reacts via the [6,6] double bond (versus the unfavorable [6,5] double bond). The resulting monocycloadducts are easily isolated in good yields. Fullerene dimeric materials are prepared efficiently via the derivatization of C<sub>60</sub> with bifunctionalized molecules. The first syntheses of fullerene dimers were reported by Wudl and co-workers using bis(diazoderivatives).<sup>1,22</sup> As a result, many other dumbbell shaped fullerene dimers have been synthesized from bisdienes using Diels-Alder cycloadditions. For example, Paquette and co-workers have prepared dumbbell-shaped systems via the use of bis-dienes (Figure 1.7).<sup>1,23</sup> By controlling the number of tethering spheres in these dumbbell-shaped dimers, information can be obtained about the communication between fullerene cages. The studies of these molecules are restricted due to their insolubility.



**Figure 1.7.** Syntheses of dumbbell-like systems via Diels-Alder cycloadditions.

Another very interesting type of cycloaddition is the 1,3-dipolar addition of azomethane ylides to  $C_{60}$ .<sup>1.24</sup> The first synthesis of this type was performed by in 1996 by Lucas and co-workers (Figure 1.8). As of yet, no interactions between fullerene cages have been observed in the ground state of these dimer compounds.<sup>1.25</sup>



**Figure 1.8.** Fullerene dimer obtained from bifunctional cycloaddition.

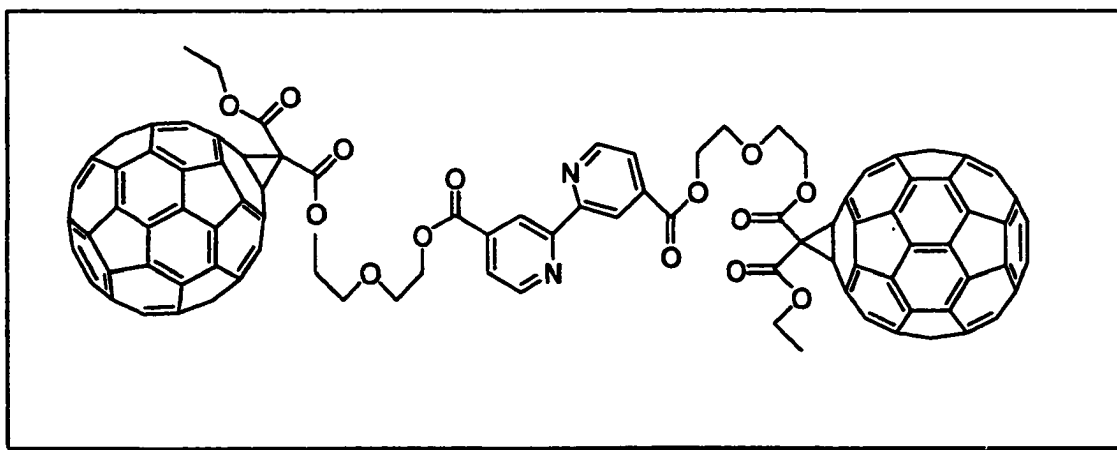
### 1.5 Dimers Formed via Electroactive Bridges

Organofullerenes that contain electroactive moieties are of significance because of the intriguing optical and electronic properties of these compounds. The electronic properties of  $C_{60}$ -porphyrin- $C_{60}$  triads have been extensively studied. These dimers are formed via Bingel macrocyclization of bismalonates<sup>1.25</sup> which contain a porphyrin tether or 1,3-dipolar cycloadditions via the corresponding formylporphyrins.<sup>1.27</sup>

Fullerene dimers containing two fullerene spheres which are attached directly or covalently through a molecular electroactive bridge have also been studied. The electronic interactions between two  $C_{60}$  units and between  $C_{60}$  and the electroactive spacer are of importance due to their electrochemical and photophysical redox

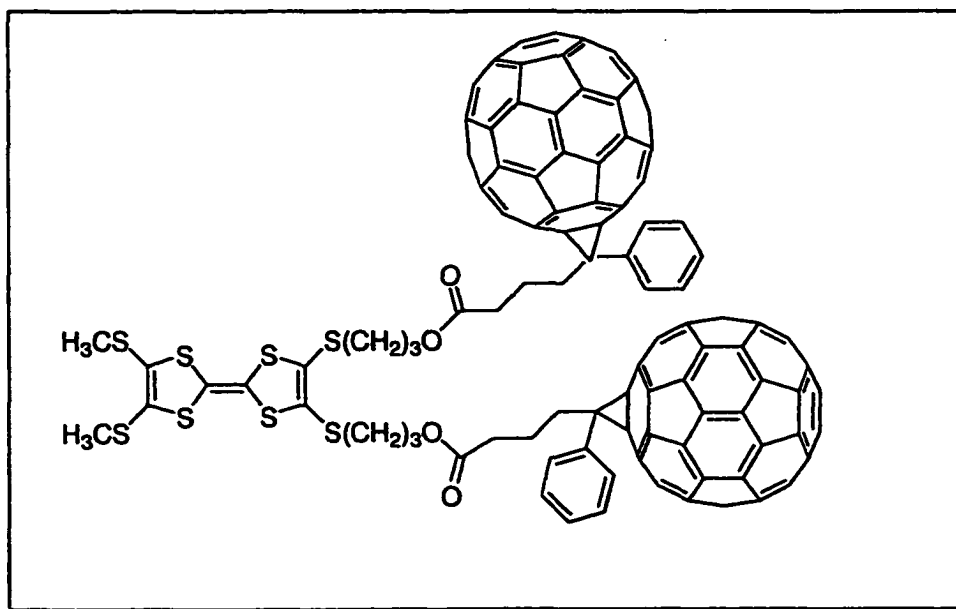
properties. Examples of electroactive bridges used include bipyridine (bpy) ligands and tetrathiafulvalene (TTF).

The bis- $C_{60}$ -bpy dimer has been synthesized via the Bingel reaction to produce dimers in which polyethoxy spacers are used to separate the methanofullerenes from the bipyridine ligands (Figure 1.9).<sup>1,28</sup> Electrochemical studies indicate that there is no interaction between  $C_{60}$  and the oligomer.



**Figure 1.9.** Structure of the bis- $C_{60}$ -bpy derivative.

The covalent attachment of the strong electron donor tetrathiafulvalene to  $C_{60}$  is useful in the preparation of photovoltaic devices. Only one example of the  $C_{60}$ -TTF- $C_{60}$  triad is reported in the literature.<sup>1,29</sup> In this synthesis, reported by Delhaes and co-workers, a TTF derivative is covalently linked to two or four  $C_{60}$  molecules through the use of flexible rings (Figure 1.10). Although no interaction is detected between the donor and acceptor systems of the molecule, these systems may be used in photophysical studies in the search for improved electronic devices.



**Figure 1.10.** Structure of the C<sub>60</sub>-TTF-C<sub>60</sub> triad.

Conducting polymers originating from the addition of polyphenylenevinylenes and polythiophenes to C<sub>60</sub> have been used to prepare polymeric voltage cells. These molecules can undergo photoinduced electron transfer.<sup>1,9</sup> Only two examples of conjugated oligomers that are end-capped with two C<sub>60</sub> moieties are known. Both of these dimers have been prepared via 1,3-dipolar cycloaddition using the corresponding diformyl oligomers.<sup>1,30,131</sup> As in the case of the fullerene porphyrin analogs, there is electrochemical studies show no interaction between the fullerene and the oligomer in the ground state. Since oligomers are well defined and able to correlate the structural effects and electronic properties of corresponding polymers, the C<sub>60</sub>-oligomer-C<sub>60</sub> analogs should be studied more intensively.

A variety of the new classes of dimeric fullerenes have been discussed. Although the main motivation for the synthesis of new fullerene dimers and polymers was to

generate novel all carbon allotropes via physical methods, some of the products obtained were too difficult to be analyzed and characterized. The preparation of new carbon allotropes containing two fullerene cages such as  $C_{119}$ ,  $C_{120}$ ,  $C_{121}$ , and  $C_{122}$  is possible through covalent fullerene chemistry. The identification of the structures of these compounds can aid in understanding the nature of fullerene polymers, since the synthesis of these dimers can allow introduction of functional groups which will aid in producing new fullerene dimers with enhanced solubility's and varying structures and properties.

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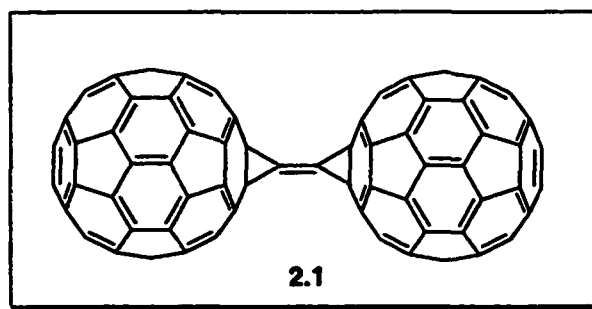


## CHAPTER 2.

### THE REACTION OF BUCKMINSTERFULLERENE WITH DIAZOTETRAZOLE. SYNTHESIS, ISOLATION, AND CHARACTERIZATION OF $(C_{60})_2C_2$ \*

#### 2.1 Introduction

A current challenge of fullerene chemistry<sup>21</sup> is the synthesis, isolation and characterization of new molecular carbon allotropes. Recent investigations include the formation of gas-phase clusters<sup>21</sup> as well as the solution-phase production of methanofullerene-acetylene hybrids<sup>22</sup> and all-carbon dimers.<sup>23,24</sup> Dimeric all-carbon fullerenes with appropriate bridging moieties might exhibit novel intercage electronic interactions or serve as precursors to coalesced fullerenes. We have successfully performed the first isolation and characterization of the dimeric allotrope  $(C_{60})_2C_2$ , (Figure 2.1) obtained via a new reaction of [60]fullerene with the atomic carbon precursor diazotetrazole,  $2^{25}$  (Scheme 2.1).

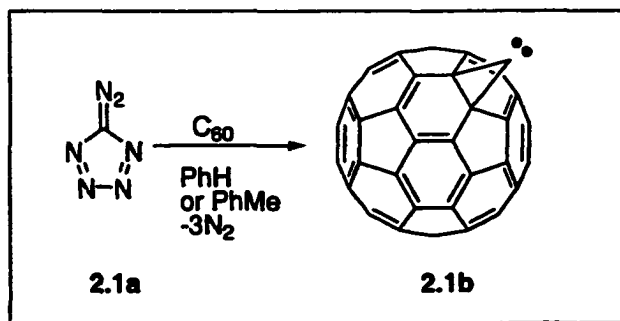


**Figure 2.1.** Structure of  $(C_{60})_2C_2$ .

\*Reprinted in part with permission from Journal of Organic Chemistry, 1998, *Volume* 63, pages 3522-3523; Taiya S. Fabre, W. Dale Treleaven, Tracy D. McCarley, Cynthia L. Newton, Rebecca M. Landry, Marcelo C. Saraiva, and Robert M. Strongin; The Reaction of Buckminsterfullerene with Diazotetrazole. Synthesis, Isolation, and Characterization of  $(C_{60})_2C_2$ .

## 2.2 Results and Discussion

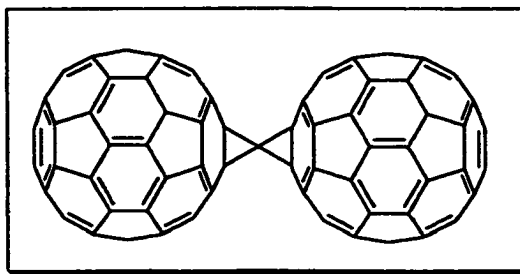
The synthesis of **2.1** was obtained via a new reaction of  $C_{60}$  with the atomic carbon precursor diazotetrazole,<sup>2,5</sup> **2.1a** (Scheme 2.1). Initially reported by Thiele in 1892,<sup>2,6</sup> Shevlin discovered a facile preparation of **2.1a** and demonstrated that this highly energetic molecule readily formed carbon atoms upon thermolysis.<sup>2,5</sup>



**Scheme 2.1.** Formation of  $C_{60}$  cyclopropylidene.

In the presence of olefins, atomic carbon produces cyclopropylidenes.<sup>2,7</sup> We proposed that the decomposition of **2.1a** in the presence of  $C_{60}$  would thus lead to direct formation of **2.1b** (Scheme 2.1). Intermediate **2.1b** has been previously reported as a precursor to  $(C_{60})_2C_2$  (Figure 2.1) and  $(C_{60})_2C$  (Figure 2.2). The methanofullerene,  $C_{61}Br_2$ , was produced during pioneering studies by Osterodt and Vögtle, in which **2.1** and **2.2** were detected by mass spectrometry.<sup>2,8</sup> Formation of **2.1a** was achieved via diazotization of 5-aminotetrazole with isoamyl nitrite and concentrated HCl in THF.<sup>2,7</sup> The resultant solution was heated to reflux in a benzene or toluene solution of  $C_{60}$ . At least fourteen fullerene products were observed via HPLC analysis.<sup>2,9</sup> We also obtained similar product distributions by either photolysis (Hanovia mercury lamp, medium pressure,

quartz filter, rt, 30 min) or upon allowing the solutions to stand at ambient temperature for 12h.

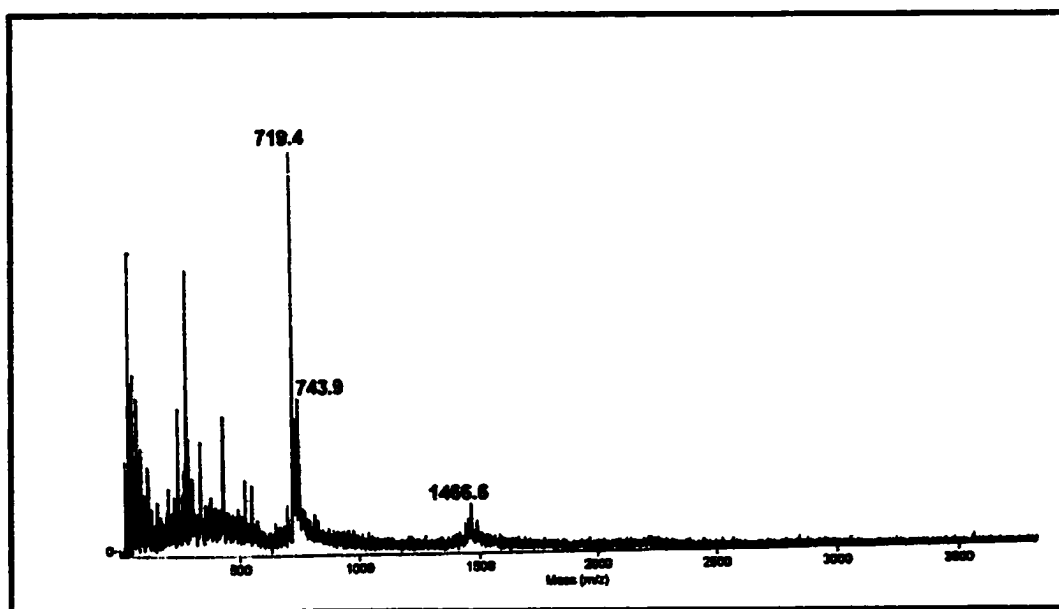


**Figure 2.2.** Structure of  $(C_{60})_2C$ .

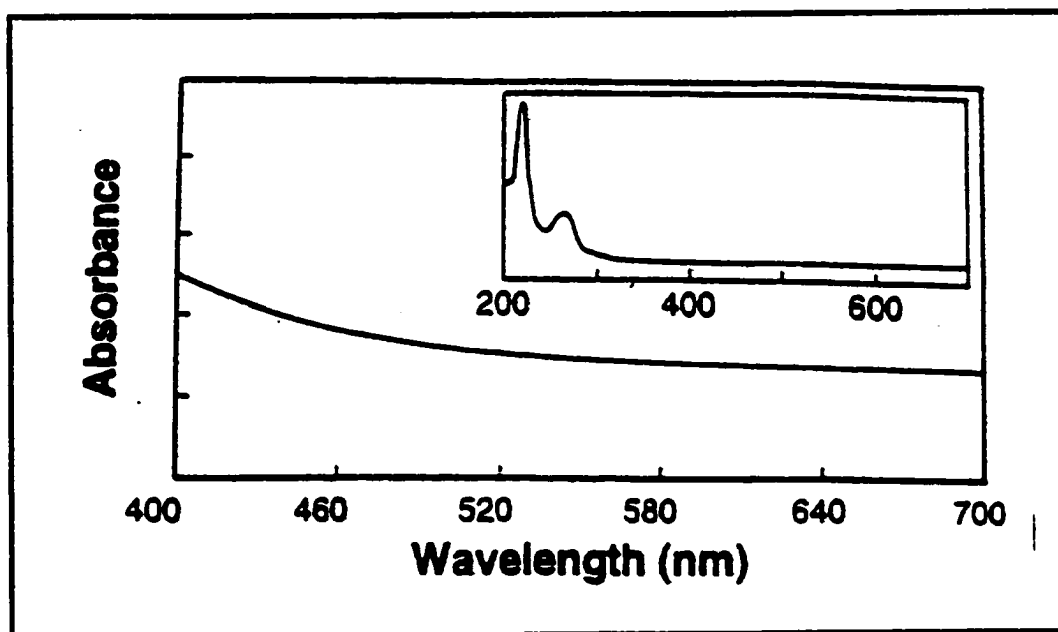
Since fullerene dimers exhibit relatively long HPLC retention times compared to  $C_{60}$  and most the corresponding monoadducts,<sup>2,6,2.10,2.11</sup> our initial focus concerned the isolation and characterization of the latest eluting material. Conversion of  $C_{60}$  to this product with the longest retention time (a black solid which forms a golden-yellow solution in toluene) has been highly capricious to date for reasons that are presently not clear. The HPLC-isolated yields range from <1-3%.

The laser-desorption time-of-flight (LD-TOF) mass spectrum (Figure 2.3) of the isolated product exhibits a parent peak for  $(C_{60})_2C_2$  (1465.3 amu calc'd., 1466.6 obs.)<sup>2,12</sup> as well as two highly prominent fragments corresponding to  $C_{62}$  (743.9 amu) and  $C_{60}$  (719.4 amu). The use of the matrix 9-nitroanthracene<sup>2,8</sup> did not produce any significant change in the mass spectrum.

The UV-vis spectrum shows two intense fullerene absorptions present at 210 nm and 260 nm (Figure 2.4). No clear absorptions appear in the region 400-700 nm.

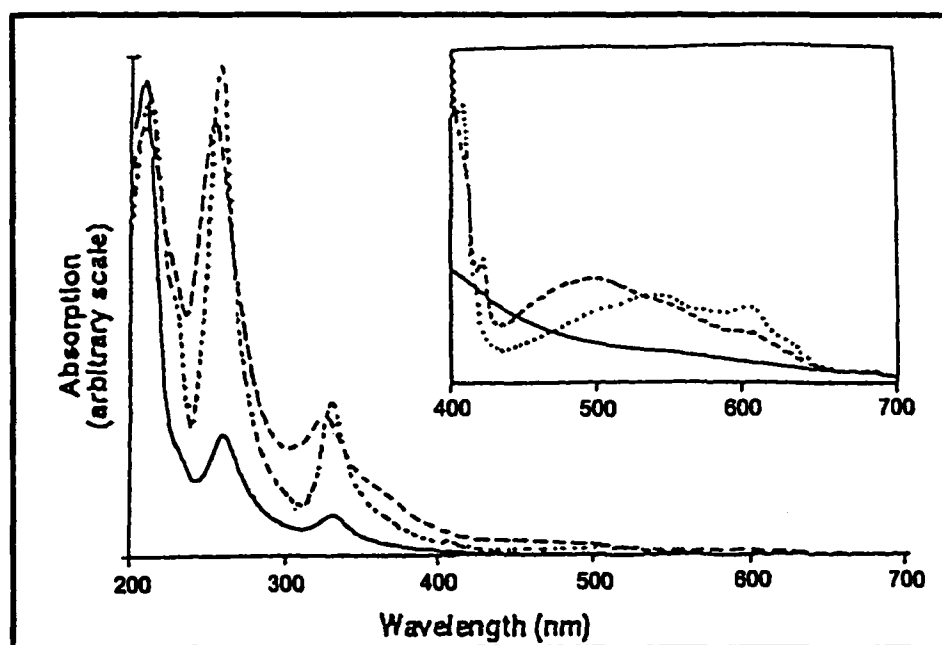


**Figure 2.3.** LD-TOF mass spectrum of **2.1**.



**Figure 2.4.** UV-vis spectrum of **2.1** from 400-700 nm in toluene  
[inset: spectra of **2.1** from 200-700 nm in hexane].

