

## The First Structurally Characterized Homofullerene (Fulleroid)

Andrew F. Kiely,<sup>†</sup> Robert C. Haddon,<sup>\*‡</sup> Mark S. Meier,<sup>\*‡</sup> John P. Selegue,<sup>†</sup> Carolyn Pratt Brock,<sup>\*‡</sup> Brian O. Patrick,<sup>†</sup> Guan-Wu Wang,<sup>†</sup> and Yongsheng Chen<sup>†</sup>

Department of Chemistry, University of Kentucky, and  
Advanced Carbon Materials Center,  
Lexington, Kentucky 40506-0055

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The reaction of fullerenes with carbenes and carbene equivalents has been studied since the earliest days of fullerene chemistry.<sup>1</sup> Addition of a carbene such as :CBr<sub>2</sub> to C<sub>60</sub> results in formation of a cyclopropane.<sup>2</sup> However, addition of “:CR<sub>2</sub>” by 1,3-dipolar cycloaddition of CR<sub>2</sub>N<sub>2</sub> followed by the loss of N<sub>2</sub> produces 2 different isomeric addition products, depending on the specific conditions. One of the products is a cyclopropane, but the other product displays electrochemical and spectroscopic behavior remarkably similar to that of C<sub>60</sub>.<sup>3</sup> This novel second isomer was formulated as a fulleroid, a compound in which the :CR<sub>2</sub>R<sub>2</sub> unit has been inserted into the framework of the fullerene. The insertion is rationalized as the addition to the fusion of a five-membered ring and a six-membered ring, followed by a norcaradiene rearrangement.<sup>1</sup> Herein we report the first crystal structure of a fulleroid and establish that, indeed, addition has occurred to the fusion of a five-membered ring and a six-membered ring and that the structure is an opened, homoconjugated annulene.<sup>4</sup> In addition, this particular compound is the first example of a crystallographically characterized C7–C8 adduct of C<sub>70</sub>.

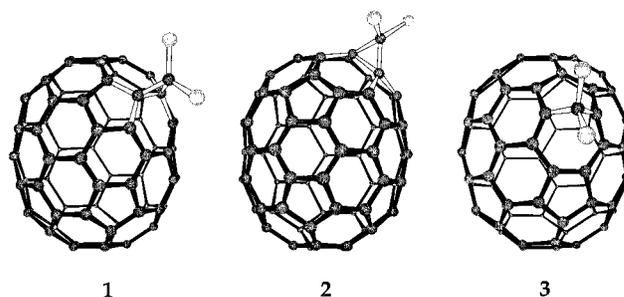
Treatment of C<sub>70</sub> with 2.5 equiv of PhHgCCl<sub>2</sub>Br in refluxing benzene produced a mixture of dichlorocarbene adducts, C<sub>70</sub>(CCl<sub>2</sub>)<sub>n</sub> (n = 1–4), and unreacted C<sub>70</sub>.<sup>5</sup> Three isomeric monoadducts, C<sub>71</sub>Cl<sub>2</sub>, were obtained in 28% combined yield by gel permeation chromatography (GPC). The C<sub>71</sub>Cl<sub>2</sub> isomers (35:37:29 ratio) were separated by HPLC, and their formulation was confirmed by mass spectrometry.<sup>6</sup>

The first isomer, **1**, displays a <sup>13</sup>C NMR spectrum comprised of 38 resonances with 4 single-intensity and 32 double-intensity sp<sup>2</sup> resonances (2 coincident), 1 double-intensity and 1 single-intensity sp<sup>3</sup> resonance. This pattern is indicative of a structure with a plane of symmetry. The presence of 2 sp<sup>3</sup> resonances indicates that the product is a methanofullerene rather than a homofullerene. There are 2 possible structures that would fit these data; 5,6-dichloromethano[70]fullerene is the most likely structure, since there are no examples of a 2,3-methano[70]fullerene with a closed C2–C3 bond.

The <sup>13</sup>C NMR spectrum of isomer **2** is comprised of 35 lines, consistent with a plane of symmetry. On the basis of the C<sub>s</sub> symmetry and the presence of 3 sp<sup>3</sup> resonances in the <sup>13</sup>C NMR,

we conclude that **2** results from addition to the C1–C2 bond. This is the only C<sub>s</sub> methanofullerene with the cyclopropane moiety in the mirror plane.

