

Reaction of C<sub>60</sub> with Chlorophenyldiazirine.  
Spectral and Electronic Properties of the C<sub>60</sub>-Chlorophenylcarbene 1:1 Adduct

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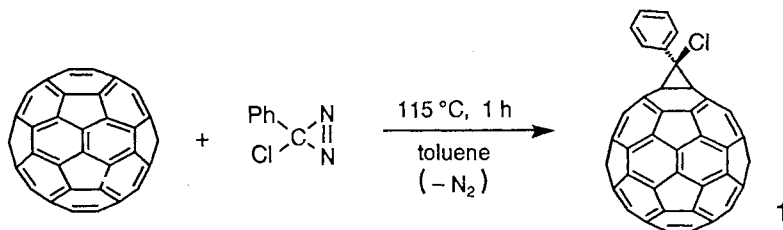
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A reaction of C<sub>60</sub> with an equimolar amount of chlorophenyldiazirine in refluxing toluene afforded the C<sub>60</sub>-chlorophenylcarbene 1:1 adduct in 37% yield. The adduct was shown to have the cyclopropane structure by <sup>13</sup>C NMR and exhibited reversible reduction waves at the potential about 0.1 V more negative and an irreversible oxidation peak at nearly the same potential as compared with those of C<sub>60</sub> itself.

Functionalization of the fullerene C<sub>60</sub> is quite important for further synthetic utilization of this unique chemical species. Although various chemical reactions of C<sub>60</sub> have so far been reported,<sup>1)</sup> there are rather limited number of studies, which describe isolation and full characterization of the products particularly suited for further derivatization.<sup>2)</sup> Since chlorophenyldiazirine<sup>3)</sup> is known as a clean source of chlorophenylcarbene which would give the product with a potentially ionizable C-Cl bond, we attempted its reaction with C<sub>60</sub>. Here we report the properties of the produced 1:1 adduct of C<sub>60</sub> and chlorophenylcarbene.<sup>4)</sup>

As a typical procedure, a solution of C<sub>60</sub> (115 mg, 0.160 mmol) and chlorophenyldiazirine (27 mg, 0.18 mmol) in 110 ml of toluene was refluxed for 1 h; the mixture was evaporated to give a dark brown solid, which was separated by the use of medium pressure liquid chromatography (hexane-toluene / silica gel) to give unchanged C<sub>60</sub> (14-32 mg, 12-28% recovery), a dark brown solid identified as the adduct **1**, C<sub>60</sub>((C<sub>6</sub>H<sub>5</sub>)CCl),<sup>5)</sup> (50 mg, 37%; 42-51% based on consumed C<sub>60</sub>), and a dark brown solid containing the bisadduct, C<sub>60</sub>((C<sub>6</sub>H<sub>5</sub>)CCl)<sub>2</sub>, as shown by FAB MS (*m/z* 968).<sup>6)</sup> In contrast to the reaction with substituted or unsubstituted diazomethane,<sup>7)</sup> no product having pyrazoline structure was isolated nor observed in the crude product by NMR or TLC.



The structure of the adduct **1** was determined based on the spectral data described below.

The EI MS spectrum exhibited molecular ion peaks ( $m/z$  844, 25%; 845, 15%; 846, 12%; 847, 5.5%; 848, 1.5%) which are in complete agreement with the theoretically predicted pattern of isotopic distribution for  $C_{60}((C_6H_5)CCl)$ , together with peaks for  $M^+ - Cl$  (809, 30%) and  $M^+ - (C_6H_5)CCl$  (720, 100%).

The  $^1H$  NMR spectrum (400 MHz,  $CS_2-(CD_3)_2CO$ ) showed only the signals for the *ortho*-protons and *meta* and *para*-protons at  $\delta$  8.13 and 7.55, respectively. In the  $^{13}C$  NMR spectrum (100 MHz,  $CS_2 - (CD_3)_2CO$ ) shown in Fig. 1, were observed three strong signals ( $\delta$  131.56, 130.35, 129.28) for proton-bearing carbons of the phenyl group, 27 signals ( $\delta$  146.53, 146.33, 145.56, 145.53, 145.45, 145.34, 145.04, 144.97, 144.93, 144.90, 144.85, 144.65, 144.03, 143.96, 143.47, 143.44, 143.35, 143.32, 142.73, 142.50, 142.45, 142.07, 141.34, 141.28, 139.76, 137.96, 135.86) corresponding to 27 sets of two equivalent carbons (marked by closed circles), four relatively weak and partially overlapped signals ( $\delta$  144.83, 144.77, 143.16, 143.12)<sup>8)</sup> for non-equivalent  $sp^2$  carbons (marked by open squares), and most importantly two signals at  $\delta$  79.13 and 58.17, which can be assigned to the aliphatic quaternary carbons of the newly formed three-membered ring. These signals are consistent with the structure **1** having one plane of symmetry, which was formed by addition of phenylchlorocarbene to the 6,6-junction bond of the  $C_{60}$  molecule. Addition of the chlorophenylcarbene to the 5,6-junction bond would result in the formation of two isomers **2** and **2'**<sup>9)</sup> unless one of them is predominantly formed over the other. From the present result, neither of these possibilities seems likely.