Typically,  $C_{60}$  monoadducts display highly distinctive bands in the visible region;<sup>2,5</sup> however, greatly diminished fine structure is well preceded in the oxo- and methylene-bridged dimeric fullerene analogs,  $C_{120}O^{2.11a}$  and  $C_{121}H_2^{2.11b}$  respectively (Figure 2.5).



**Figure 2.5.** UV-vis spectrum of  $C_{60}$  (...),  $C_{60}O$  (---), and  $C_{120}O$  (-) in hexane (visible region in toluene).

The 100 MHz  $^{13}C$  NMR spectrum affords evidence for the proposed  $D_{2h}$  symmetry of  $(C_{60})_2C_2$ , formed as a result of dimerization of **2.1b**. After several attempts we finally<sup>2.13</sup> acquired a spectrum with adequate signal/noise ratio on a small (0.1 mg) sample synthesized from 10-15% carbon-13 enriched  $C_{60}$ . The  $^{13}C$  labeled NMR sample co-elutes at 20.2 min from the HPLC with non-labeled samples that consistently produce the  $(C_{60})_2C_2$  parent peak in the mass spectrometer. Prolonged NMR acquisition times and poor solubility precluded our use of 1,2-dichlorobenzene- $d_4$  as lock solvent. The spectrum (Figure 2.6) exhibits 15 of the 16 expected resonances (in the region 136-

150 ppm) (Table 2.1); however, we assign two resonances as overlapping (intense peak at 145.1 ppm). The single upfield resonance (60.1 ppm) can be attributed to the skeletal cyclopropane carbons, which integrate to four carbons. The cyclopropylmethylene bridging carbons, at natural abundance, are not observed.

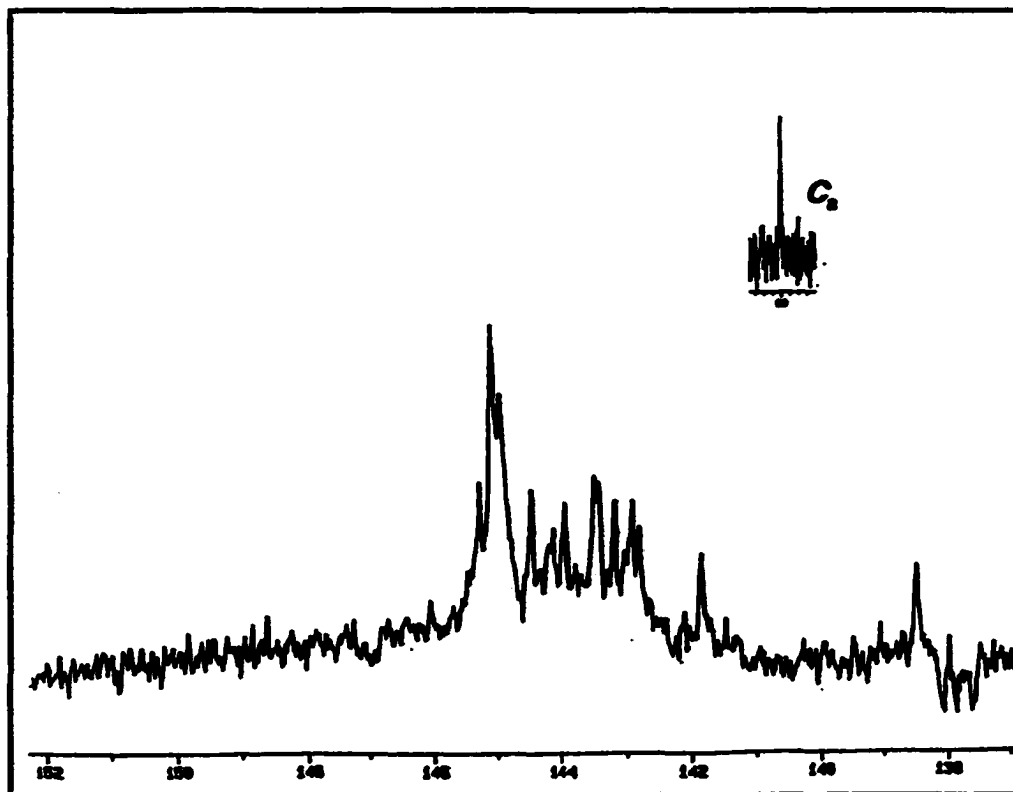


Figure 2.6.  $^{13}\text{C}$  NMR spectrum of 2.1.

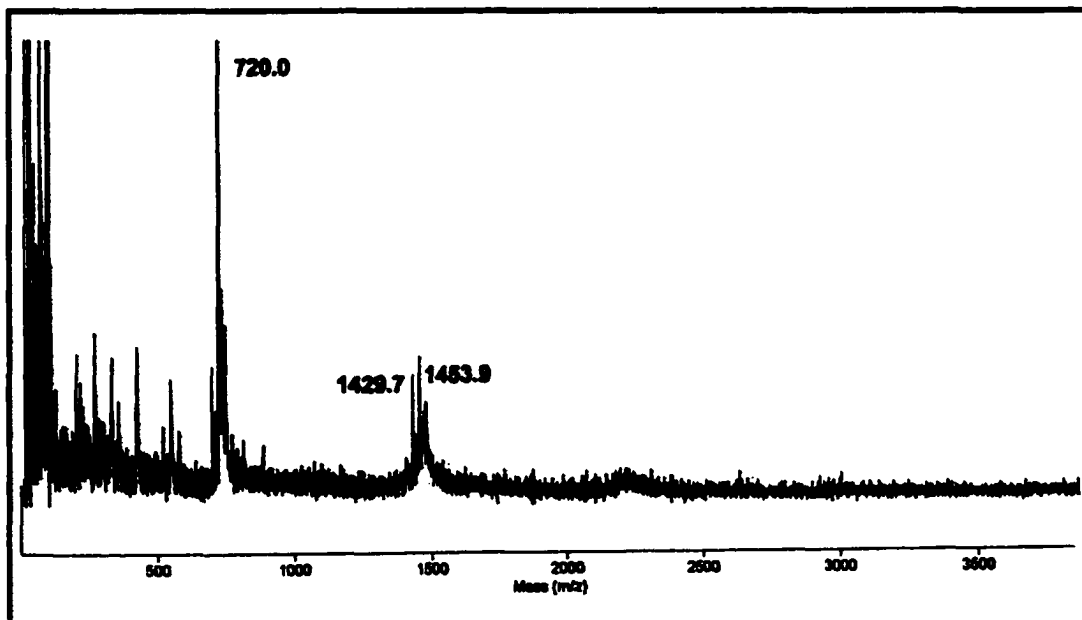
Other products formed in the reaction of 2.1a and  $\text{C}_{60}$  include those found in fractions isolated from a cluster of peaks with HPLC retention times<sup>29</sup> centered at 11 min (100% toluene mobile phase). The LD-TOF mass spectrum of this material (Figure 2.7) exhibits formation of the recently isolated  $\text{C}_{119}$ <sup>2,14</sup> (1429.3 amu calc'd., 1429.7 obs.) as well as sought-after allotrope  $(\text{C}_{60})_2\text{C}$  (1453.3 amu calc'd., 1453.9 obs.), (Figure 2.2). One current challenge is determining the origin of  $\text{C}_{119}$  and  $(\text{C}_{60})_2\text{C}$ ; i.e., and

determining if the species are produced in the mass spectrometer from isolable precursors or can be directly obtained via the reaction of C<sub>60</sub> and 2.1a.

**Table 2.1.** <sup>13</sup>C NMR data for 2.1 (*o*-dichlorobenzene-*d*<sub>4</sub>).

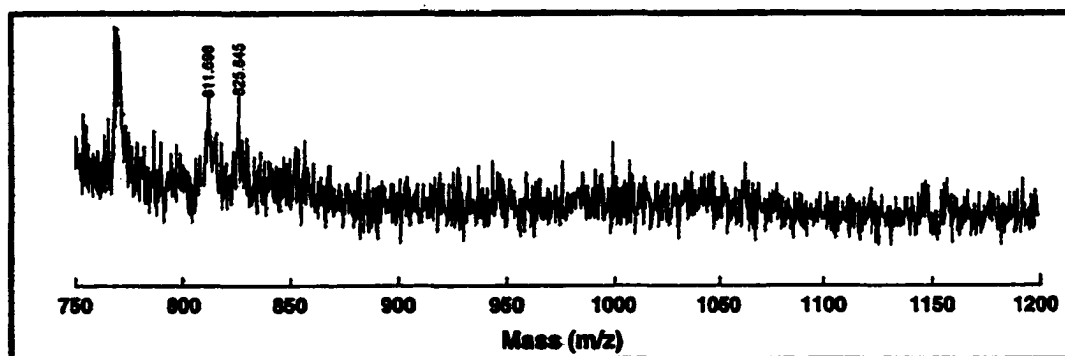
Compound 1					
$\delta$ (ppm)	#C	$\delta$ (ppm)	#C	$\delta$ (ppm)	#C
145.31	8	143.95	8	142.81	8
145.12 <sup>a</sup>	16	143.51	8	141.86	8
144.97	8	143.30	8	138.51	8
144.49	8	143.20	8	60.10	4
144.30	4	143.00	4		
144.15	6	142.93	8		

(a) Represents close or overlapping resonances



**Figure 2.7.** LD-TOF mass spectrum of C<sub>119</sub> and C<sub>121</sub>.

Mass spectrometric analysis indicates the presence, also in fractions of material centered at 11 min., of either  $C_{61}(C_6H_6)$ , or  $C_{61}(C_7H_8)$ , (Figure 2.8), whose selective appearance is dependent on the choice of benzene or toluene as reaction solvent, respectively.<sup>2,15</sup> Importantly, the formation of solvent adducts offers further evidence of the reaction intermediate **2.1b**, the monomer of **2.1**.



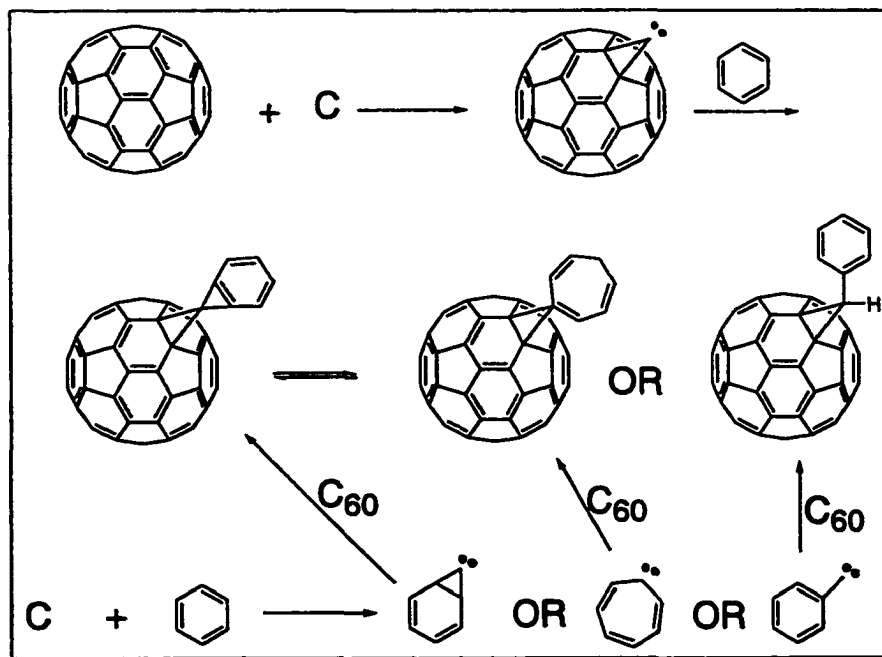
**Figure 2.8.** LD-TOF mass spectrum of solvent adducts of  $C_{60}$ .

The formation of solvent adducts could occur via carbene addition or insertion of **2.1b** to solvent. Alternatively, the  $C_{60}$  + carbon = solvent products might potentially arise via initial reaction of atomic carbon with benzene or toluene followed by trapping  $C_{60}$  (Scheme 2.2). We also cannot rule out the potential formation of and  $C_{122}$  via insertion of  $C_2$  between two  $C_{60}$  molecules.

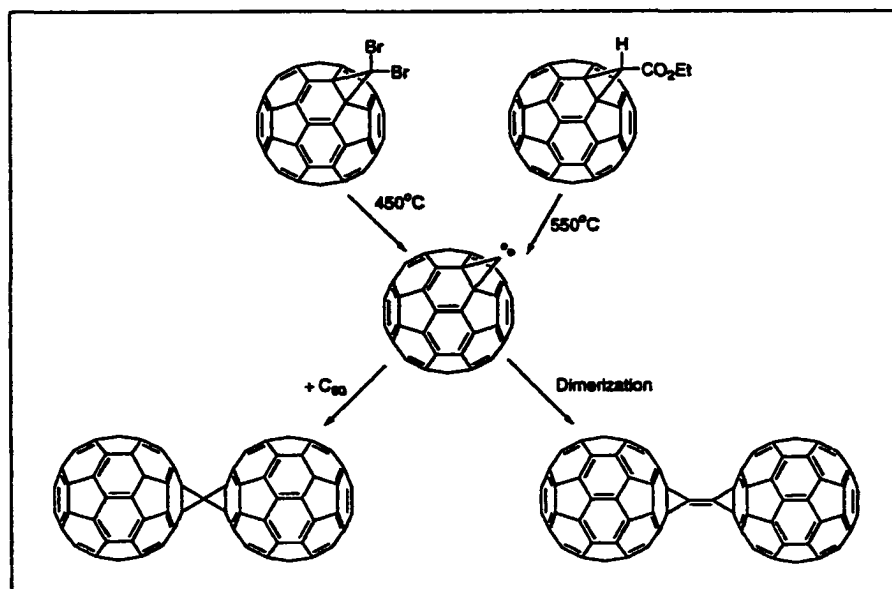
Following our report Dragoe and co-workers published an alternative synthesis of  $C_{121}$  and  $C_{122}$ .<sup>2,16</sup> The reaction was performed via a solid state thermolysis of  $C_{60}CBr_2$  and  $C_{60}$  at  $450^\circ C$  (Scheme 2.3). The product obtained was a mixture detected by gel permeation chromatography. The yield of  $C_{121}$  was reported as 10% and the yield of



$C_{122}$  was decreased with an increase in the  $C_{60}/C_{60}CBr_2$  ratio. Scanning tunneling microscopy was used to prove the existence of dumbbell like structures.



**Scheme 2.2.** Pathways for the reaction of solvent molecules and carbon with  $C_{60}$ .



**Scheme 2.3.** Drago's synthesis of  $C_{121}$  and  $C_{122}$ .

## 2.3 Conclusions

We have performed the first synthesis of  $(C_{60})_2C_2$  (2.1) in isolable amounts. We have presented spectroscopic evidence consistent with a dimeric  $D_{2h}$ -symmetric structure. The reaction of  $C_{60}$  with diazotetrazole also leads to several other products observed by mass spectrometry, including the carbon allotropes  $C_{119}$  and  $(C_{60})_2C$  as well as  $C_{61}(C_6H_6)$  and  $C_{61}(C_7H_8)$ .

## 2.4 Experimental Procedures

**General.** Isotopically labeled (10-15%  $^{13}C$ ) fullerenes were purchased from MER Corporation, Tucson, Az. Enriched  $C_{60}$  was isolated via the method of Tour<sup>2,17</sup>. The remaining chemicals were reagent grade (Aldrich) and were used without further purification. The  $^{13}C$  NMR spectrum was acquired with a Bruker AM-400 spectrometer. A Beckman DU-7 spectrophotometer was used to obtain UV-vis spectra. All laser-desorption mass spectra were acquired with a PerSeptive Biosystems Voyager linear laser-desorption time-of flight mass spectrometer equipped with a nitrogen laser (337 nm) and operated in positive ion mode. The accelerating voltage was held at 28 kV. A one-point calibration of the mass spectrometer was performed using  $C_{60}$ .

**Preparation of  $(C_{60})_2C_2$  (2.1).** Diazotetrazole was formed via slow addition of concentrated HCl (0.4 mL) to a solution of 5-aminotetrazole monohydrate (0.082 g, 0.79 mmol, 11 equiv) in THF (1.5 mL) followed by addition of isoamyl nitrite (0.1 mL, 0.74 mmol, 11 equiv) at 5 °C.<sup>2,7</sup> This solution was poured into diethyl ether (2 mL) and water (2 mL). The layers were quickly separated and the organic layer immediately added to a solution of  $C_{60}$  (0.050g, 0.069 mmol, 1 equiv) in benzene or toluene (40 mL) and heated to reflux. Upon cooling, the mixture was filtered through a 1 inch pad of

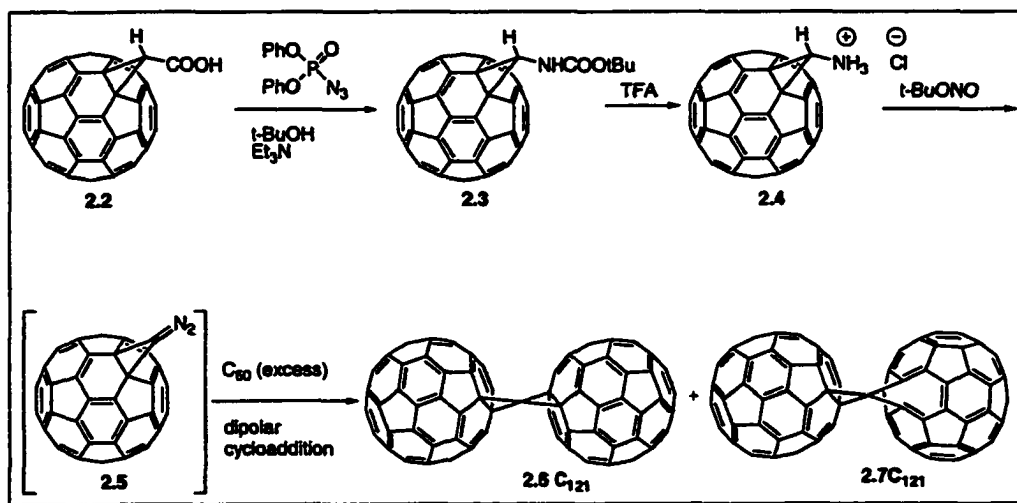
SiO<sub>2</sub> with toluene as elutant. Fourteen HPLC peaks were observed (Cosmosil Buckyprep column, 4.6 x 250 mm, 10% hexane/toluene mobile phase, flow rate 1 mL/min, monitored at  $\lambda=325$  nm): 15.0 (C<sub>60</sub>), 17.9, 18.8, 20.5, 21.4, 24.9, 28.0, 29.6, 33.3, 34.9, 39.1, 41.4, 46.4, 50.9, 56.9 and 63.0 (2.1) min. (C<sub>60</sub>)<sub>2</sub>C<sub>2</sub> (2.1) was isolated employing 100 % toluene as the mobile phase (20.2 min retention time) and obtained in 3 % yield (3.0 mg, 0.0021 mmol). C<sub>119</sub>, 2.2, and solvent adducts were observed by LD-TOF mass spectrometry in fractions isolated from a cluster of peaks centered at 11.0 min. The carbon-13 NMR data for 2.1 is shown in Table 2.1.

## 2.5 Future Studies

A great challenge in synthesizing dimeric fullerenes is to overcome relatively poor yields and solubility, factors which greatly hinder product characterization. One proposed objective for future work is an extensive investigation of new organic syntheses of fullerene dimers. The expected outcomes are (i) improved yields (ii) alternative syntheses of isomeric products to aid in product characterizations and (iii) the development of mild new synthetic methods.

We plan to isolate and study the other products of the reaction of carbon and C<sub>60</sub> and improve yields and control product distribution. For example, we have recently employed milder (one-pot) atomic carbon reaction conditions which afford a new (potentially) dimeric product in 40 % yield. Our collaborators at the University of Tokyo have already begun working with us towards characterizing and isolating carbon/C<sub>60</sub> reaction products via MALDI, nano-, electrospray and TGA mass spectrometry as well as automated HPLC isolation and purification.

