

## Synthesis and characterization of C<sub>60</sub> adducts with benzyne, dichlorocarbene, dienes, and oxygen

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We studied cycloaddition reactions of C<sub>60</sub> with benzyne, dichlorocarbene, and typical dienes and oxidation of C<sub>60</sub> with a perbenzoic acid. All of the products were isolated by HPLC and characterized by negative ion FAB MS. <sup>13</sup>C NMR analyses suggest that the anthracene, cyclopentadiene and dichlorocarbene adducts have closed structures at the 6-ring/6-ring junction.

### 1. Introduction

Studies on physics and chemistry of fullerenes [1] have been extensive since the method of macroscopic synthesis of fullerenes was discovered in 1990 [2]. While the physical properties of fullerenes have attracted much attention [3,4], the chemistry of fullerenes is also very attractive [5]. Several functionalizations of fullerenes [6-9] have been reported. We report here addition reaction of benzyne to C<sub>60</sub> [10] and Diels-Alder reactions of C<sub>60</sub> with several typical dienes [11]. We also examined addition reaction of dichlorocarbene to C<sub>60</sub> [12] and oxidation of C<sub>60</sub> with a perbenzoic acid.

### 2. Addition Reaction of Benzyne to C<sub>60</sub>

The addition reaction of benzyne was published elsewhere [10]. The products were separated on an HPLC (LC 908, Japan Analytical Industry Co., Ltd.) by using gel permeation columns (Jaigel 1H+1H) and chloroform as an eluent.

The negative ion FAB mass spectra of the four products were measured on a TSQ 700 (Finningan Mat Co., Ltd.). Samples were ionized from a matrix of *m*-nitrobenzyl alcohol by a Xe beam with an energy of 8 kV. We could observe molecular ion peaks ascribable to C<sub>60</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>n</sub> (n=1-4). The <sup>1</sup>H NMR spectra of these products were measured on a JNM-GX-270 (JEOL Co., Ltd.). The spectrum of C<sub>60</sub>(C<sub>6</sub>H<sub>4</sub>) showed a typical AA'BB' coupling

pattern due to the *o*-phenylene moiety. Hoke *et al.* reported the benzyne addition to C<sub>60</sub> [13] which is consistent with our results. The <sup>1</sup>H NMR spectra of the multi-adducts were rather complicated, indicating that the multi-adducts consist of the corresponding mixture of isomers.

### 3. Diels-Alder Reactions of C<sub>60</sub> with Dienes

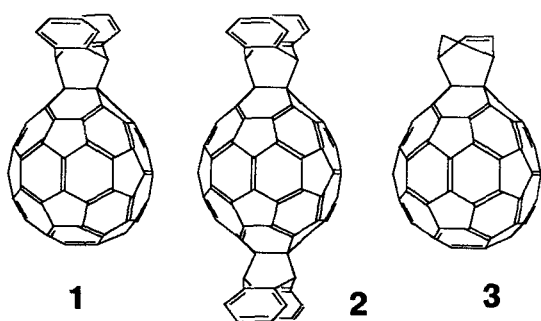
Diels-Alder reactions of C<sub>60</sub> have been reported recently by some groups [14] and they mentioned that mass spectral characterization of the adducts was hampered by their fragmentation into component molecules. We found that the Diels-Alder addition products between C<sub>60</sub> and several typical dienes can be characterized unequivocally by FAB mass and NMR spectroscopy. Although the isolation of the anthracene mono-adduct of C<sub>60</sub> has very recently been reported [15], we will discuss further the molecular structure of the mono- and di-adducts from the <sup>13</sup>C NMR data.

The addition reaction of C<sub>60</sub> with anthracene was published elsewhere [11]. The products were separated by HPLC (Jaigel 1H+1H) and toluene as an eluent, to give the mono-adduct C<sub>60</sub>(C<sub>14</sub>H<sub>10</sub>) and di-adduct C<sub>60</sub>(C<sub>14</sub>H<sub>10</sub>)<sub>2</sub>.