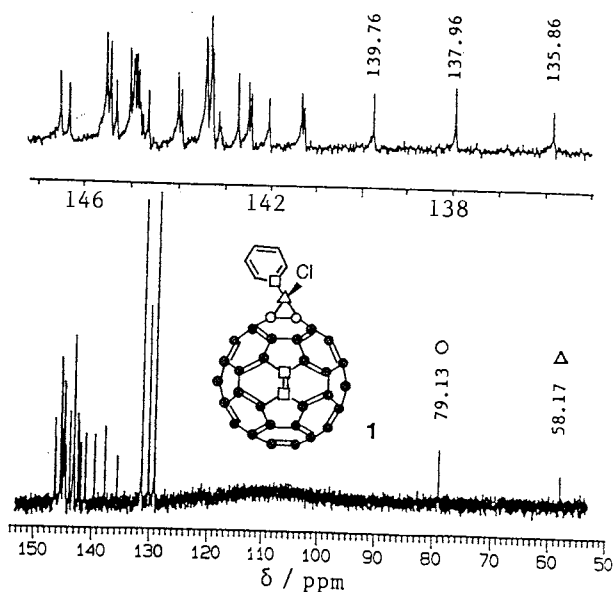
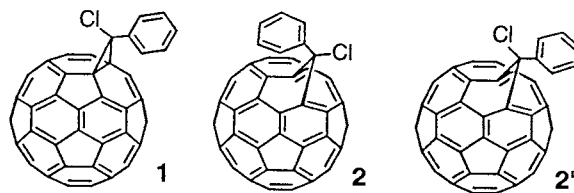


Fig. 1. The  $^{13}C$  NMR spectrum of **1**, together with the range of 135-147 ppm expanded.

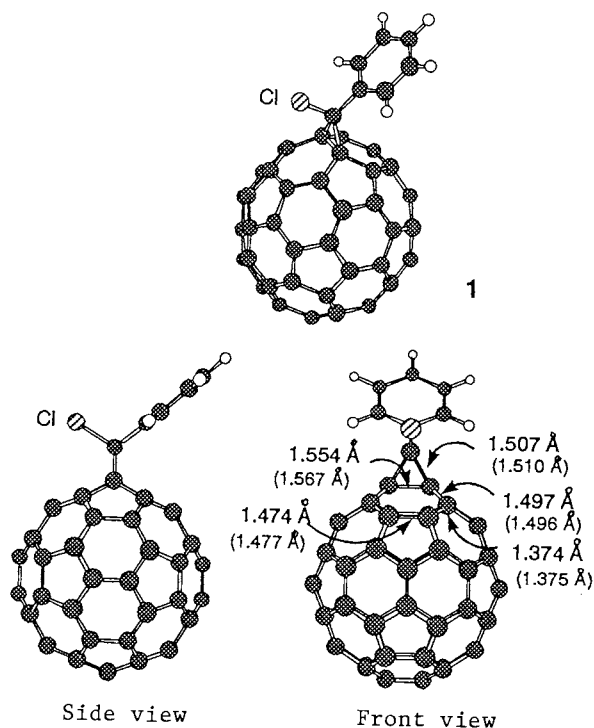


Fig. 2. The structures of **1** calculated by PM3; the values obtained by AM1 are in parentheses.

Actually, ab initio molecular orbital calculations (HF/3-21G//AM1)<sup>10</sup> indicated that the structure **1** is more stable than the structures **2** and **2'** by 8.0 and 8.4 kcal/mol, respectively. The methano-[10]annulene-type open structure was not on the potential minimum. The calculated structure of **1** (PM3)<sup>11</sup> is shown in Fig. 2 together with some values for calculated bond lengths.

The electronic spectrum of **1** exhibited the UV absorption similar to that of C<sub>60</sub> itself and the long-wavelength visible absorption extending to a maximum at 687 nm as shown in Fig. 3.

The cyclic voltammetry of the adduct **1** in benzonitrile exhibited at least three reversible reduction waves (Fig. 4) and one irreversible oxidation peak. The values of redox potential are shown in Table 1 together with those for C<sub>60</sub> and the [4+2] adduct of C<sub>60</sub> with anthracene, **3**,<sup>12</sup> for comparison. It is clearly seen that **1** is about 0.1 V less reducible than C<sub>60</sub>, but the oxidizability of **1** is almost the same as C<sub>60</sub>. This is in contrast to the adduct **3**, which is 0.1 V more oxidizable than C<sub>60</sub> possibly due to the intramolecular electronic interaction between the  $\pi$ -conjugated system and the rigidly held two benzene rings.