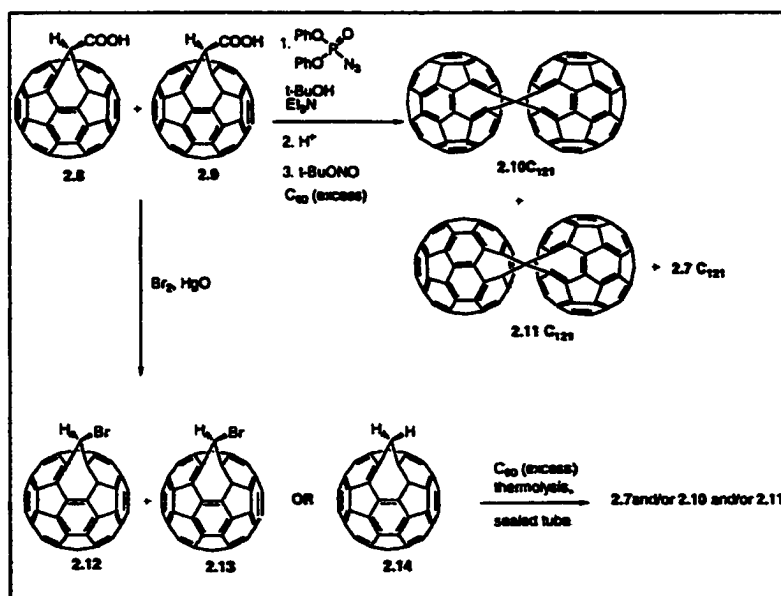
We plan to develop new fullerene chemistry. One goal is to produce the new diazomethanofullerene **2.5** via the methanofullerene amine salt **2.4** to be obtained via the carbamate **2.3** from known **2.2** (Scheme 2.4). The proposed conversion of **2.2** to **2.3** is via a classic carbon-nitrogen rearrangement; thus numerous alternative reagents and conditions are available in case, for instance, the azide moiety reacts preferentially with the fullerene sphere.<sup>2,18</sup> Key intermediate **2.5** should react with  $C_{60}$  to furnish the  $C_{121}$  isomers **2.6** and **2.7** and the  $C_{122}$  analogues. The advantage of producing  $C_{121}$  via this new proposed method is that it is potentially more controlled, milder approach than previously reported both by us (*vide supra*)<sup>2,19</sup> and our collaborators in Tokyo (solid-phase high temperature thermolysis).<sup>2,16</sup>



**Scheme 2.4.** Proposed synthesis of  $C_{121}$ .

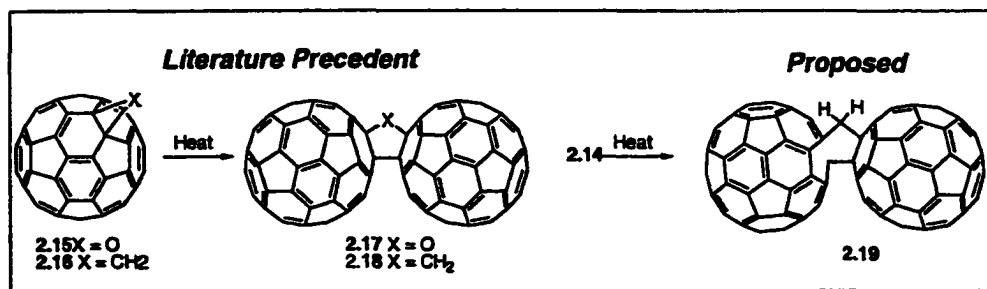
We are also proposing a new means to attain enriched amounts of fulleroid isomers of  $C_{121}$ . The production of enriched amounts of these isomers via alternative methods should greatly aid the characterization of complex product mixtures obtained by present methods (*vide supra*).<sup>2,19,2,16</sup> It would further promote property studies of

these isomers including electronic interactions between the fullerene cages<sup>2,20</sup> (i.e., potentially better, but presumably at least different orbital overlap relative, for example, to spiropentane 2.6). Fulleroid dimers should also be easier to convert to unique coalesced (merged-cage) fullerenes,<sup>2,21</sup> based on their already partially-opened structures. Our approach, based on known fulleroid starting materials 2.8 and 2.9<sup>2,22</sup> (using chemistry exactly as described above for isomer 2.2) should directly afford 2.7, 2.10, and/or 2.11 in solution. Alternatively, Hunsdieker reaction<sup>2,23</sup> of 2.8 and 2.9 followed by thermolysis should yield bromofulleroids 2.7, 2.10, and/or 2.11 via the thermolysis methods developed by our collaborators in Tokyo (Scheme 2.5).<sup>2,16</sup> An alternative route to 2.8 and 2.9 is via treatment of C<sub>60</sub> with bromodiazomethane.<sup>2,24</sup> A potential problem with 2.8 and 2.9 is that they might isomerize<sup>2,22,2,25</sup> to the corresponding cyclopropanes upon heating prior to reacting with C<sub>60</sub>. If this should occur, parent fulleroid 2.14,<sup>2,26</sup> which doesn't thermally convert to the cyclopropane isomer, could be employed. Compound 2.14 can be made on multigram scale.<sup>2,27</sup>



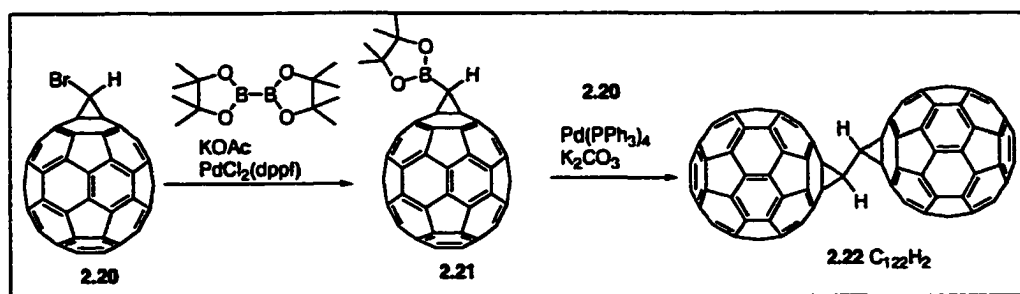
**Scheme 2.5.** Proposed synthesis of coalesced fullerenes.

Milder heating of **2.14** in the presence of  $C_{60}$  could also afford a unique  $C_{121}H_2$  coalescence (already partially cage-opened) precursor, **2.17** (Scheme 2.6). This would be in accord with known reactions to afford  $C_{120}O^{2.28,2.29}$  and  $C_{121}H_2^{2.28}$ . Physical property studies of each of the proposed targets described in this section (coalescence, intercage electronic interactions, solid state structures) would be collaborative efforts.



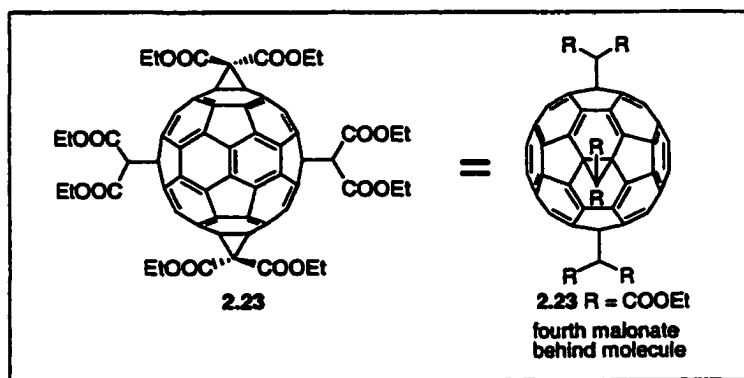
**Scheme 2.6.** Proposed synthesis of  $C_{121}H_2$ .

Another potential goal will be the application of mild Suzuki coupling methods<sup>2.30</sup> towards the synthesis of bridged dimers (Scheme 2.7). It is known that halocyclopropanes can undergo Suzuki coupling reactions.<sup>2.31</sup> Our research group has previously employed Suzuki couplings towards the synthesis of oligomeric arenes and three-dimensional conjugated organic materials.<sup>2.32</sup> This study would lead to not only new routes to dimers but unique fullerene functionalization chemistry. Preliminary studies of the Suzuki reactions of **2.20** are presented in Chapter 3.



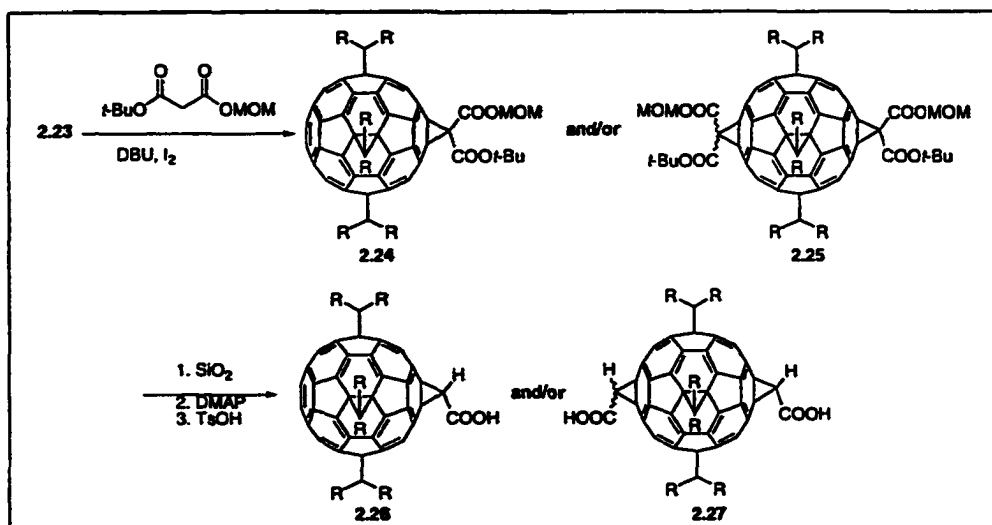
**Scheme 2.7.** Proposed synthesis of bridged dimers via Suzuki coupling.

In order to attain conducting materials or fullerene tubes to be produced via coalescence of cage-linked subunits, the synthesis of longer oligomeric materials will be necessary. The synthesis of oligomeric analogues of the dimers poses huge challenges involving product solubility, isolation and characterization. A goal will thus be the synthesis of materials with pendant solubilizing moieties. The placement of solubilizing groups on the  $C_{60}$  sphere presents the problem of reaction regioselectivity. In order to overcome this difficulty, we plan to employ known **2.23**<sup>2,33</sup> (Figure 2.9) as our main oligomerization template since it is well-known that reactions typically occur at the remaining octahedral sites of malonate-derived fullerenes.<sup>2,34</sup> Compound **2.23** has only two equivalent octahedral sites remaining, both of which are symmetry-equivalent.



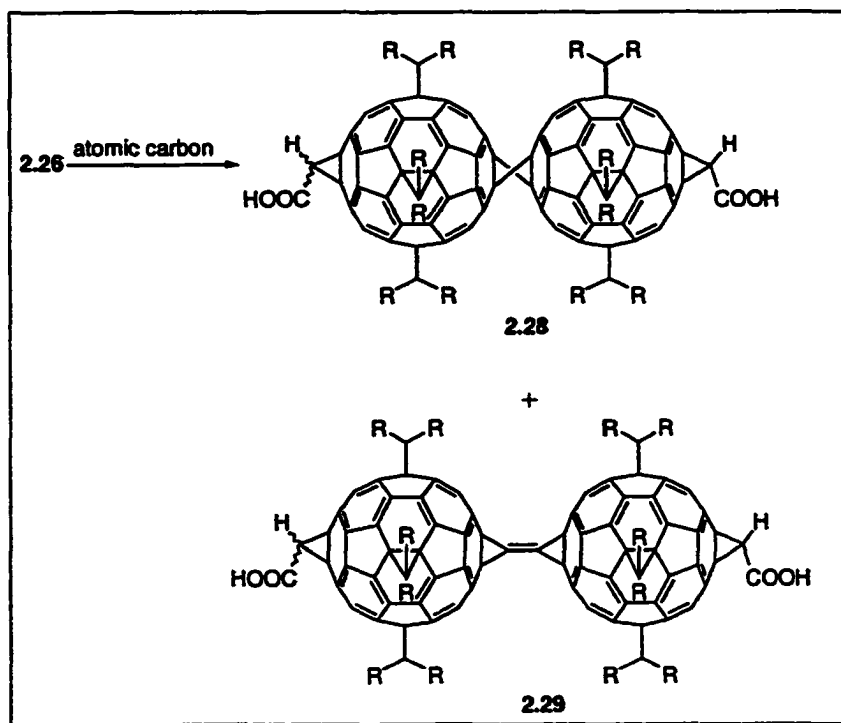
**Figure 2.9.** Structure of malonate fullerene derivative.

Studies would begin with the transformation of known compound **2.23** to **2.24** and **2.25** via Bingel reaction<sup>2,35</sup> with the mixed diester (Scheme 2.8). Hydrolysis of the MOM ester on silica gel<sup>2,36</sup> followed by decarboxylation with DMAP<sup>2,34</sup> and hydrolysis of the *t*-butyl ester with TsOH<sup>2,37</sup> should afford **2.26** from **2.23** and **2.26** from **2.24**.



**Scheme 2.8.** Proposed synthesis of oligomeric fullerene adducts.

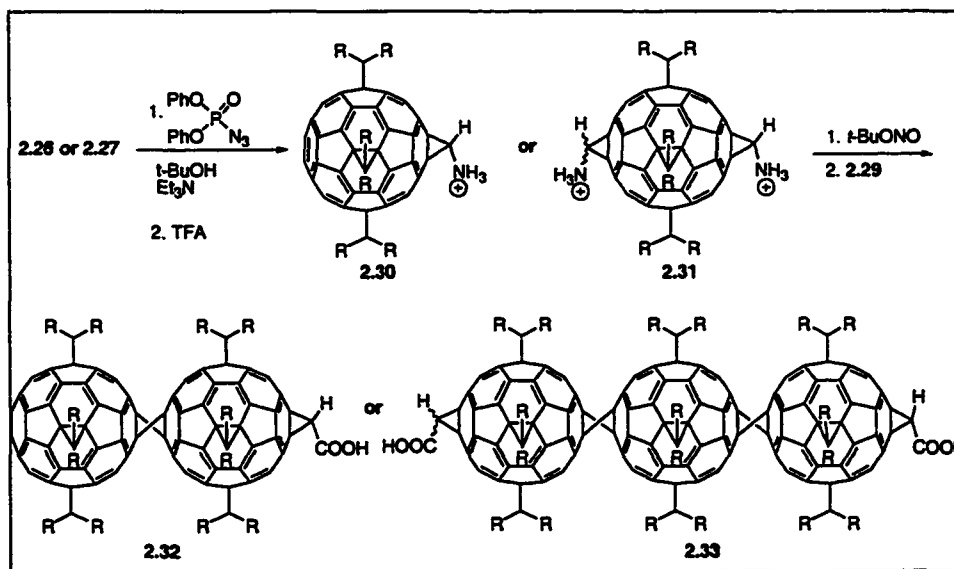
The reaction of **2.26** with atomic carbon via our published protocols<sup>2,19</sup> should furnish the relatively soluble dimers **2.28** and **2.29** (Scheme 2.9).



**Scheme 2.9.** Proposed synthesis of solubilized fullerene dimers.

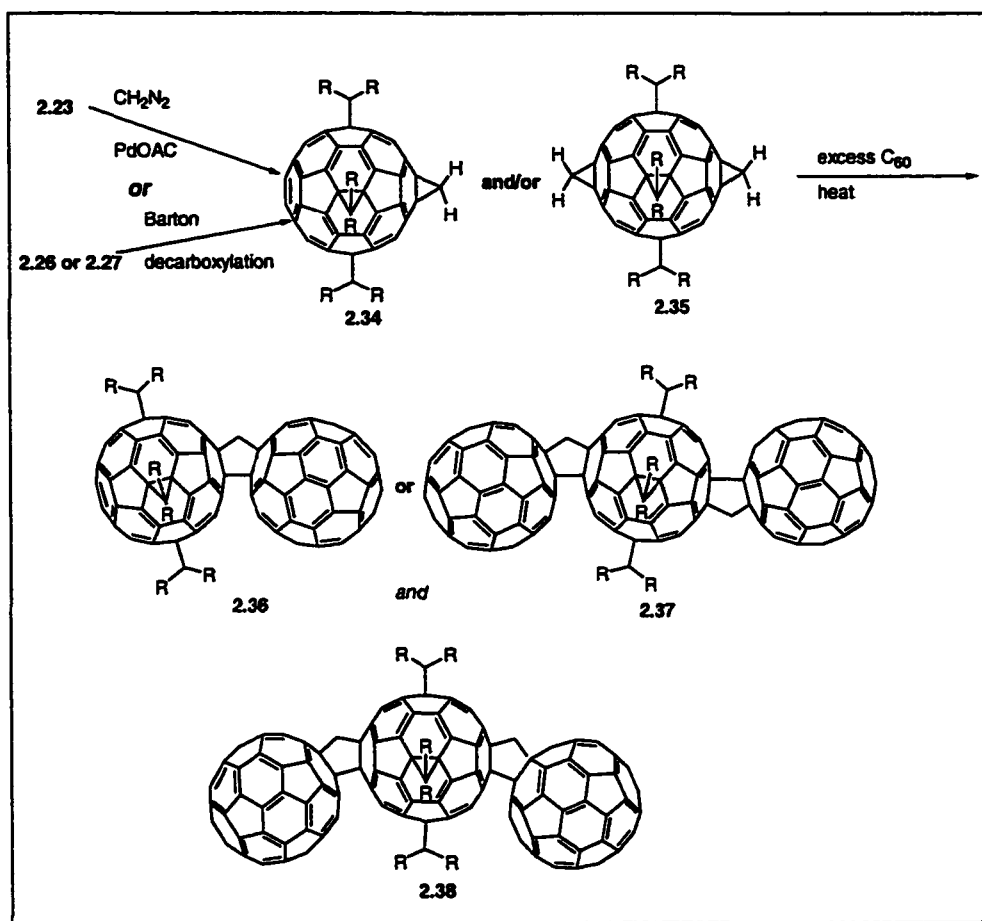


We will employ our proposed new fullerene reaction, employing a rearrangement followed by diazotization, to afford soluble bis- and tris-fullerenes **2.32** and **2.33** from **2.30** and **2.31**, respectively (Scheme 2.10). The relative proportions of **2.30** and **2.31** should be controllable by reaction stoichiometries. In any case, they will be separable. For the transformation of **2.31** to **2.33**, excess **2.26** would be used.