The negative ion FAB mass spectra of the mono- and di-adducts exhibited weak molecular ion peaks at *m/z* 898 for C<sub>60</sub>(C<sub>14</sub>H<sub>10</sub>)<sup>-</sup> and at *m/z* 1076 for C<sub>60</sub>(C<sub>14</sub>H<sub>10</sub>)<sub>2</sub><sup>-</sup> together with an intense peak at *m/z* 720 due to the fragment C<sub>60</sub><sup>-</sup>.

The mono-adduct has 3 and 21 resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra respectively [16].

These spectra indicate that the product has a  $C_{2v}$  symmetry **1** and that the cycloaddition occurs at the reactive 6-ring/6-ring junction like other adducts reported. The chemical shifts ( $\delta_c$  58.4 and 72.4) of the mono-adduct are reasonably assigned to the bridging tetravalent carbons. The former signal is due to the methine carbons at the pendant bridgehead. The latter is ascribable to the quaternary bridgehead carbons of the  $C_{60}$  moiety. This assignment is rationalized by the similarity of the chemical shifts of the diene adducts [14] and benzyne adduct [13] which have the corresponding closed propellanic structure. Wudl *et al.* reported that  $C_{61}\text{Ph}_2$  and  $C_{61}\text{H}_2$  had the methanoannulene structures and that the chemical shifts of all the carbons in the  $C_{60}$  moiety appeared in the fulleroid region ( $\delta_c$  120-160) [8]. These facts strongly indicate that the anthracene adduct has a closed structure and not an open structure like bridged annulenes. The di-adduct, purified by HPLC followed by repeated reprecipitation from  $\text{CS}_2$  solution with hexane, exhibited 3  $^1\text{H}$  and 13  $^{13}\text{C}$  signals in the NMR spectra [17]. The trans-polar  $D_{2h}$  structure **2** is proposed for the di-adduct.



Similarly, the reaction of  $C_{60}$  with cyclopentadiene gave the mono- and di-adducts. These products gave molecular ion peaks at  $m/z$  786 and 852 respectively, in the FAB mass spectra. The mono-adduct showed 4  $^1\text{H}$  and 35  $^{13}\text{C}$  signals in the NMR spectra [18]. The  $C_s$  structure explains these data satisfactorily. The adduct has a closed structure in the  $C_{60}$  sphere as indicated by the chemical shift analysis similar to the case of the anthracene adducts;

the position of the addition on the  $C_{60}$  moiety cannot be determined by  $^{13}\text{C}$  NMR data alone. Raghavachari *et al.* pointed out that the addition at a 6,6-"double" bond prefers closed structures but that the addition at a 5,6-"single" bond open structures [19]. Therefore, the proposed structure **3** seems to be plausible.

The addition reaction of  $C_{60}$  with hexachlorocyclopentadiene gave a mono-adduct, which exhibited molecular ion peaks around  $m/z$  993 with a characteristic isotope pattern in its mass spectrum.

The adducts with 2,3-dimethylbutadiene (DMBD) could not be isolated because of the autoxidation. After the reaction of  $C_{60}$  and DMBD followed by the removal of the solvent, the mass spectrum of the residue was measured immediately. It showed peaks corresponding to  $M+16$  and  $M+32$  (Figure 1). The generation of the accompanying products was suppressed under nitrogen, and their relative abundance increased in the air. Therefore, the new products were concluded to be air-oxidized products. Their mass spectra of the final products exhibited two series of several peaks due to  $C_{60}(\text{DMBD})_n\text{O}_m$  ( $n=1,2$ ;  $m=1-6$ ). Tandem MS/MS measurements of the parent ion at  $m/z$  818 due to  $C_{60}(\text{DMBD})\text{O}$  gave the peaks of fragments at  $m/z$  736 and 82 ascribable to  $C_{60}\text{O}$  and DMBD respectively. This fact indicates that the autoxidation occurred on the  $C_{60}$  and not on the pendant butene moiety.