The similarity of the UV/vis spectrum of **3** to that of C<sub>70</sub> suggested that this isomer was a fulleroid rather than a methanofullerene (Figure 1).<sup>7,8</sup> This assignment was confirmed by its <sup>13</sup>C NMR spectrum, which consists of 36 lines: 5 single intensity resonances (4 sp<sup>2</sup> and 1 sp<sup>3</sup>), 30 double-intensity sp<sup>2</sup> resonances, and 1 quadruple-intensity sp<sup>2</sup> resonance. The presence of only 1 sp<sup>3</sup> resonance indicates that this isomer is a fulleroid, and the number of resonances indicates a structure with C<sub>s</sub> symmetry.



There are two possible fulleroids with the C<sub>s</sub> symmetry of **3**: one formed by addition of dichlorocarbene to the C7–C8 bond and one by addition to the C2–C3 bond. The greater double-bond character of the C7–C8 bond makes this the more reasonable site of attack by dichlorocarbene.<sup>9</sup> C2–C3 fulleroids are known,<sup>8</sup> but only as products from the decomposition of C1–C2 pyrazolines, rather than as products of direct attack by carbenes.<sup>10</sup>

The assignment of structure **3** as a C7–C8 fulleroid was confirmed by X-ray crystallography.<sup>11</sup> This compound crystallizes from toluene/pentane in space group P2<sub>1</sub>/c with two C<sub>71</sub>Cl<sub>2</sub> molecules and one pentane molecule in the unit cell. The C7–C8 addition regiochemistry of **3** is clear from the crystal structure; the critical C7–C8 distances (2.136(6) Å and 2.139(6) Å for the two independent molecules) are clearly nonbonded. Pairs of C<sub>71</sub>Cl<sub>2</sub> molecules interact across inversion centers through their Cl atoms; the intermolecular Cl–Cl distances are 3.432(2) Å and 3.612(2) Å for the two independent pairs of molecules. These

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(11) Crystals were grown by vapor diffusion of *n*-pentane into a toluene solution of C<sub>71</sub>Cl<sub>2</sub>: *a* = 17.867(1) Å, *b* = 10.730(1) Å, *c* = 37.886(1) Å,  $\beta$  = 96.75(1)°, *V* = 7225.9(9) Å<sup>3</sup>, space group P2<sub>1</sub>/c, *Z* = 8 at 110(1) K. A hemisphere of data having  $\theta$  = 25.0° (23 001 reflections; 12 658 unique observations) was measured on an Nonius Kappa-CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation. The asymmetric unit was found to contain two C<sub>71</sub>Cl<sub>2</sub> molecules and one molecule of solvent, which was C<sub>5</sub>H<sub>12</sub> 88(1)% of the time and toluene 12(1)% of the time. The structure was refined anisotropically with the program SHELXL93 [1369 variables; 7 restraints (pentane 1,2 and 1,3 C–C distances); fixed geometry and one overall *U*<sub>iso</sub> for the toluene molecule; calculated positions for the H atoms] to *R* = 0.089 (on *F*); the 8032 reflections having *I* > 2 $\sigma$  and *wR* = 0.144 (on *F*<sup>2</sup>; 12 647 reflections). The value of *R* is a little higher than usual because of the large number of atoms, the significant thermal motion, and the solvent disorder, all of which reduce the average intensity of the reflections. The value of *wR*, however, is very satisfactory, and the esds for the C–C bonds are nearly all 0.006 Å. Lengths of chemically equivalent bonds in the two halves of the two independent molecules agree slightly better than expected. The average esd for the means is 0.003 Å.

<sup>†</sup> University of Kentucky.

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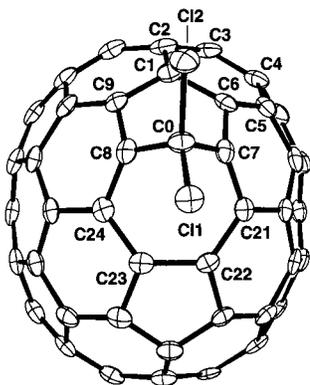
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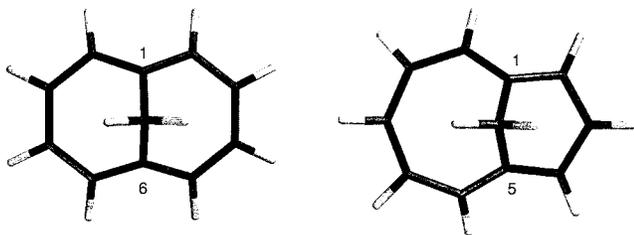
(6) To verify that **3** was not generated by rearrangement of **1**, a sample of pure **1** was subjected to refluxing benzene in the presence of PhHgBr for 18 h. No change was observed.