**Scheme 2.10.** Proposed synthesis of bis- and tris- fullerene adducts with solubilizing groups.

Compound **2.23** will also be utilized towards the synthesis of bis- and tris-cyclopentanofullerenes **2.38** and **2.37** (Scheme 2.11). Cyclopropanation at the octahedral sites of **2.23** should furnish **2.34** and **2.35**, employing palladium acetate/diazomethane.<sup>2.25</sup> The corresponding fulleroids may be of interest as well. To obtain the corresponding fulleroids, diazomethane could be used without palladium.<sup>2.26</sup> An alternative proposed approach to **2.34** and **2.35** derives from the Barton decarboxylation of **2.26** and **2.27** (*N*-hydroxypyridine-2-thione, tributyltin hydride).<sup>2.38</sup>

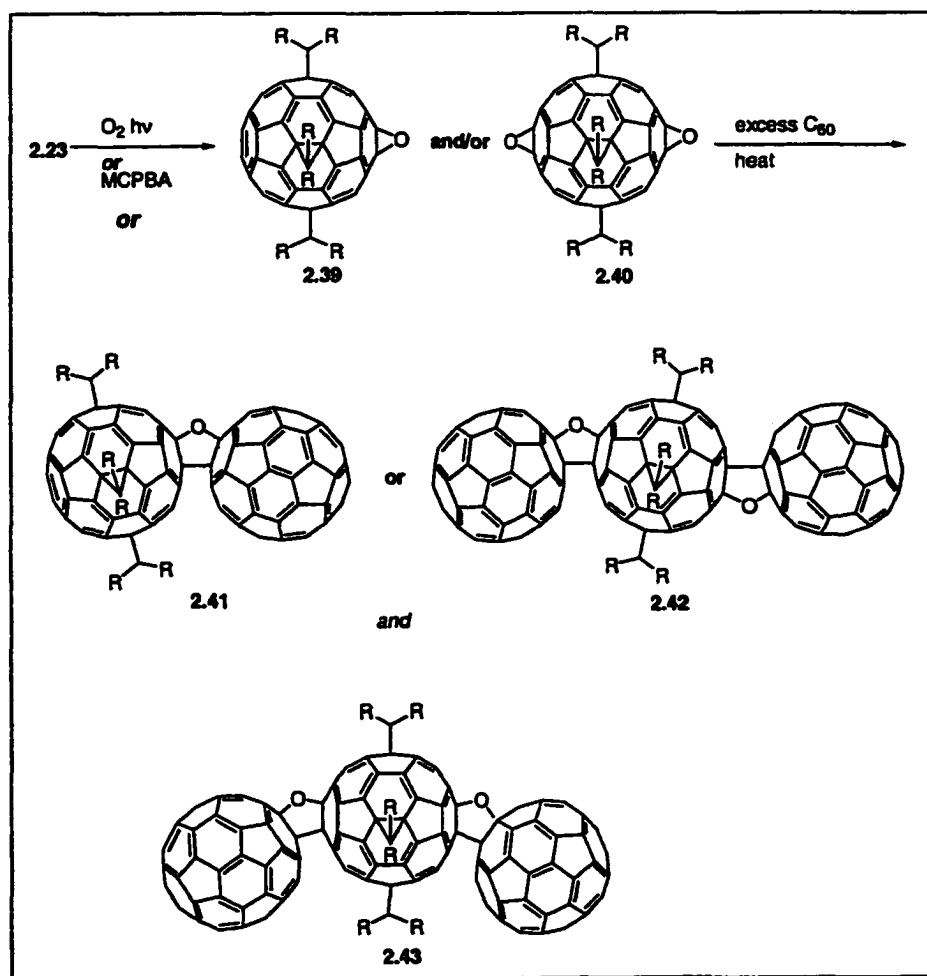


**Scheme 2.11.** Proposed synthesis of bis- and tris- cyclopentafullerenes.

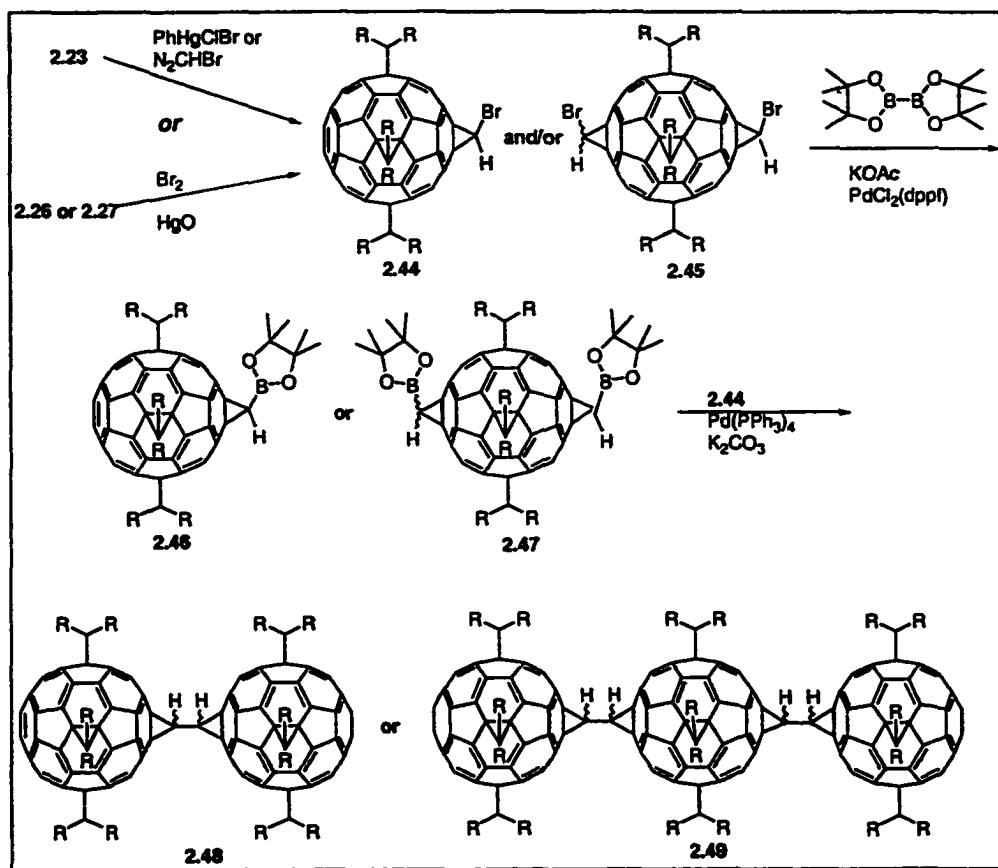
In a similar fashion, the oxygenated analogues (2.39-2.41) of 2.38 and 2.37 will be obtained via epoxidation of 2.23 followed by thermolysis (Scheme 2.12). The bis- and tris-fullerenes 2.48 and 2.49 will be synthesized via bromocarbene reaction of 2.23 (Seyferth conditions or bromodiazomethane) or, alternatively, Hunsdieker reaction of 2.26 or 2.27 followed by Suzuki coupling chemistry (Scheme 2.13).

The fundamental properties of the unique di- and trimeric materials produced would be studied (with our collaborators in Japan and Europe) to probe (i) electrochemical properties, including retro-Bingel reactions (precedented to remove malonate groups with related monomeric fullerenes to furnish the parent

hydrocarbons),<sup>2,39</sup> electron accepting character and electronic communication between the fullerene spheres as well as (ii) solid state structure and thermal behavior (e.g., orientational ordering transitions), allied with microscopy and X-ray scattering studies and (iii) coalescence of the spheres via treatment with heat and/or radiation.



**Scheme 2.12.** Proposed synthesis of oxygenated analogs of **2.38** and **2.37**.



**Scheme 2.13.** Proposed synthesis of bis- and tris- fullerenes.

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- 2.4 Gromov, A.; Ballenweig, S.; Geisa, S.; Lebedkin, S.; Hull, W. E.; Kratschmer, W. *Chem. Phys. Lett.* **1997**, 267, 460.
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- 2.12 PerSeptive Biosystems Voyager linear laser-desorption time-of-flight mass spectrometer equipped with nitrogen laser (337 nm): instrument error = 0.1%.
- 2.13 The  $^{13}C$  NMR spectrum was acquired with 1,020,499 scans, a 0.5s relaxation delay, and 0.1 equiv of  $Cr(acac)_3$  spin relaxant in the sample solution.
- 2.14 Gromov, A.; Ballenweig, S.; Giesa, S.; Lebedkin, S.; Hull, W. E.; Kratschmer, W. *Chem. Phys. Lett.* **1997**, 267, 460.
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## CHAPTER 3.

### PROGRESS TOWARDS THE DEVELOPMENT OF NEW SYNTHETIC METHODOLOGY TOWARDS THE FIRST SUZUKI COUPLING OF ARYLBORONIC ACIDS TO METHANOFULLERENES

#### 3.1 Introduction

One of the future research goals presented in Chapter 2 was the investigation of new coupling chemistry to afford fullerene-derived electronic materials. We have begun investigating methanofullerene carbon-carbon bond formation via palladium-catalyzed cross coupling reactions. Coupling reactions between organoboron compounds and organic halides or triflates, the Suzuki coupling reaction, is versatile due to the availability of reagents and mild reaction conditions. Some of the advantages of the Suzuki coupling reactions are: (1) being largely unaffected by the presence of water, (2) enduring a wide range of functional groups, and (3) proceeding regio- and stereoselectively. Suzuki couplings are also efficient for industrial processes since the inorganic by-products produced are non-toxic and easily removable.<sup>3,1</sup> There have been no reports of a successful Suzuki coupling employing a methanofullerene.

We have begun investigating Suzuki couplings using the monohalocarbene C<sub>60</sub> derivative, 1'-bromo-1,2-methano[60]fullerene (Figure 3.1).

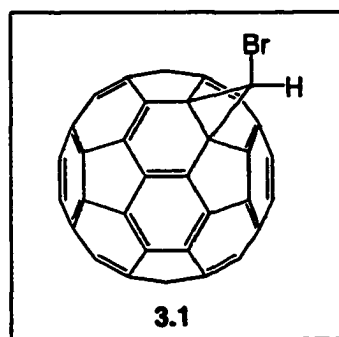
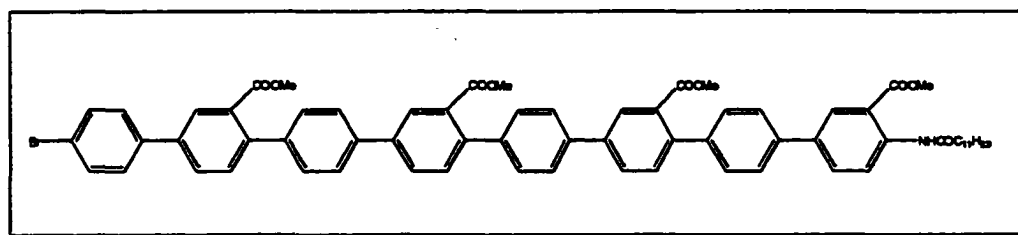


Figure 3.1. Structure of 1'-bromo-1,2-methano[60]fullerene.



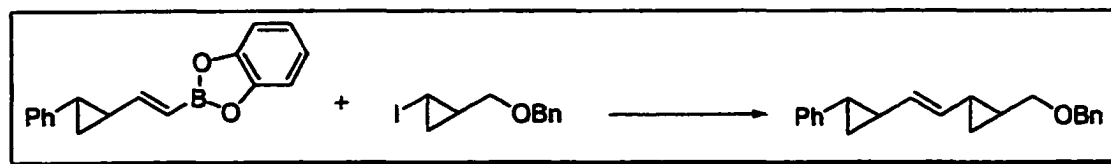
This compound was first synthesized by our collaborators, Dragoe and co-workers at the University of Tokyo.<sup>3,2</sup> Compound 3.1 may also be used as an intermediate for the formation of the C<sub>61</sub> carbene which can be used for addition-substitution reactions.

Our research group at LSU has previously published two accounts of new Suzuki coupling methodology which feature the creation of oligophenylene-derived molecular wires (Figure 3.2).<sup>3,3</sup> The reaction of appropriately-functionalized coupling partners could thus potentially lead to oligomeric or polymeric fullerenes with applications as novel conducting and optical materials. These studies are aligned with our reported dimerization reactions offering alternative pathways to forming cage-joined fullerenes.



**Figure 3.2.** Oligo(*p*-phenylene) rigid rod.

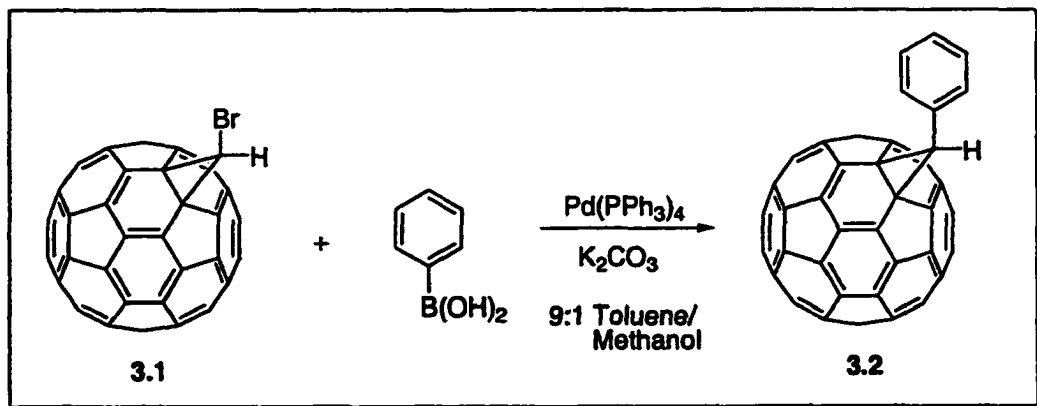
We envisioned that 3.1 would indeed serve as a suitable Suzuki coupling partner since cyclopropyl halides have been successfully used as reacting partners with boronic acids (Scheme 3.1)<sup>3,4</sup>



**Scheme 3.1.** Suzuki coupling of cyclopropyl halide with boronic acid.

### 3.2 Results and Discussion

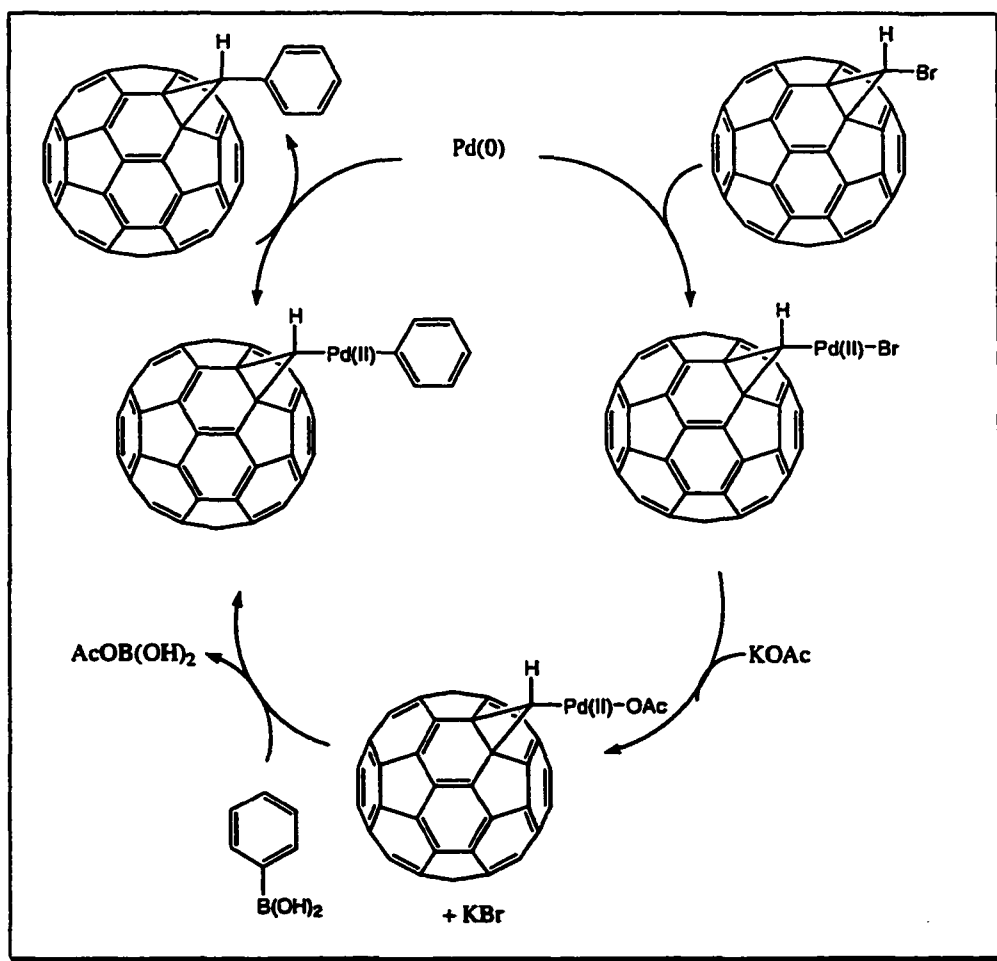
The Suzuki coupling of 3.1 with phenylboronic acid was attempted in our research group (Scheme 3.2).



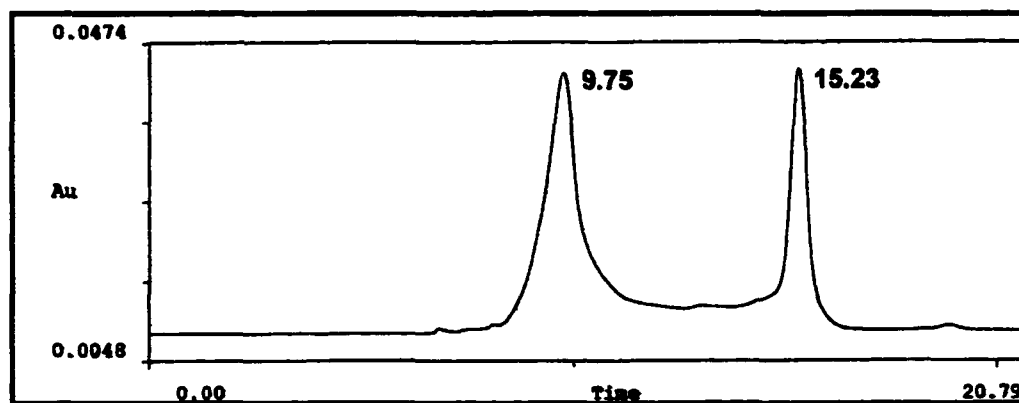
Scheme 3.2. The reaction of 3.1 with phenylboronic acid.

Compound 3.1 (1 equiv) was reacted with phenylboronic acid (1.2 equiv) using a solvent system of 9:1 toluene/H<sub>2</sub>O since fullerenes are soluble in toluene and the base was soluble in water. The reaction mixture was heated for 3 hours at 70° C followed by filtration to remove the catalyst and azeotropic removal of water.

We envision a mechanism analogous to that for standard Suzuki reactions (Scheme 3.3). Oxidative addition<sup>3,5</sup> of the monobromomethanofullerene to a palladium(0) complex gives a stable trans- $\sigma$ -palladium(II) complex. This is followed by the addition of the base, which results in another stable trans- $\sigma$ -palladium complex, which then reacts with the phenylboronic acid via transmetalation. The resulting palladium(II) complex is then converted into 3.2 via reductive elimination. The product from the reaction was analyzed via HPLC using a C18 column. The HPLC trace showed two separate peaks, which were, isolated (Figure 3.3).



**Scheme 3.3.** Proposed mechanism for the formation of 3.2.



**Figure 3.3.** HPLC trace of reaction mixture.

The synthesis of compound **3.2** was done as a model reaction and is currently under extensive characterization. If phenylboronic acid was successfully coupled to  $C_{60}$ , this constitutes the first Suzuki coupling to a methanofullerene. This procedure lays the groundwork for continuing studies in our group.

### 3.3 Experimental Procedures

Preparation of  $C_{67}H_6$ (**3.2**). Phenylboronic acid (0.0028g, .02362 mmol, 1.2 equiv), tetrakis(triphenylphosphine) palladium(0) (0.003g, 0.00059 mmol, 0.03 equiv),  $K_2CO_3$  (0.006g, 0.04330 mmol, 2.2 equiv) and  $C_{61}HBr$  (0.016g, 0.01968 mmol, 1 equiv) obtained from our collaborators in Tokyo,<sup>3,2</sup> were dissolved in 25mL of 9:1 toluene: water. The reaction mixture was heated at 70°C for 3 hours. The resulting mixture was filtered through a silica plug to remove the catalyst. The water was removed by azeotroping the toluene/water mixture. TLC analysis was performed on the resulting mixture using a solvent system of 50:50 hexane:toluene. These studies indicated that the product formed was less polar than the starting material.

Using a C18 HPLC column with a 60:40 toluene:methanol solvent system and a flow rate of 7 mL /min, two peaks were observed at 9.75 minutes and 15.23 minutes. Both peaks were isolated and reinjected on a Cosmosil buckyprep column with a 100% toluene solvent system and a flow rate of 1 mL/min. The 9.75 minute peak from the C18 column contained a mixture of peaks between 3 – 4.2 minutes and a peak at 7.36 minutes. The 15.23 minute peak from the C18 column produced a peak at 7.37 minutes. The 15.23 minute HPLC trace appeared to be more soluble than the starting material in toluene, even though it co-eluted at the same retention time with the starting compound. The characterization of these compounds is ongoing in our laboratory.

### **3.4 Future Work**

Currently, the full characterization of **3.2** is ongoing in our research group.

Our products have been sent to our collaborators at the University of Tokyo for extensive analysis including comparison to known product standards, as produced by other methods. We believe that the formation of **3.2** was potentially successful due to the fact that our product has a higher solubility in toluene than the starting material. We plan to investigate other boronic acids and boronate esters as coupling partners towards the goals discussed on page 29 in Chapter 2.

### **3.5 References**

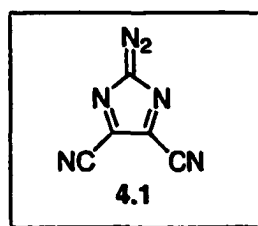
- 3.1 Suzuki, A. *J. Organomet. Chem.*, **1999**, 576, 147.
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## CHAPTER 4.