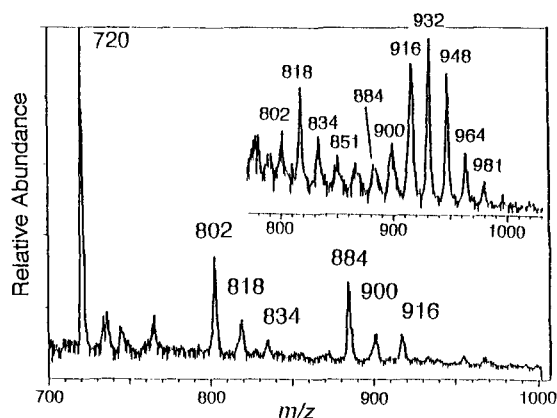


Figure 1 Negative ion FAB mass spectrum of the crude mixture for the addition reaction of  $C_{60}$  and 2,3-dimethylbutadiene. Inset: FAB mass spectrum of a series of autoxidized products from the di-adduct.

#### 4. Addition Reaction of Dichlorocarbene to C<sub>60</sub>

We examined the addition reactions of dichlorocarbene to C<sub>60</sub>. The adduct C<sub>60</sub>(CCl<sub>2</sub>) may give many functionalized fullerenes.

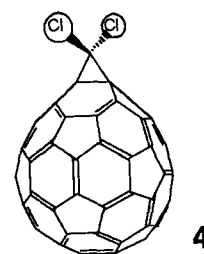
A mixture of 18.3 mg of C<sub>60</sub>, 46.8 mg of sodium trichloroacetate (10-fold excess), 20 ml of benzene, and 4 ml of diglyme was vigorously refluxed for 6 h under argon. The solution turned from purple to reddish brown. After an aqueous work-up followed by the evaporation of the solvent under reduced pressure, the products were separated on an HPLC (Jaigel 1H+1H). The isolated products were as follows in the order of the retention time (formulae were determined by their mass numbers and the yields of multi-adducts are shown as a mixture of isomers, see below): 1.5 mg (6%) of a tri-adduct C<sub>60</sub>(CCl<sub>2</sub>)<sub>3</sub>, 5.2 mg (22%) of a di-adduct C<sub>60</sub>(CCl<sub>2</sub>)<sub>2</sub>, 5.4 mg (25%) of a mono-adduct C<sub>60</sub>(CCl<sub>2</sub>), and 8.4 mg (43%) of C<sub>60</sub> recovered. Fractions containing a slight amount of tetra- or more-addition products were obtained in some cases. The mono-adduct is pink and other adducts are orange in solution.

The negative ion FAB mass spectra of the first, second, and third fractions showed molecular ion peaks around *m/z* 969, 886, and 803 respectively, accompanied by characteristic isotope patterns due to the chlorine atoms. The reaction products were assigned from these results. An intense peak at *m/z* 720 of the fragment C<sub>60</sub><sup>-</sup> was observed for all cases.

The <sup>13</sup>C NMR spectra of the mono-adduct exhibited 18 signals [20]. The signals at δ<sub>c</sub> 64.1 and 80.1 are ascribable to >CCl<sub>2</sub> and the bridgehead carbons, respectively. All of the other signals were observed in the fulleroid region (δ<sub>c</sub> 139-145). These findings indicate the following two structural informations. First, the molecule has a C<sub>2v</sub> symmetry which shows 17 resonances from the C<sub>60</sub> moiety; the addition occurred at the reactive 6-ring/6-ring junction as previously reported. An alternative C<sub>s</sub> isomer given by reaction at a 5-ring/6-ring junction is expected to have 32 resonances from the C<sub>60</sub> moiety and this is eliminated. Second, the chemical shift of the bridgehead carbons in the C<sub>60</sub> moiety is consistent with a closed

cyclopropane structure [13,14,21] and not with an open methanoannulene structure [8]. The resonances of the bridgehead carbons of the cyclopropane in the fullerene sugars were reported to appear in δ<sub>c</sub> 77-80 [21] in good accordance with the present study. In addition, the UV-vis absorption of C<sub>60</sub>(CCl<sub>2</sub>) [22] was practically the same as that of the fullerene sugar [21]. The structure 4 satisfies these results.