**Figure 1.** Ellipsoid plot (50% probability surfaces) of the front half of **3**.

attractive Cl $\cdots$ Cl interactions probably explain ordering of the fullerenes and the relatively small atomic displacements.<sup>12</sup>

Addition of dihalocarbene to C<sub>60</sub>, where the carbon atoms have pyramidalization angles similar to that of C1 and C2 of C<sub>70</sub>,<sup>13</sup> generates a methanofullerene as the only isolable monoadduct, with no indication of addition to a [6,5] ring fusion.<sup>2,6</sup> In contrast, the C7–C8 bond of C<sub>70</sub> undergoes the addition of benzyne, the first example of direct addition across any [6,5] ring fusion in a fullerene.<sup>14</sup> Scott and co-workers report that dichlorocarbene adds to the fullerene analogue corannulene and propose that the mechanism for addition involves initial attack at a [6,5] ring fusion.<sup>15</sup> A theoretical study on the Diels–Alder addition of butadiene to C<sub>70</sub> found that the C7–C8 bond was, after the C1–C2 and C5–C6 bonds, the most reactive in the molecule.<sup>16</sup> A likely pathway for this heretofore unobserved addition involves initial formation of a [6,5] methanofullerene followed by a rapid norcaradiene rearrangement to the [6,5] fulleroid.



The use of sodium trichloroacetate rather than PhHgCCl<sub>2</sub>Br results in a mixture that contains mostly **1**, with a small amount of **2** and little to none of **3**. The trichloromethyl anion is an intermediate in the generation of dichlorocarbene from trichloroacetate,<sup>17</sup> and this anion may provide an alternative pathway for the formation of methanofullerenes in these reactions. This

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**Table 1.** Key Bond Lengths and  $\pi$ -orbital Misalignment Angles ( $\phi$ ) in **3**

bond	bond length (Å)	$\phi$ (deg)	bond	bond length (Å)	$\phi$ (deg)
C1–C6	1.466(1)	9.4	C7–C21	1.419(3)	26.0
C6–C7	1.450(2)	31.0	C21–C22	1.427(2)	17.0
C7–C8	2.135(1)		C22–C23	1.458(1)	0

**Table 2.** Selected Pyramidalization Angles ( $\theta_p$ ) in **3**

carbon atom	pyramidalization angle ( $\theta_p$ )	carbon atom	pyramidalization angle ( $\theta_p$ )
C1	10.5	C21	6.8
C6	8.9	C22	9.2
C7	6.2		

result also provides further evidence for the role of dichlorocarbene in the generation of **3** from PhHgCCl<sub>2</sub>Br.

The role of homoconjugation has been an important question in the electronic structure of the fullerenes.<sup>18</sup> By using the 3D-HMO theory, it is possible to answer this question directly from the structure. The orientation and hybridization of the carbon atoms may be obtained analytically from the geometry. A reduced resonance integral ( $\rho$ ) for any pair of carbon atoms in a molecule can then be obtained by calculating the overlap integral and scaling by the overlap between the  $\pi$ -orbitals in benzene. Application of this procedure to two known annulenes and to **3** gives the following: 1,6-methano[10]annulene (homonaphthalene),  $\rho_{1,6} = 0.40\beta$ ; and 1,5-methano[10]annulene (homoazulene),  $\rho_{1,5} = 0.24\beta$ ; **3**,  $\rho_{7,8} = 0.43\beta$ . Thus, the extent of homoconjugation in **3** exceeds that in the free-standing annulenes, and it is clearly appropriate to refer to “fulleroids” as homofullerenes.

Selected bond lengths,  $\pi$ -orbital misalignment angles, and pyramidalization angles for **3** are given in Tables 1 and 2. As seen in previous studies,<sup>18</sup> the insertion of the bridging methylene absorbs curvature and reduces the pyramidalization in the annulene perimeter, while greatly increasing  $\pi$ -orbital misalignment (although not to the same extent as in the [60]fulleroid).

In conclusion, we have prepared a C7–C8 homofullerene by addition of dichlorocarbene to C<sub>70</sub>. The C7–C8 bond has opened to produce a homoconjugated annulene. These results suggest that dichlorocarbene will be useful in derivatizing the less pyramidalized parts of higher fullerenes and nanotubes, which are inert to many of the reagents currently used to functionalize C<sub>60</sub> and C<sub>70</sub>.<sup>19</sup>

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**Supporting Information Available:** Experimental procedures, <sup>13</sup>C NMR data, absorption spectra, and the structure report for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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