### THE REACTION OF C<sub>60</sub> WITH 2-DIAZO-4,5-DICYANOIMIDAZOLE

#### 4.1 Introduction

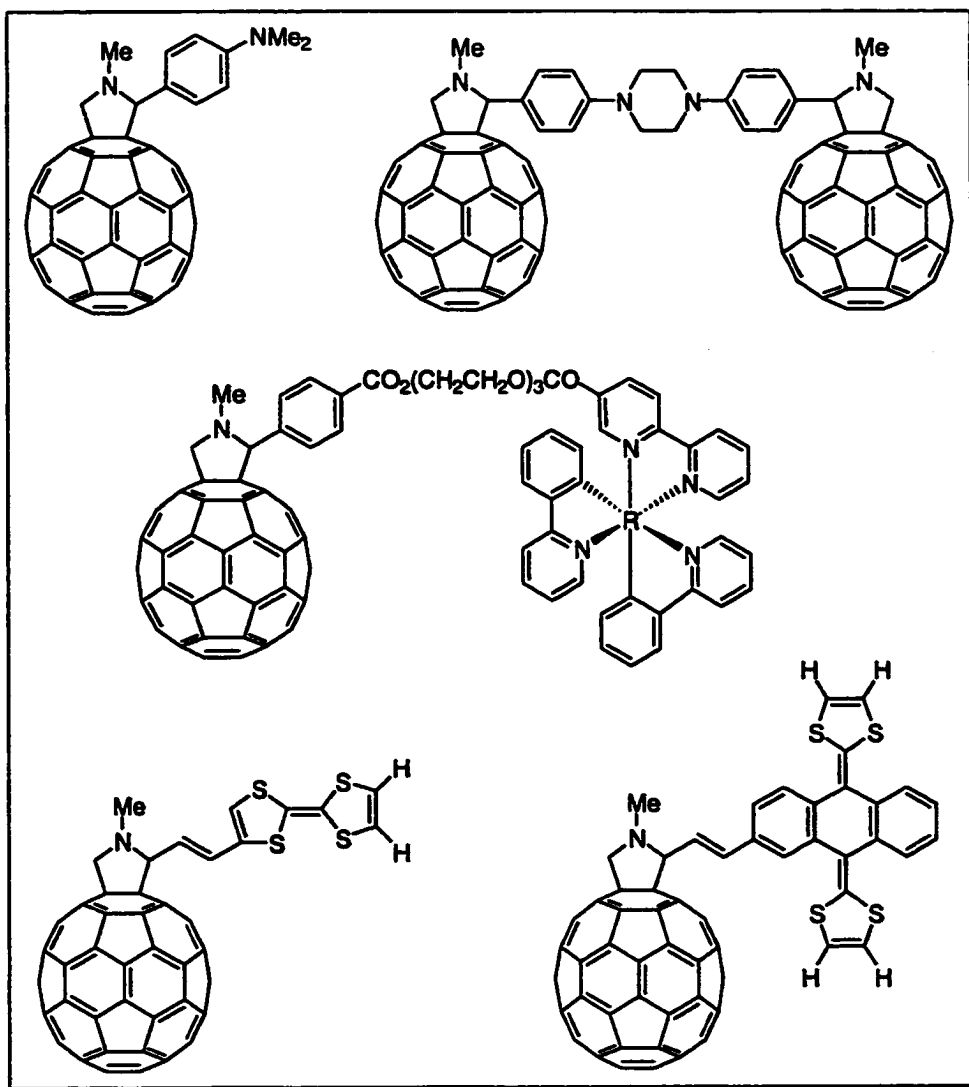
We detected numerous (at least 14) products in the reaction of C<sub>60</sub> with atomic carbon produced by thermolysis of the azoazole diazotetrazole (Chapter 2).<sup>4.1</sup> In order to more fully understand the details of the complex reaction we decided to investigate the interaction of C<sub>60</sub> with other azoazole heterocycles. In collaboration with Professor Paul Rasmussen of the University of Michigan we undertook a study of the reaction of 2-diazo-4,5-dicyanoimidazole (Figure 4.1) with C<sub>60</sub>. Professor Rasmussen has had a long-standing interest in studying nitrogen content materials derived from heterocyclic precursors such as 2-amino-4,5-dicyanoimidazole.



**Figure 4.1.** Structure of 2-diazo-4,5-dicyanoimidazole.

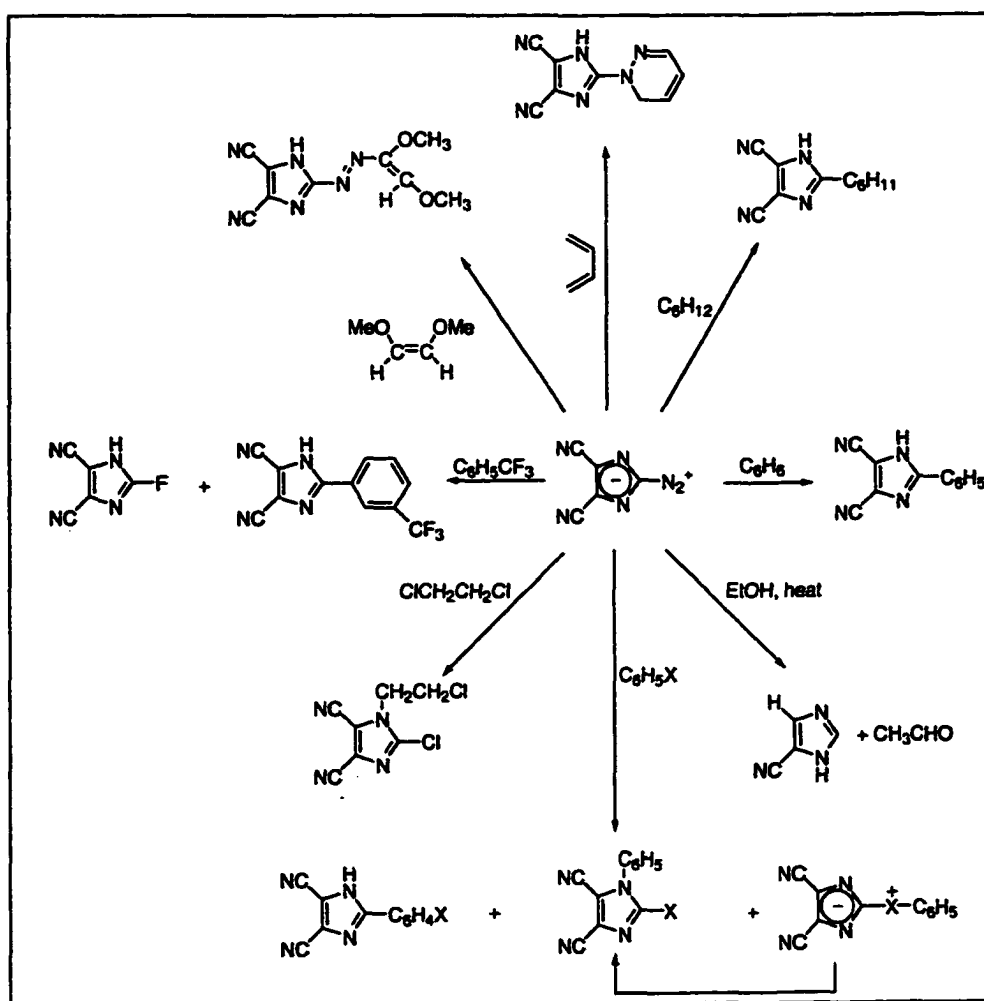
Of further interest is the perturbation of a dicyanoimidazole substituent on the electronic properties of C<sub>60</sub>. There is great current interest in tuning the properties of fullerenes via the appendage of donor or acceptor groups. This work could relate fullerene chemistry to classical benzene chemistry. The addition of electron

withdrawing moieties to fullerenes may have application in charge and light-induced electron transfer. This may prove important in both materials science and biochemistry.<sup>4.2</sup> Most prior efforts have afforded fullerenes with electron donating substituents. The effect of electron withdrawing groups on the electron poor fullerene cage has been less studied. They have been proposed, for instance, as components of photovoltaic cells (Figure 4.2).<sup>4.3</sup>



**Figure 4.2.** Examples of modified fullerenes with enhanced electron affinities.

Dicyanoimidazole compounds are synthesized using the hydrogen cyanide (HCN) tetramer diaminomaleonitrile (DAMN). The synthesis of DAMN was reported by Woodward.<sup>4,4</sup> Sheppard and Webster later divulged the synthesis of 2-diazo-4,5-dicyanoimidazole (4.1).<sup>4,5</sup> Although diazo heterocycles are usually known as moderate to weak electron acceptors, the presence of the cyano groups stabilize 4.1.<sup>4,6</sup> 2-diazo-4,5-dicyanoimidazole is an electrophilic reagent that undergoes a variety of reactions:<sup>4,5</sup> (Scheme 4.1)

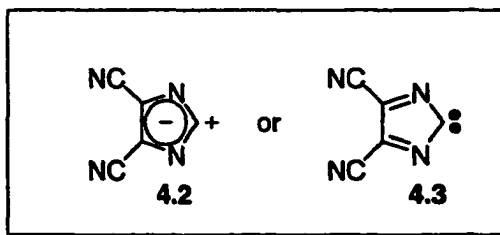


**Scheme 4.1.** Reactions of diazodicyanoimidazole.



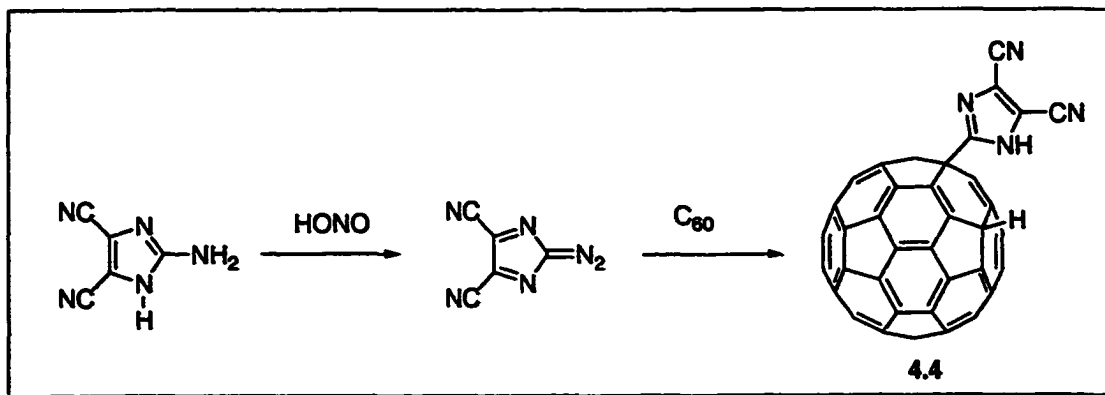
## 4.2 Results and Discussion

Upon thermal reactions promoting loss of  $N_2$  from compound 4.1, a species is generated which can take one of two proposed forms (Figure 4.3). Electrophilic addition to  $C_{60}$  is relatively rare and can result in 1,4-adducts<sup>4,7</sup> while carbene addition results in 1,2 (cyclopropane or annulene-type)-addition patterns.



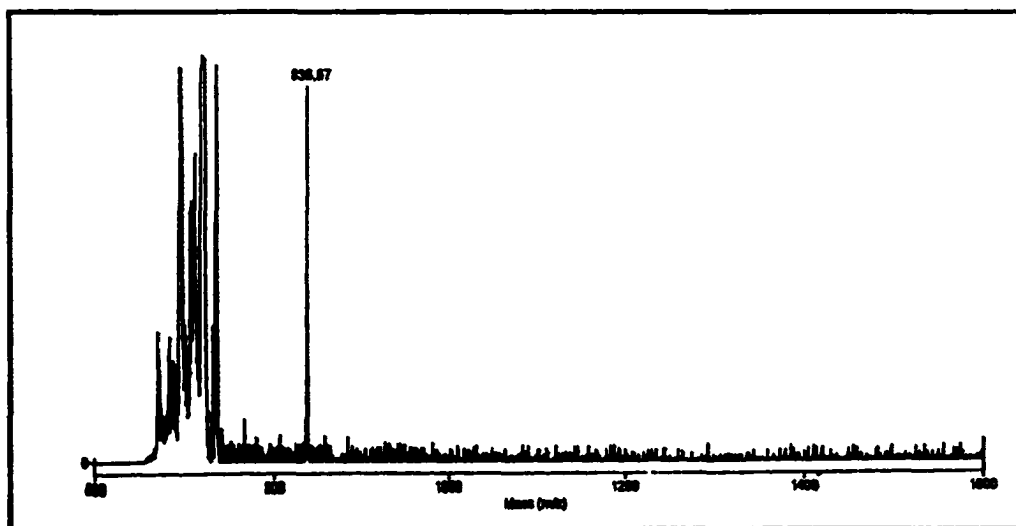
**Figure 4.3.** Intermediates formed from the thermolysis of diazodicyanoimidazole.

The formation of 4.4 (Scheme 4.2) begins with the diazotization of 2-amino-4,5-dicyanoimidazole with  $NaNO_2$  and  $HCl$  in  $H_2O$ .  $C_{60}$  is dissolved in benzene and added to the solution of the diazonium salt and the resultant mixture is heated at reflux. The major monoadduct was isolated using flash column chromatography and observed by HPLC analysis.



**Scheme 4.2.** The reaction of  $C_{60}$  with 2-diazo-4,5-dicyanoimidazole.

The FAB negative ion mass spectrum of **4.4** exhibits a peak at 836.67 (M-H) indicating monosubstitution of the heterocyclic addend.

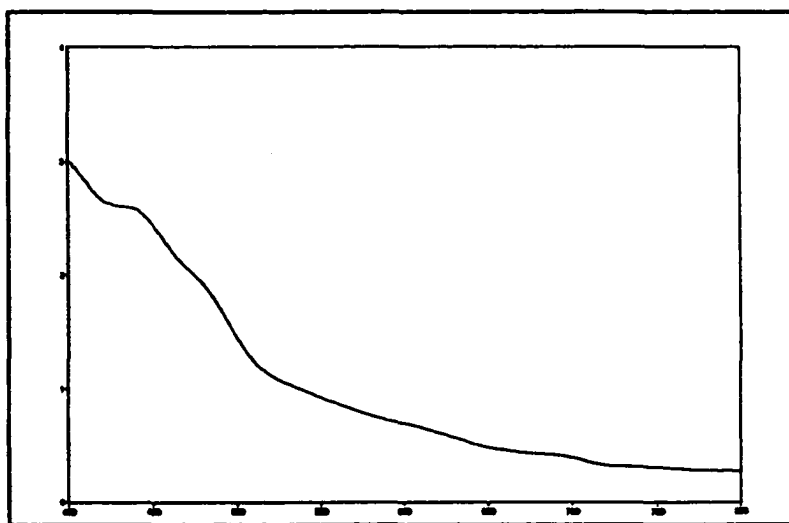


**Figure 4.4.** FAB negative ion mass spectrum of **4.4**.

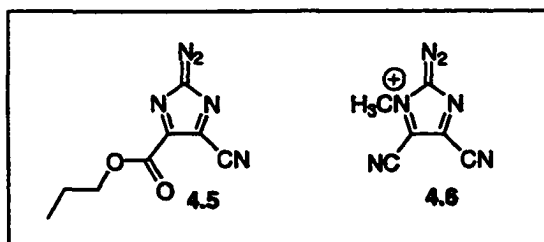
The UV-vis spectrum of **4.4** is characteristic of 1,4-monoadducts, displaying a broad absorption at 440 nm (Figure 3.4). Most diazoalkanes add to  $C_{60}$  furnishing 1,2-adduct cyclopropane and/or annulene (fulleroid or homofullerene) structures which each exhibit highly characteristic, distinct UV-vis spectra.<sup>3,8</sup> The 1,2-derivative of diazodicyanoimidazole would embody a spirocyclopropyl or annulene structure in which the heterocyclic addend would not be aromatic.

The reaction of  $C_{60}$  with other diazoimidazoles **4.5** or **4.6** (Figure 4.5) also results in the formation of isolable products whose UV-vis spectra resembles that of **4.4**. Diazodicyanoimidazole addition to  $C_{60}$  may thus be a general method towards the controlled formation of relatively less-encountered 1,4 fullerene adducts.

Further evidence for the structure assignment of **4.4** derives from NMR spectroscopy. We acquired the  $^{13}C$  NMR via the reaction of 2-diazo-4,5-dicyanoimidazole with a 10-15 % randomly carbon-13 enriched sample of  $C_{60}$ .

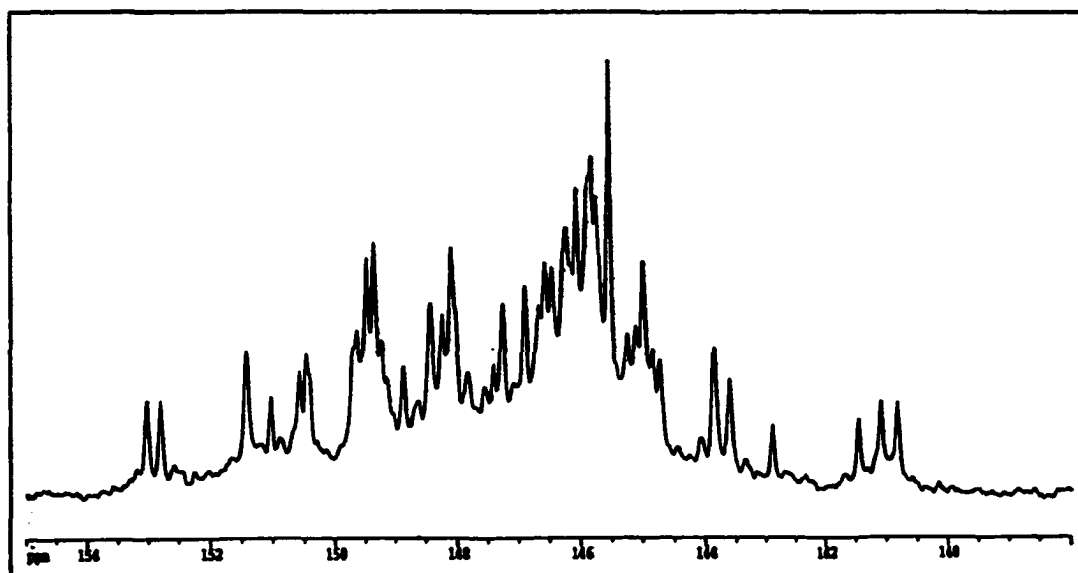


**Figure 4.5.** UV-vis spectrum of 4.4 in toluene.

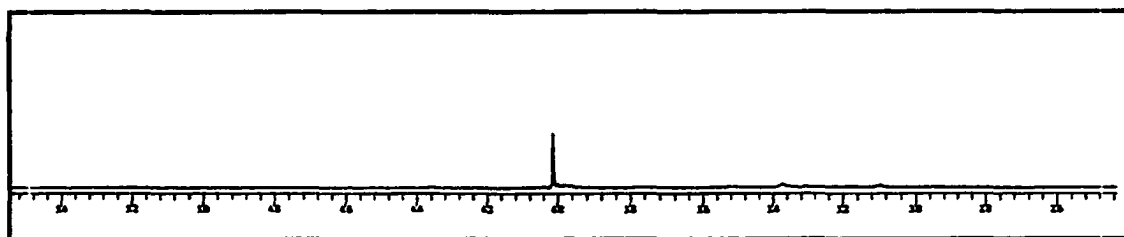


**Figure 4.6.** Structures of analagous imidazoles.

The  $^{13}\text{C}$  NMR of 4.4 exhibits 53 fullerene resonances (of the expected 60) in the aromatic region (Figure 3.6) along with two  $\text{sp}^3$  resonances at 73.9 and 77.9 ppm. The unlabeled heterocycle resonances were too weak to be observed. In addition, the  $^1\text{H}$  NMR spectrum of 4.4 displays a singlet at 4.01 ppm (Figure 3.7), consistent with the chemical shift of protons directly attached to the  $\text{C}_{60}$  sphere. The IR spectrum of 4.4 exhibits the typical fullerene absorptions. The cyano stretches are too weak to be assigned.



**Figure 4.7.** 100 MHz  $^{13}\text{C}$  NMR spectrum of 4.4.



**Figure 4.8.** 250 MHz  $^1\text{H}$  NMR spectrum of 4.4.

### 4.3 Conclusions

In conclusion, we have performed the synthesis of an isolable amount of the less encountered 1,4 monoadduct resulting from the addition of 2-diazo-4,5-dicyanoimidazole to [60]fullerene. We have presented spectroscopic evidence consistent with 1,4 adduct formation. Initial studies with related diazo imidazoles indicate the formation of similar 1,4 adducts and these experiments are ongoing in our laboratory.

#### 4.4 Experimental Procedures

**General.** Isotopically labeled (10-15%  $^{13}\text{C}$ ) fullerenes were purchased from MER Corporation, Tucson, Az. Enriched  $\text{C}_{60}$  was isolated via the method of Tour. All chemicals were reagent grade (Aldrich) and were used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were acquired with Bruker AC-200, Bruker AC-250, or Bruker AM-400 spectrometers. A Beckman DU-7 spectrophotometer was used to obtain UV spectra. FAB mass spectra were acquired with a Finnigan MAT 900 double focusing mass spectrometer or a Finnigan TSQ-70 triple quadrupole mass spectrometer equipped with a liquid SIMS ionization source.