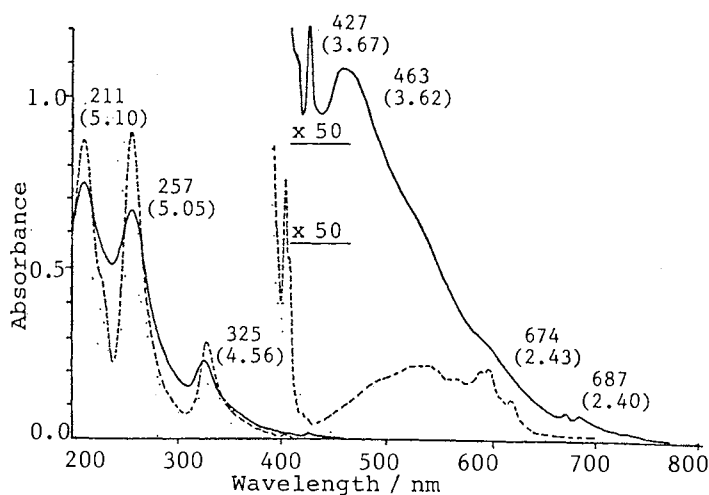


Fig. 3. The UV-Vis spectra of **1** (—) and C<sub>60</sub> (----) in cyclohexane (both concentration,  $6.0 \times 10^{-6}$  M).

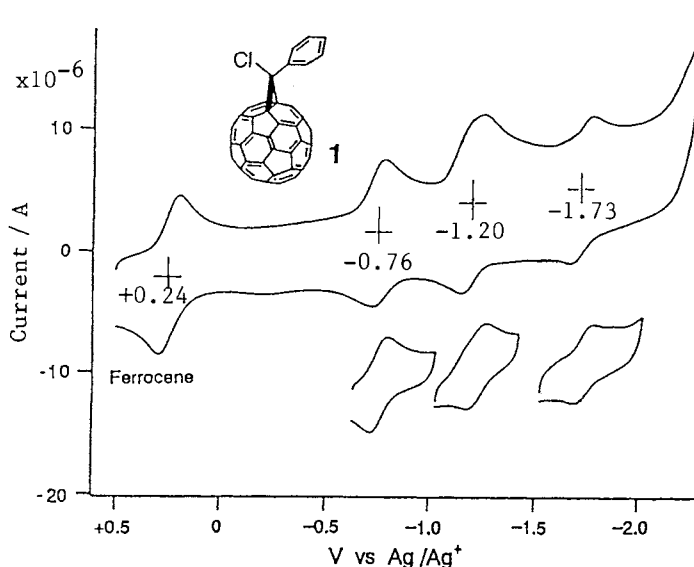
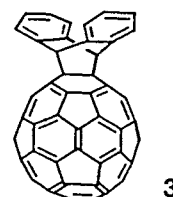


Fig. 4. The cyclic voltammogram of **1** in C<sub>6</sub>H<sub>5</sub>CN with 0.05M Bu<sub>4</sub>NBF<sub>4</sub>; scan rate, 0.1 V s<sup>-1</sup>. Also shown are wave patterns of individual redox waves.

Table 1. Comparison of the Redox Potential (V vs. ferrocene / ferrocenium) for C<sub>60</sub>, **1**, and **3** in Benzonitrile with 0.05 M Bu<sub>4</sub>NBF<sub>4</sub>

Compd	E <sub>ox</sub> <sup>a)</sup>	E <sub>red</sub> <sup>1 b)</sup>	E <sub>red</sub> <sup>2 b)</sup>	E <sub>red</sub> <sup>3 b)</sup>
C <sub>60</sub>	+1.41	-0.93	-1.36	-1.85
<b>1</b>	+1.39	-1.00	-1.44	-1.97
<b>3</b> <sup>c)</sup>	+1.31	-1.05	-1.45	-2.03

a) Irreversible (E<sub>pa</sub>). b) Reversible (E<sub>1/2</sub>). c) Ref. 12.



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- 5) **1**; mp >400 °C. IR (KBr)  $\nu$  1560, 1541, 1508, 1446, 1428, 1184, 752, 739, 718, 691, 582, 551, 526 cm<sup>-1</sup>. Anal. Found: C, 90.44; H, 0.53; Cl, 3.67%. Calcd for C<sub>67</sub>H<sub>5</sub>Cl: C, 95.21; H, 0.60; Cl, 4.19%. The repeated analyses on the recrystallized (CS<sub>2</sub>-pentane) and completely vacuum-dried sample constantly gave the low carbon contents (90.43%, 90.18%), presumably due to incomplete combustion.
- 6) When the reaction was carried out using 10-fold excess of the diazirine, a mixture of poly-carbene adducts, C<sub>60</sub>((C<sub>6</sub>H<sub>5</sub>)CCl)<sub>n</sub> (n = 1-8), was obtained as shown by FAB MS.
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- 8) It is assumed that one more one-carbon signal is hidden in larger signals.
- 9) The methanoannulene-type open structure is known to be more stable than the closed cyclopropane structure for the 5,6-addition product: for example, see Ref. 7c.
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