**Preparation of  $\text{C}_{65}\text{N}_4\text{H}_2$  (4.4).** The formation of 2-diazo-4,5-dicyanoimidazole was achieved via the addition of  $\text{NaNO}_2$  (0.120 g, 1.739 mmol, 25 equiv, in .25 mL  $\text{H}_2\text{O}$ ) and concentrated  $\text{HCl}$  (0.9 mL) to a solution of 2-amino-4,5-dicyanoimidazole (0.160 g, 1.20 mmol, 1.4 equiv) in  $\text{H}_2\text{O}$  (1.8 mL). To this solution was added 1mL of  $\text{CCl}_4$ . The resultant mixture was added to  $\text{C}_{60}$  (0.050 g, 0.069 mmol, 1equiv) in benzene (25 mL) and heated to reflux. Compound 4.4 was isolated (0.010g, 20%) via flash column chromatography using a gradient elution beginning with 100% hexane and ending with 100% toluene.  $^1\text{H}$  NMR (250 MHz, toluene- $d_6$ )  $\delta$  4.01;  $^{13}\text{C}$  NMR (100 MHz, carbon disulfide) [(a) indicates overlapping resonances]  $\delta$  140.82, 141.09, 141.45, 142.90, 143.60, 143.86, 144.07, 144.73, 144.85(a), 144.99(a), 145.11(a), 145.25(a), 145.54(a), 145.75(a), 145.83(a), 146.06(a), 146.23(a), 146.46(a), 146.57(a), 146.90, 147.27, 147.41, 147.55, 147.83, 148.09, 148.24, 148.43, 148.63, 148.86, 149.23(a), 149.36(a), 149.48(a), 149.64, 150.47, 150.58, 151.03, 151.42, 152.79, 153.03; uv  $\lambda_{\text{max}}$  440 nm (Toluene) FAB MS 836.67 obs.(M-H), (838.03 calc'd).

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## CHAPTER 5.

### PROGRESS TOWARDS UNDERSTANDING THE COLOR AND FLUORESCENCE DETECTION OF BIOMOLECULES WITH NOVEL CHROMOPHORES

#### 5.1 Introduction

In addition to our work involving  $C_{60}$  our efforts have also focused on other relatively large benzenoid molecules. In 1872 von Baeyer studied the condensation reaction of benzaldehyde and resorcinol. His aim was to synthesize new dyes. The red solution color of his product changed to violet in the presence of base.<sup>5.1</sup> It is now well-known that von Baeyer produced the first resorcinarenes, cyclic tetrameric macrocycles based on resorcinol.<sup>5.2</sup>

We recently reported the synthesis of resorcinarenes that afford the most versatile color sensing of specific saccharides observed to date.<sup>5.3</sup> The sugars are a challenging class of compounds due to the similarity of their structures. The visual sensing of saccharides should aid in monitoring disease states or the products of fermentation processes. Our group's stereoisomeric **5.1** and **5.2**, derived from the condensation of 4-formylphenylboronic acid and resorcinol are recent examples<sup>5.4</sup> and **5.3** is a brominated substructure.<sup>5.5</sup> The resorcinarenes are remarkable molecules whose impact in the disciplines of molecular recognition, materials science and supramolecular chemistry has been the subject of extensive study and recent reviews.<sup>5.2</sup> Despite the great attention they have received, prior to our studies there had never been a report of resorcinarenes exhibiting saccharide sensing that can be observed by visual inspection.

The development of a resorcinol based color test that was specific for ketoses, was reported by Seliwanoff in 1887.<sup>5.6</sup> Other resorcinol-based color tests were later developed but they were based on harsh methods such as the use of highly toxic and

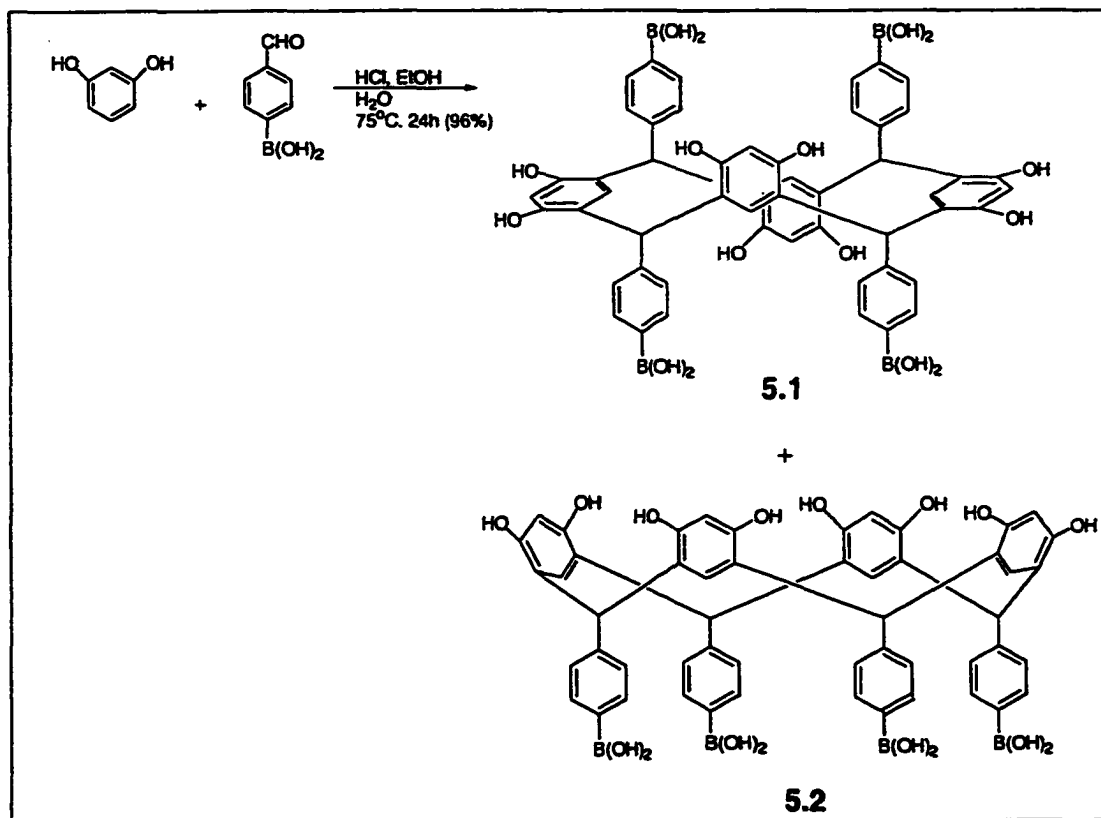
corrosive reagents.<sup>5.7,5.8</sup> In the 1990's Shinkai and co-workers made significant progress towards the enhanced visible detection of saccharides based on chromophore-functionalized arylboronic acids<sup>5.9</sup> or the affinity of nitrogen-containing chromophores for arylboronic acids.<sup>5.10</sup>

Since the resorcinarenes promoted the first known binding of sugars in apolar solvents<sup>5.11</sup> and boronic acids are the basis for carbohydrate affinity chromatography, our group decided to combine boronic acids and resorcinarenes into single molecular frameworks. We thus reasoned that these materials would afford powerful and unique new sugar receptors. We are the only research group to synthesize boronic acid resorcinarene molecules and to demonstrate their utility as sugar visualization agents. Some of the advantages of using resorcinarenes are: (1) ease of resorcinarene synthesis on a multigram scale<sup>5.12</sup> and (2) amenability of resorcinarenes to structure variation<sup>5.4,5.5,5.13</sup>.

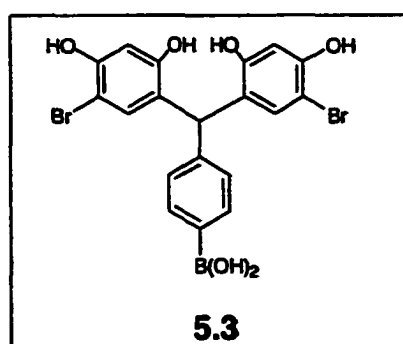
A major focus of our research is to determine (1) the cause of the color formation of the resorcinarene products and (2) the origin of the selective color formation of solutions containing analytes. We can also apply these methods to neutral oligosaccharides which to date have no general visual detection methods.<sup>5.14</sup> Current detection methods for these oligosaccharides require total hydrolysis to monosaccharides or their prior covalent attachment to a chromophore.<sup>5.14</sup>

Compounds 5.1, 5.2, and 5.3 were first synthesized in our laboratory (Figure 5.1 and Figure 5.2).<sup>5.4,5.5</sup> They have been observed to lead to fast, characteristic color changes of specific saccharide solutions which may be observed visually. The coloration process is selective, quantifiable, and reproducible.



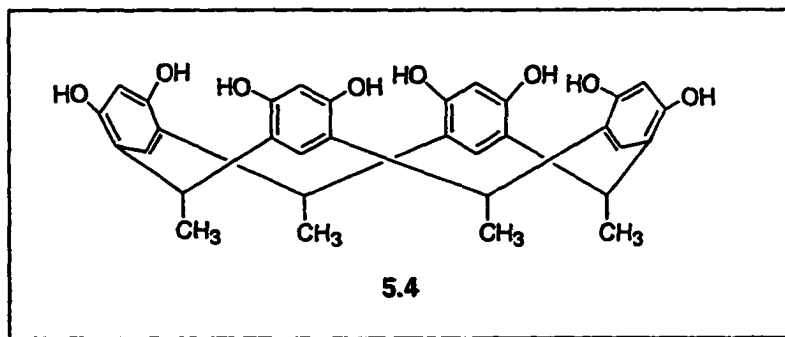


**Figure 5.1.** Synthesis of resorcinarenes.



**Figure 5.2.** Other resorcinol based colorimetric sensor.

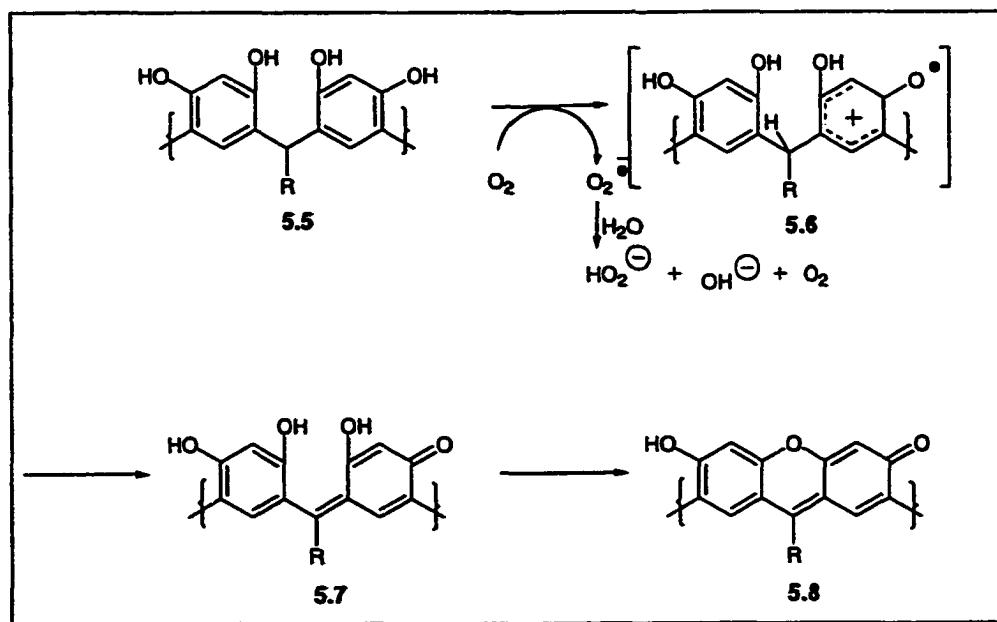
Additionally, experiments with resorcinarene compounds which lack boronic acid moieties also exhibit visual sensing properties with saccharides (Figure 5.3).



**Figure 5.3.** A parent resorcinarene without boronic acids.

Several observations have arisen from our sensing studies with 5.1, 5.2, and 5.3. First, the visual sensing of saccharides appears applicable to a variety of readily-available resorcinol condensation products, including those without boron. Second, the color patterns for different sugars can be altered by changing the framework of the receptor. Third, our method which involves heating the receptors in aqueous DMSO with analytes, is convenient. This method enables direct correlations between concentration and fluorescence and/or absorbance intensities in the visible region. This may allow for monitoring of unknown sugar levels. Fourth, the free hydroxyls are necessary for color formation.<sup>5.15</sup> Fifth, the presence of O<sub>2</sub> enhances the color formation of the solution with the receptor. Sixth, the pH-induced color formation and concomitant changes promoted by added acid or base (as observed first by von Baeyer<sup>5.1</sup>) is extremely faint unless the chemosensors are first heated. Some of these and the following observations lead us to hypothesize that oxidized resorcinarenes are responsible for solution color changes.

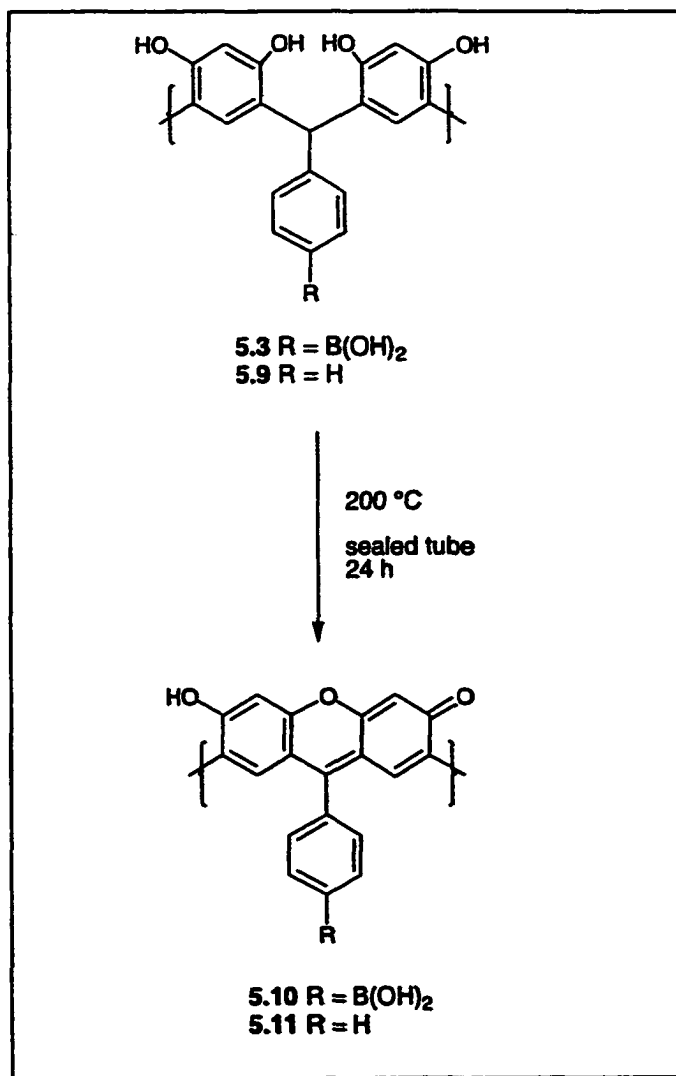
The intensity of the colors of our purified chemosensors appear and increase with heating or (longer term) standing in DMSO solutions in air. The colors of the solutions of resorcinol condensation products are most enhanced in the oxidizing solvent DMSO, the presence of oxygen and studies in which 5.3 is the receptor. Compound 5.3 should be more prone to oxidation than the resorcinarenes due to relatively less strain produced upon the formation of the quinone. We found that this molecule affords the most vivid solution colors in the presence or absence of analytes which we have observed to date.<sup>5.5</sup> Oxidizable phenolic hydroxyls are key to this process since methylated or acylated derivatives of 5.1, 5.2, and 5.3 do not produce any solution color under our conditions. A proposed mechanistic pathway for the oxidation is shown in Scheme 5.1.



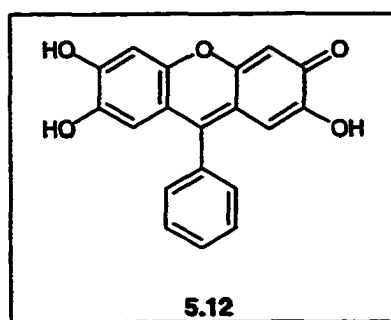
**Scheme 5.1.** Proposed mechanism for the transformation of the resorcinol condensation products to colored products.

Since the presence of O<sub>2</sub> significantly enhances the absorbance intensities of the chemosensors, we propose that O<sub>2</sub> participates in the oxidation of our molecules and is in turn reduced to superoxide (Scheme 5.1). It is generally known that superoxide converts to peroxide ions which are responsible for further oxidations. This is the first stage in certain photooxidation mechanisms.<sup>5,16</sup> The presence of hydroxyquinone structures such as **5.7** must be taken into consideration. Energy minimization studies of **5.1** and **5.2** reveal that a xanthene resorcinarene i.e., **5.8**, is ca. 30 Kcal/mol higher in energy than the unoxidized species. The corresponding hydroxyquinones i.e., **5.7** are ca. 15 Kcal/mol higher. In order to attain a xanthene material absorbing at 535 nm, bond rupture of the macrocycles to an acyclic oligomer(s) under the oxidative conditions might occur.

Model compounds **5.10** and **5.11** have been synthesized in our research group (Scheme 5.2).<sup>5,3,5,8</sup> Xanthene dye compound **5.10** was isolated as part of a crude reaction mixture via 24 h heating of **5.3** in air under standard thermolysis conditions.<sup>5,3,5,8</sup> The oxidation of **5.3** was also performed with ferric ammonium sulfate produced **5.10**. Crude <sup>1</sup>H NMR showed qualitative conversion to **5.10** and **5.11**. These compounds were also observed via a related xanthene synthesis procedure which also entails heating in a sealed tube.<sup>5,16</sup> Both xanthenes **5.10** and **5.11** exhibit a  $\lambda_{\text{max}}$  at 535 nm. This is essentially the same  $\lambda_{\text{max}}$  value we observe for colored **5.3** (and **5.1**, **5.2** and **5.4**) in DMSO and is in agreement with the commercially available **5.12**. The similarity of the  $\lambda_{\text{max}}$  values suggests that the structure of the visible region absorbing species in the resorcinarene macrocycles may have a xanthene chromophore such as **5.8** (Scheme 5.1).



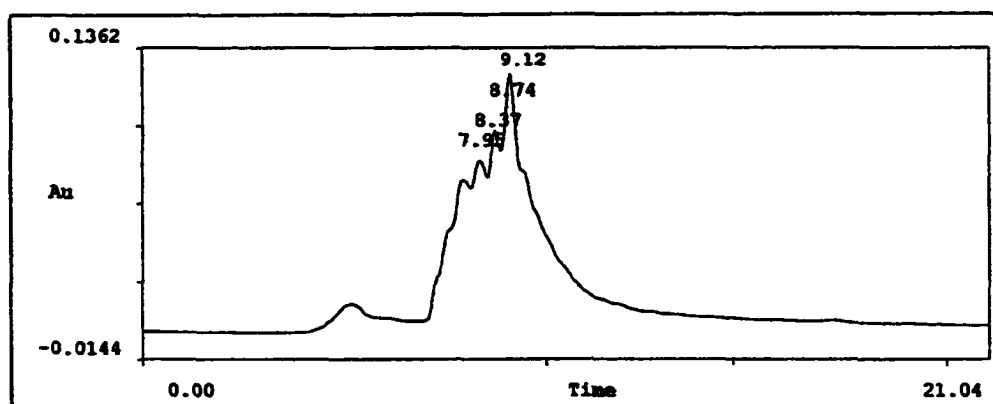
**Scheme 5.2.** Synthesis of model compounds for comparison with xanthene dyes.



**Figure 5.4.** 9-phenyl-2,3,7-trihydroxy-6-fluorone.

## 5.2 Results and Discussion

A first goal is to isolate the colored molecules formed in the macrocycle solutions. We are currently studying HPLC methodology towards this end. Using HPLC analysis with a C18 column and a solvent system of 100% acetonitrile, we obtained several peaks for the most polar material (semi-purified by flash chromatography) from a solution containing **5.4** which was subjected to prolonged heating in DMSO and air (Figure 5.5). This material was the colored fraction and exhibited the characteristic  $\lambda_{\text{max}}$  which we typically observe for xanthenes and colored solutions of resorcinarenes. Other HPLC conditions tried to date include employing a solvent system of 80% methanol/water but were unsuccessful.

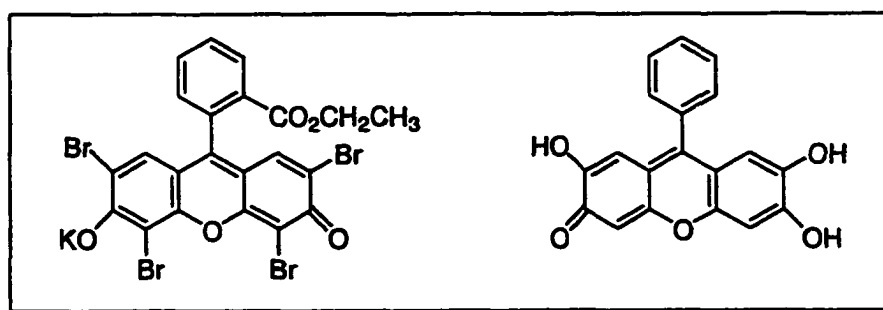


**Figure 5.5.** HPLC trace of oxidized **5.4**.

Clearly, improved conditions will be needed in order to isolate the chromophoric products from the colored solutions. This work is ongoing in our research group.

The second main issue is the cause of the color change in response to the presence of analytes. While boronic acid-containing dyes which change color in the presence of sugars are known, there is no report of commercial xanthene dyes xanthene

giving direct color responses to sugar analytes. Our hypothesis is that if the resorcinarenes form xanthene chromophores which are responsible for the colorimetric effects we observe, then xanthene dyes themselves should also produce color responses to sugars under our conditions. If this is true, the study of the interaction of xanthenes with sugars should shed important light on our new color detection mechanism. The xanthenes would thus serve as useful "models" for studying the chromogenic process and possibly embody unique, commercially available color detection agents in their own right (Figure 5.6).



**Figure 5.6.** Structures of ethyl eosin (left) and 9-phenyl-2,3,7-trihydroxy-6-fluorone.

The selective color sensing of sugars is promoted by the highly colored polar material that derives from heating **5.2** in air.<sup>5.1.5.3</sup> A recent similar study in our group with **5.10** reveals that it promotes similar color changes upon thermolysis with sucrose, glucose or fructose ( $10^{-3}$  M) to **5.3** using our published conditions. Xanthene dyes are of great importance in photochemistry and photomedicine.<sup>5.18</sup> They are used in photographic technology, tunable lasers and fluorescence depolarization diagnostic devices. The xanthene dyes have been used as both electron acceptors and as electron donors (to initiate free radical polymerizations), depending on the reacting species

(Scheme 5.3 and 5.4).<sup>5,15</sup> Again, there have been no prior reports of saccharide-induced color changes.

The fluorone dye proved to be the most interactive with our analytes, with ethyl eosin promoting little or no color changes by visual inspection. Matrix assisted laser desorption mass (MALDI) spectrometry was employed to analyze the products via the interaction of the fluorone with our analytes (Table 5.1) (Appendix B).

Using MALDI-MS we have observed evidence for the addition of analytes to the fluorone dye (and, importantly, not to ethyl eosin) which interact with our analytes via radical formation. These results are summarized in Table 5.1. We detected the addition of two molecules of potassium to tribenzylamine and one molecule of potassium to sucrose in the presence of the fluorone. The addition of one molecule of sodium was observed in the mass spectrum of fructose or glucose plus fluorone.

<sup>1</sup>H NMR studies also indicate the formation of the sugar degradation product, 5-hydroxymethyl furfural upon heating glucose, fructose or sucrose under our conditions. Furfural addition to fluorone was detected in the mass spectra of fluorone and glucose, maltotriose, maltotetraose and maltohexaose. In the case of maltotriose, maltotetraose, and maltohexaose, a peak for the addition of the furfural and maltose was observed.

Sucrose and some of the oligosaccharides (maltose, maltotriose, maltotetraose, maltopentaose) were observed to fragment to glucose and then interact with the dye. Some of our analytes were seen to undergo fragmentation which involve losing glucose. The mass spectrum of maltotetraose included a peak corresponding to the absence of two molecules of glucose but the addition of sodium and potassium whereas mass spectrum of maltohexaose detected the loss of two molecules of glucose.

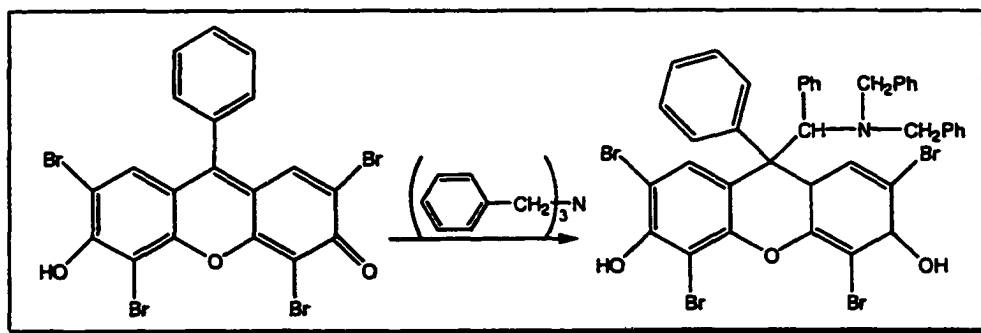


**Table 5.1. MALDI Mass Spectral Data for the interaction of 5.12 with analytes.**

Analyte (mol.wt.)	Calc'd Mass (M)	Obs. Mass	Comments
a) Tribenzylamine 287.40	607.7	687.68	M + 2K
b) Tetrabutyl- ammonium bromide 322.36	562.78	563.66	
c) Sucrose 342.30	662.60	1) 701.94 2) 522.80	1) M + K 2) Glucose + Na
d) Fructose 180.16	500.46	523.91	M + Na
e) Glucose 180.16	500.46	1) 522.87 2) 446.41	1) M + Na 2) M – Glucose + Furfural
f) Maltose 342.30	662.60	1) 685.92 2) 522.94	1) M + Na 2) Glucose + Na
g) Maltotriose 504.44	824.70	1) 789.45 2) 523.76	1) Maltose + furfural 2) Glucose + Na
h) Maltetraose 666.58	986.88	1) 1103.09 2) 522.90 3) 446.74	1) M - 2Glucose + Na + K 2) Glucose + Na 3) Maltose + Furfural
i) Maltopentaose 828.72	1149.02	1) 852.10 2) 522.92	1) M – 2Glucose + Na +K 2) Glucose + Na
j) Maltohexaose 990.86	1311.16	1) 950.55 2) 446.35	1)M – 2 Glucose 2)Maltose + Furfural

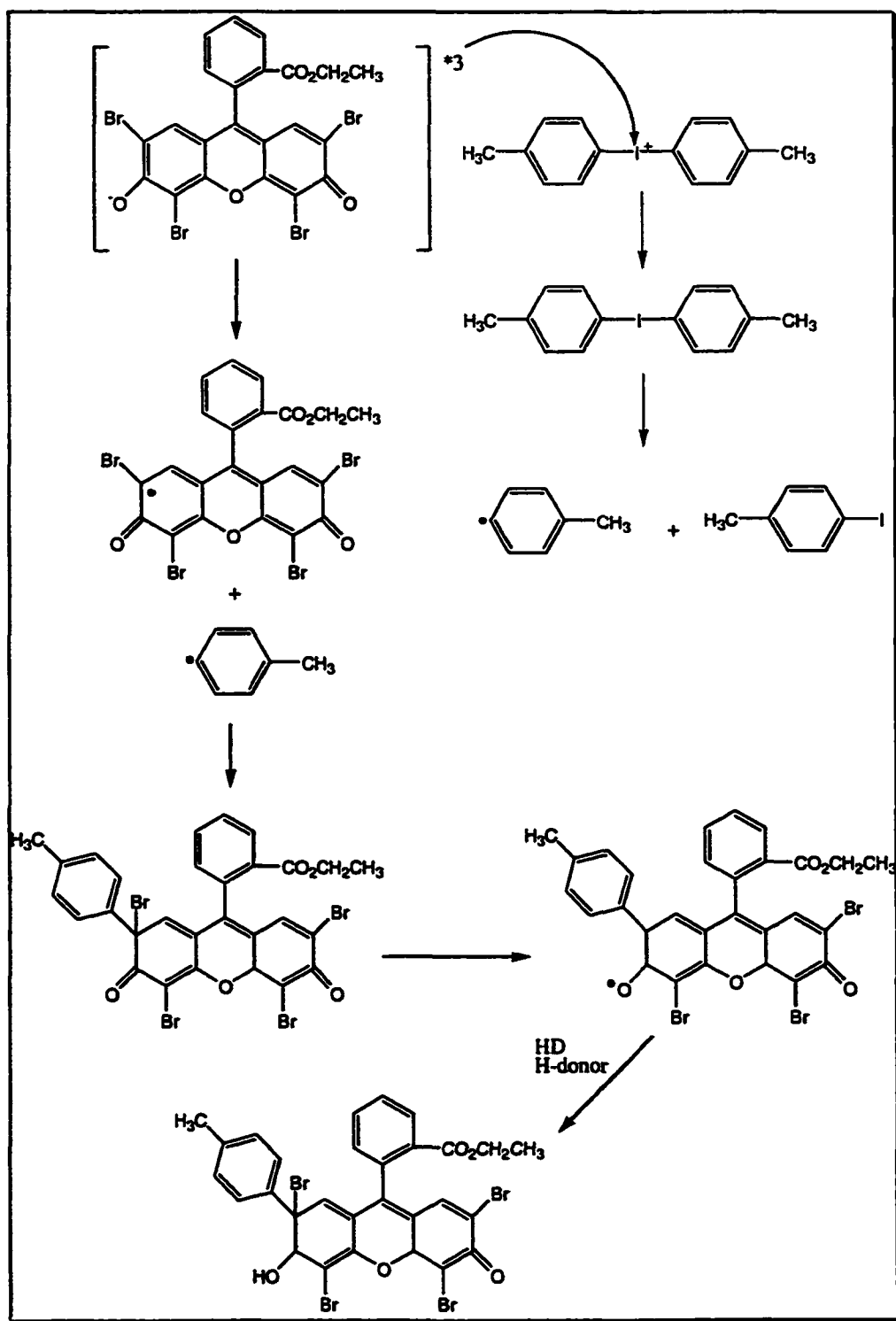
(Na = Sodium(22.99), K = Potassium(39.10), 5-(hydroxymethyl)furfural(126.11))

The evidence suggests that a free radical process takes place when the saccharides and chemosensors are heated (in the presence of O<sub>2</sub> and light). It is known in the literature with certain xanthenes, under visible light initiating conditions, act as electron donors and/or acceptors depending on the reacting partner.<sup>5,19</sup>



**Scheme 5.3.** Xanthene dye species acting as an electron acceptor.

We thus propose that, at least in some cases, the carbonyl of the sugar acts as an acceptor and the colored chemosensors act as electron donors, analogous with the xanthene dyes,<sup>5,19</sup> which promotes observable color changes of the solutions. Alternatively, the sugar hydroxyls may also take part in the process.



**Scheme 5.4.** Xanthene dye species acting as an electron donor.

### 5.3 Experimental Procedures

**General.** All chemicals were reagent grade (Aldrich or Lancaster) and used without further purification. MALDI experiments were performed with a Bruker Proflex III Maldi Mass Spectrometer using anthracene as a matrix. HPLC analysis was performed using a Milton Roy system which includes a CM4000 solvent delivery system, A1000 autoinjector, Spectrometer 3000 wavelength detector, and a Spectrometer 5000 photodiode array detector.

**Preparation of samples for MALDI analysis.** The fluorone dye (0.001g, 0.003 mmol) was dissolved in 5 mL of a 9:1 DMSO:H<sub>2</sub>O solution. A 1.0 mL aliquot was heated in the presence of the corresponding analyte (1 equiv) for 3 minutes. The solvent was removed *in vacuo*. MALDI-MS analysis was performed on all samples using methanol as the solvent and anthracene as the matrix (Table 5.1, Appendix B).

**Analysis of colored material.** The colored material was injected on a C18 HPLC column using a flow rate of 7.0 mL/min and a solvent system of 100% acetonitrile.

### 5.4 Future Work

We have developed a process for the visual sensing of saccharides. By using HPLC and MALDI-MS the interactions between the dye and saccharides or oligosaccharides may be examined and the products may be characterized. Further development of HPLC separation protocols are needed to characterize the resorcinarene-derived colored materials.

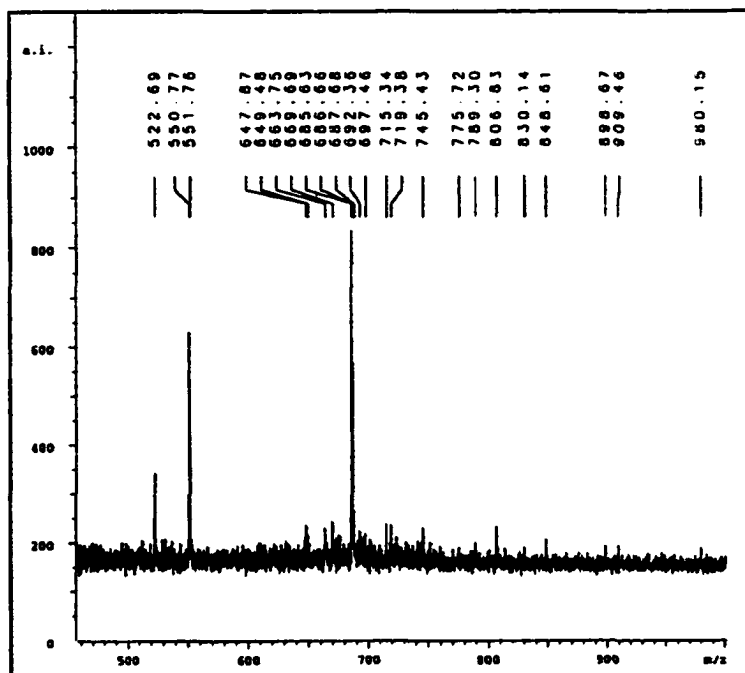
### 5.5 References

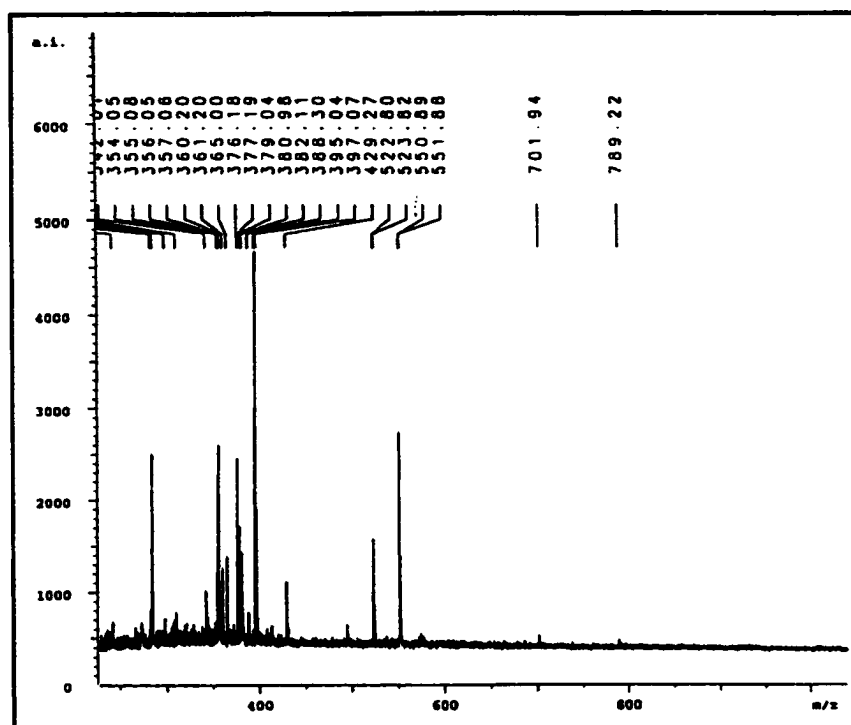
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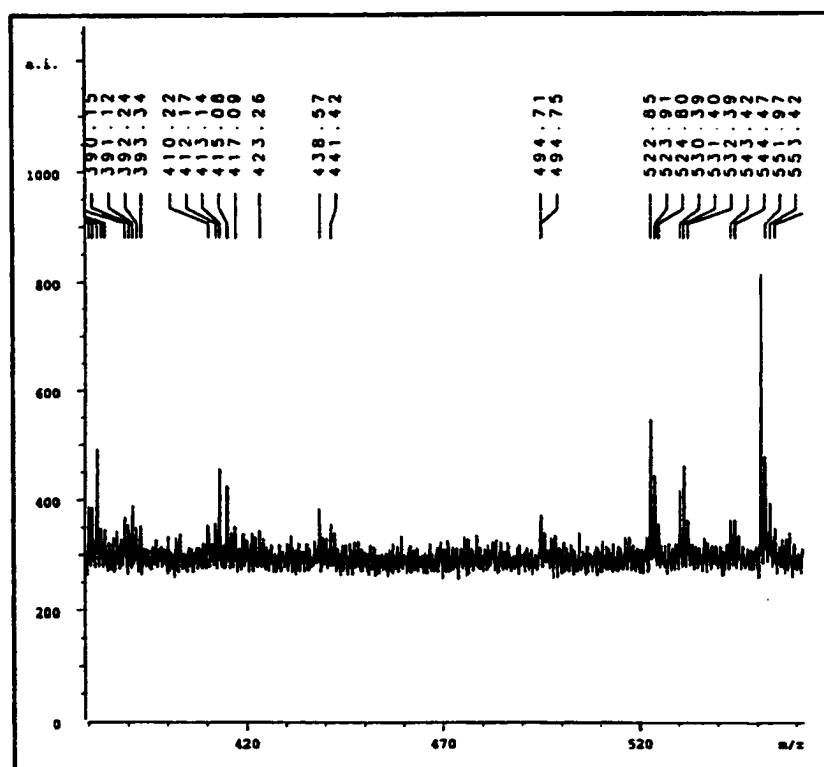
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## APPENDIX A: MASS SPECTRAL DATA





**Figure A:3:** Mass spectrum for the interaction of 5.12 with sucrose.



**Figure A:4** Mass spectrum for the interaction of 5.12 with fructose.



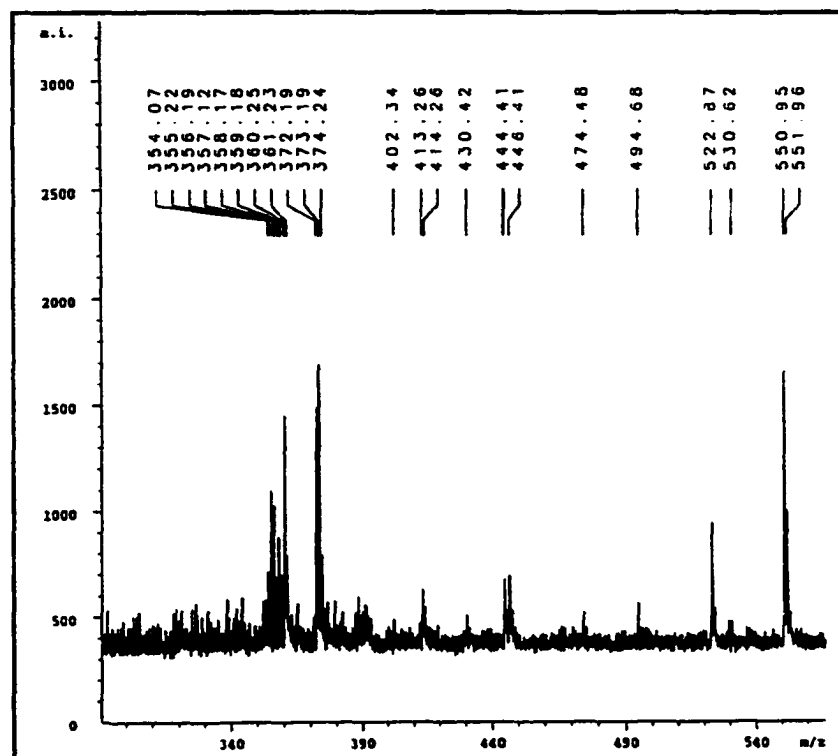


Figure A.5: Mass spectrum for the interaction of 5.12 with glucose.

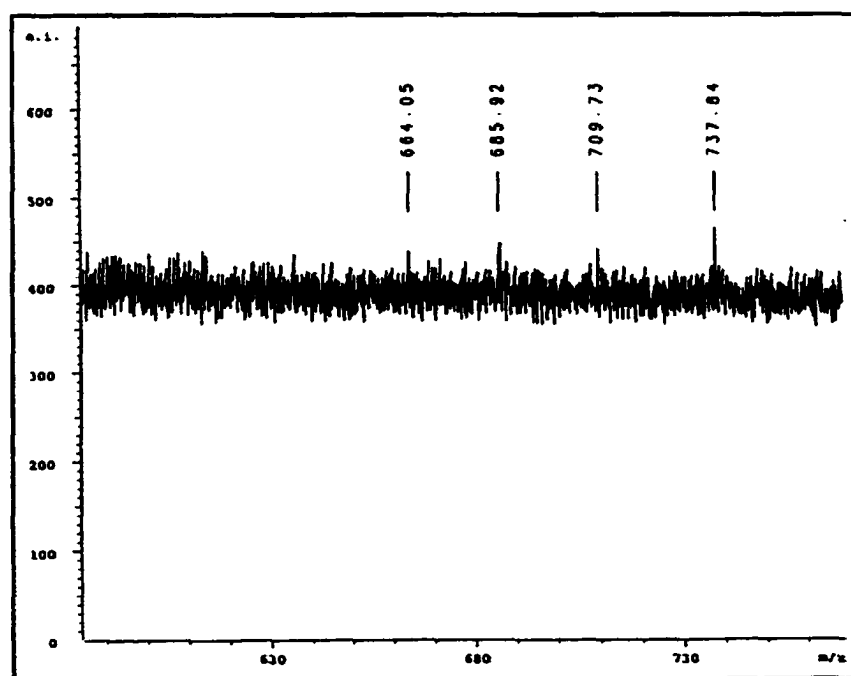
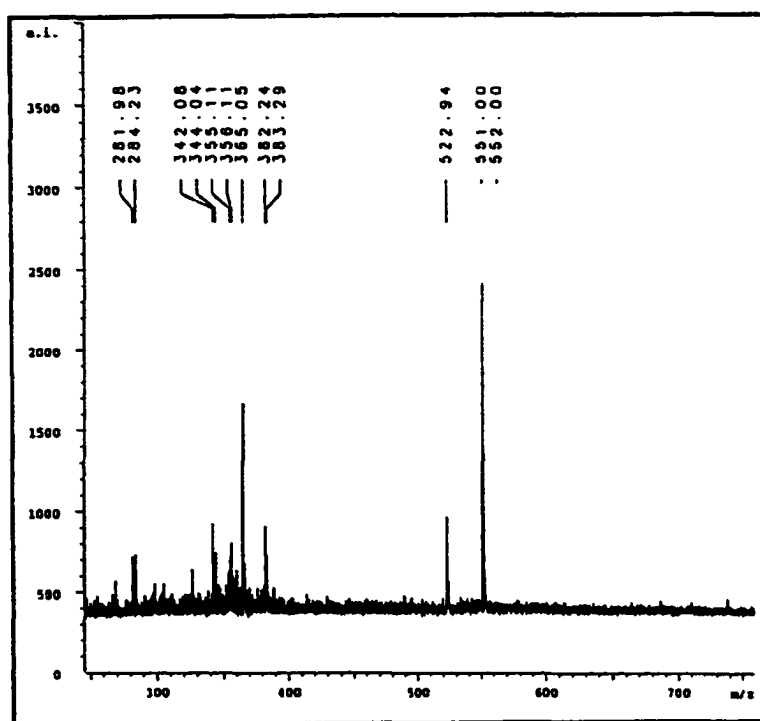
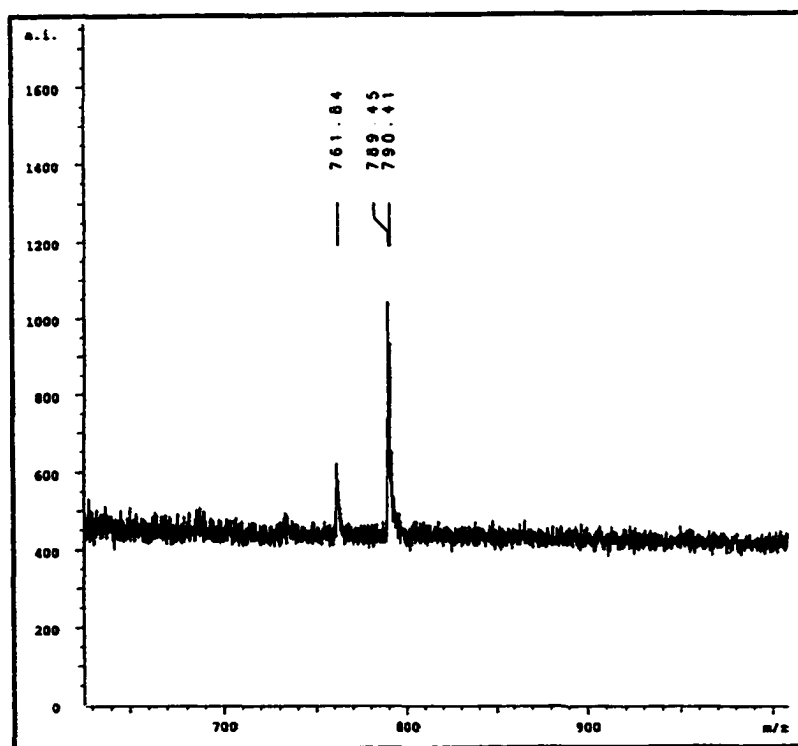


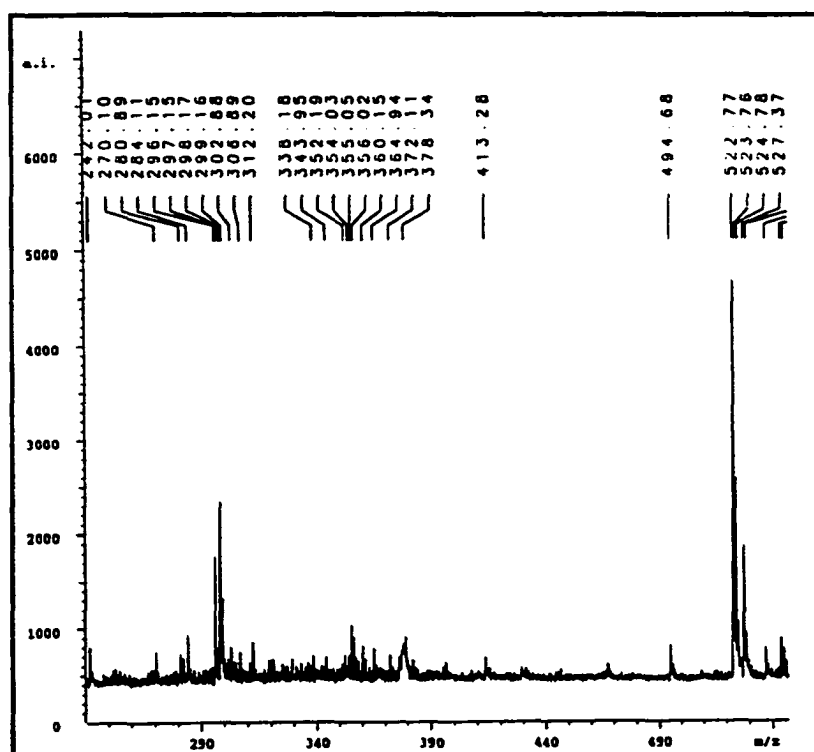
Figure A.6: Mass spectrum for the interaction of 5.12 with maltose.



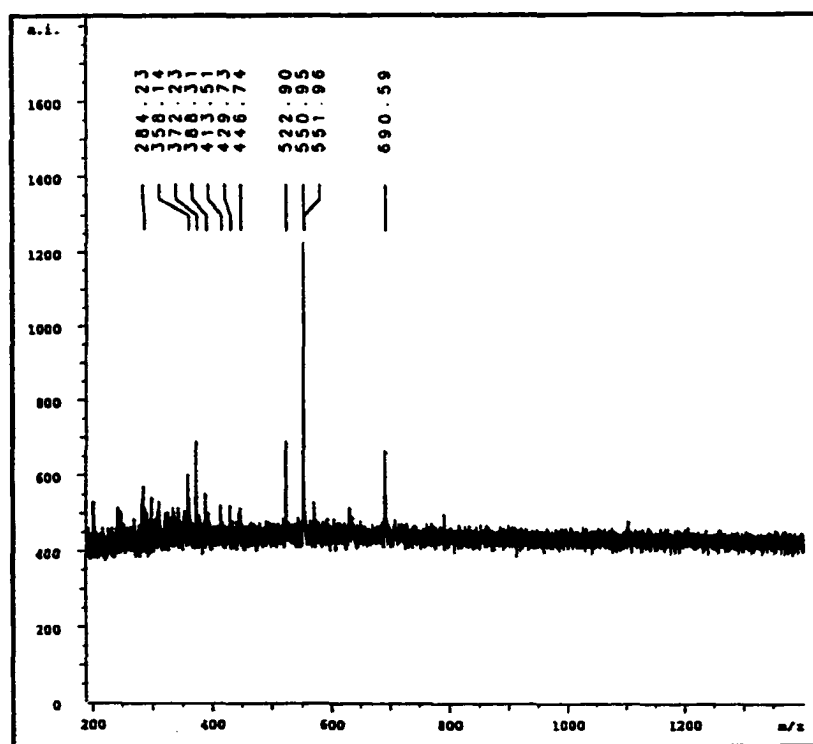
**Figure A.7: Mass spectrum for the interaction of 5.12 with maltose.**



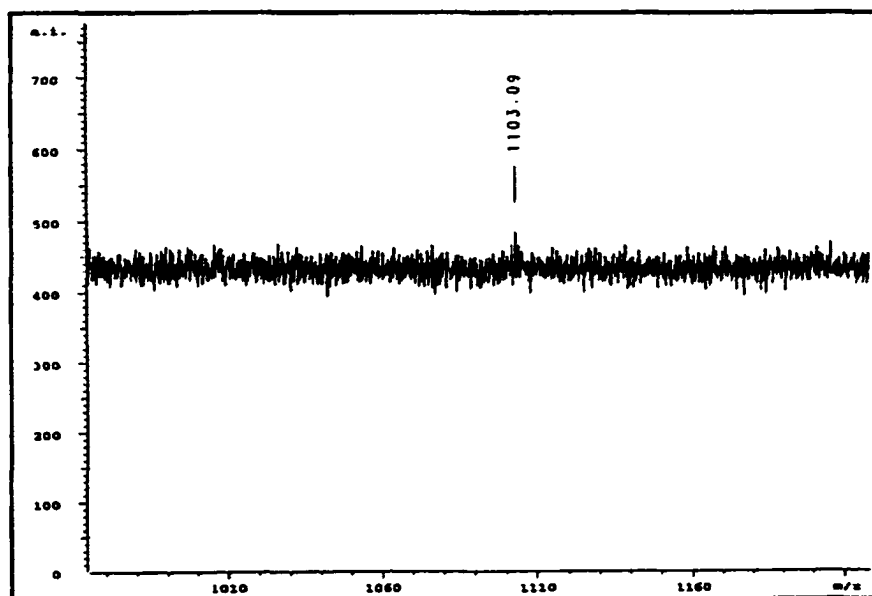
**Figure A.8: Mass spectrum for the interaction of 5.12 with maltotriose.**



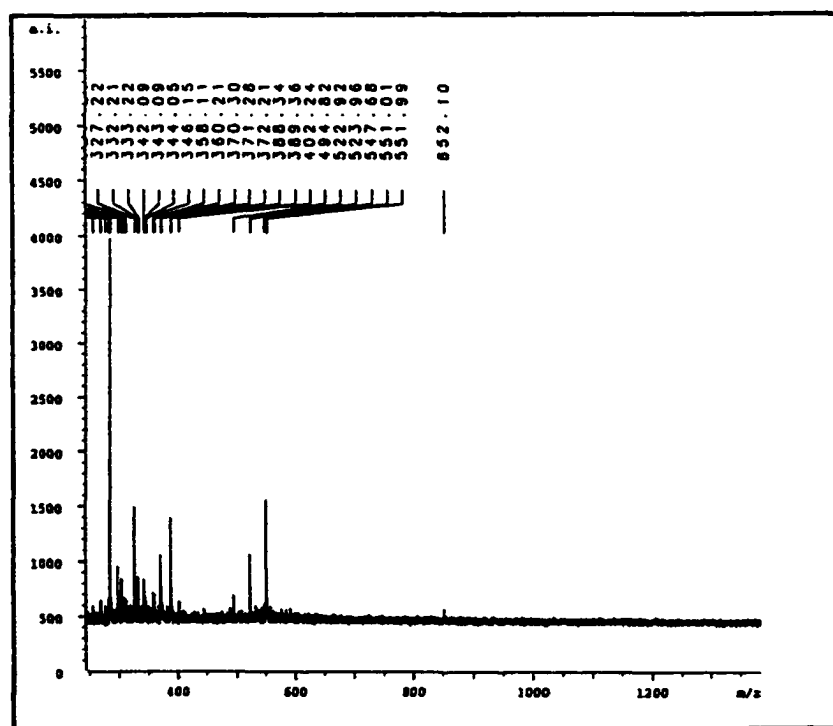
**Figure A.9: Mass spectrum for the interaction of 5.12 with maltotriose.**



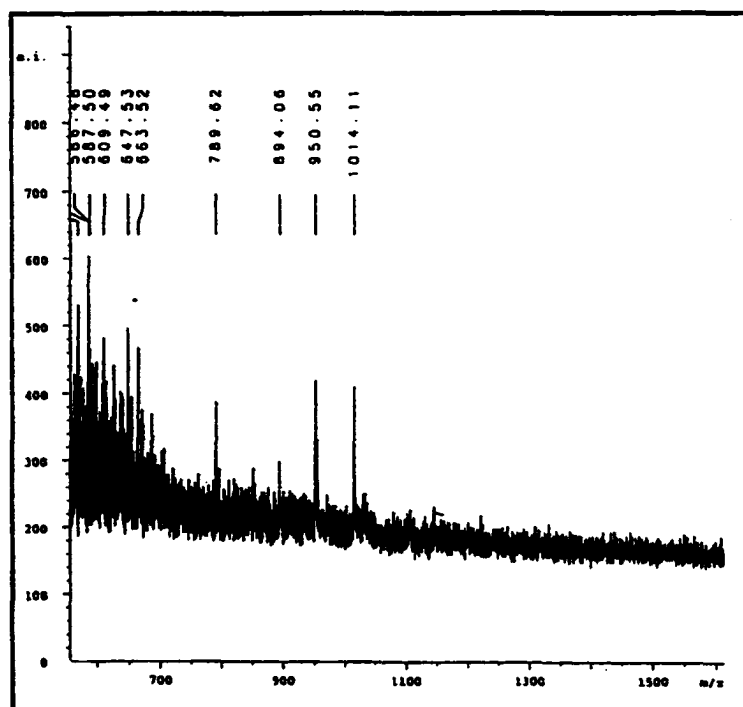
**Figure A.10: Mass spectrum for the interaction of 5.12 with maltotetraose**



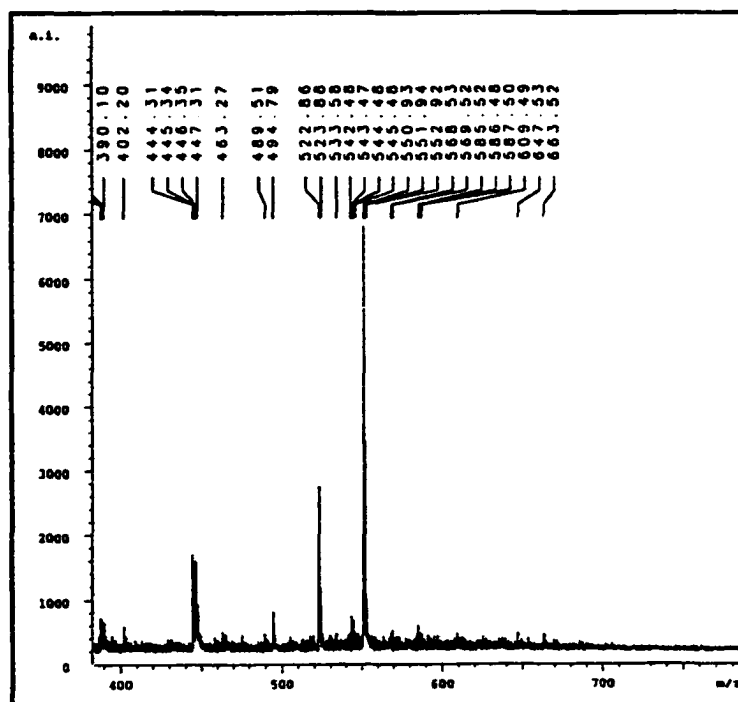
**Figure A.11:** Mass spectrum for the interaction of 5.12 with maltotetraose.



**Figure A.12:** Mass spectrum for the interaction of 5.12 with maltopentaose.



**Figure A.13:** Mass spectrum for the interaction of 5.12 with maltohexaose.



## APPENDIX B: LETTERS OF PERMISSION



LOUISIANA STATE UNIVERSITY  
AND AGRICULTURAL AND MECHANICAL COLLEGE  
Department of Chemistry

January 3, 2001

American Chemical Society  
1155 16th St., N.W.  
Washington, DC 20036

To Whom It May Concern:

I am writing to obtain permission for the use of my contributions to an article published in *The Journal of Organic Chemistry*. I am a graduate student in the Department of Chemistry at Louisiana State University. I am the first author on the article and would like to include my contributions to the article in my doctoral dissertation. The article is "The Reaction of Buckminsterfullerene with Diazotetrazole. Synthesis, Isolation, and Characterization of C<sub>122</sub>." Vol. 63, pp. 3522-3523.

Thank you for your consideration of this request.

Sincerely,

Taiya S. Fabre

Phone: (225) 578-3573

Fax: (225) 388-3458

E-mail: tsfabre@yahoo.com



## American Chemical Society

Publications Division  
Copyright Office

1155 Sixteenth Street, NW  
Washington DC 20036  
Phone: (1) 202-872-4368 or -4367  
NEW: Fax: (1) 202-776-8112 E-mail: [copyright@acs.org](mailto:copyright@acs.org)

FAX: 225-388-3458

DATE: January 11, 2001

### MEMORANDUM

TO: Taiya S. Fabre, Louisiana State University, Department of Chemistry  
Baton Rouge, LA 70803

FROM: C. Arleen Courtney, Assistant Copyright Administrator *C. Arleen Courtney*

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9/1/98

## **VITA**

**Taiya Nicole Sprull was born in Baton Rouge, Louisiana, on May 1, 1973. She graduated fifth in the class of 1991 at Port Allen High School in Port Allen, Louisiana. She was the recipient of a myraid of awards and honors including the Dow Chemical Company and Placid Refining Company Science Scholarship.**

**In the fall of 1991, she enrolled at Xavier University in New Orleans, Louisiana. While at Xavier, Taiya became a Minority Access to Research Careers Scholar (MARC). She conducted x-ray crystallographic research under the direction of Dr. Cheryl Stevens. A chemistry honors graduate, she received a bachelor of science degree in chemistry (American Chemical Society certified) in 1995.**

**In the fall of 1995, Taiya married Jason John Fabre Jr. and entered the graduate program in the Department of Chemistry at Louisiana State University (LSU) in Baton Rouge, Louisiana. While at LSU, Taiya synthesized and characterized new organic electronic architectures under the supervision of Dr. Robert Strongin. She is a member of Delta Sigma Theta Sorority, Inc., the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, and the American Chemical Society. Taiya is currently a candidate for the Doctor of Philosophy in organic chemistry.**



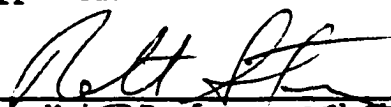
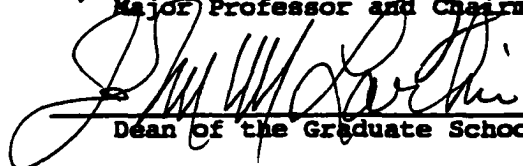
DOCTORAL EXAMINATION AND DISSERTATION REPORT

**Candidate:** Taiya Sprull Fabre


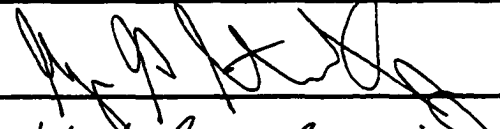

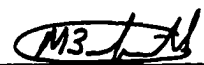
**Major Field:** Chemistry

**Title of Dissertation:** Synthesis, Isolation, and Characterization of  
Novel Organic Electronic Architectures

**Approved:**

  
\_\_\_\_\_  
Major Professor and Chairman  
  
\_\_\_\_\_  
Dean of the Graduate School

**EXAMINING COMMITTEE:**

  
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**Date of Examination:**

February 19, 2001  
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