The <sup>13</sup>C NMR spectrum of C<sub>60</sub>(CCl<sub>2</sub>)<sub>2</sub> was rather complicated, indicating that it is a mixture of positional isomers having similar HPLC retention times. Their separation seems to be difficult by usual chromatographic methods.



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#### 5. Oxidation of C<sub>60</sub> with *m*-Chloroperbenzoic Acid

The mass spectra of oxidized fullerenes C<sub>60</sub>O<sub>n</sub> and C<sub>70</sub>O<sub>n</sub> were reported in 1991 [23]. The isolation and characterization of C<sub>60</sub>O have been reported [24]. We have also succeeded in the isolation of C<sub>60</sub>O and C<sub>60</sub>O<sub>2</sub> and found novel mass fragmentation in C<sub>60</sub>O<sub>2</sub>. The benzene solution (30 ml) containing 39 mg of C<sub>60</sub> and 13-fold excess amount of *m*-chloroperbenzoic acid was gradually warmed and finally refluxed for 2 h. After basic aqueous work-up and evaporation of the solvent, a small portion of the residue was separated by HPLC (Jaigel 1H+1H) eluted with toluene. Two oxidized products C<sub>60</sub>O (0.9 mg) and C<sub>60</sub>O<sub>2</sub> (0.3 mg) were separated after 13 recycles along with recovering similar amount of C<sub>60</sub>. The FAB mass spectra of the products showed the peaks at *m/z* 736 and 752, respectively. Interestingly, the fragment ions C<sub>58</sub><sup>-</sup> and C<sub>56</sub><sup>-</sup> were observed (*m/z* 696 and 672 respectively) in the mass spectra of C<sub>60</sub>O<sub>2</sub>, suggesting CO and/or CO<sub>2</sub> elimination from the product.

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- $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (2H, s, bridgehead CH), 7.46-7.49, 7.76-7.79 (4H +4H, AA'BB', *o*-phenylene).  $^{13}\text{C}$  NMR (68 MHz,  $\text{CDCl}_3\text{-CS}_2(1:1)$  / 0.02 M  $\text{Cr}(\text{acac})_3$ )  $\delta_c$  58.41(2, CH), 72.41(2), 125.74 (4, CH), 127.25(4, CH), 136.93(4), 139.81(4), 141.43 (4), 141.49(4), 141.88(4), 142.11(4), 142.42 (4), 142.84(2), 144.49(4), 145.20(6), 145.26 (8), 146.04(4), 146.30(4), 147.40(2), 155.40 (4). The carbon abundances shown in parentheses were estimated from the peak integrals. The signals at  $\delta_c$  145.20 and 145.26 were unresolved.
- $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.10 (4H, s, bridgehead CH), 7.50-7.53, 7.84-7.87 (8H and 8H, AA'BB', *o*-phenylene).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3\text{-CS}_2(1:3)$  / 0.02 M  $\text{Cr}(\text{acac})_3$ )  $\delta_c$  58.39(4, CH), 70.26(4), 125.73(8, CH), 127.16 (8, CH), 137.22(8), 140.43(8), 141.63(8), 141.78(4), 144.08(8), 145.17(8), 145.24(8), 147.06(4), 153.74(8).
- $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.52 (1H, d of t,  $J=9.3$ , 1.5 Hz,  $\text{CH}_A\text{H}_B$ ), 3.43 (1H, br d,  $J=9.3$  Hz,  $\text{CH}_A\text{H}_B$ ), 4.48 (2H, m, bridgehead CH), 7.05 (2H, m, vinyl CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3\text{-CS}_2(1:3)$  / 0.02 M  $\text{Cr}(\text{acac})_3$ )  $\delta_c$  45.07 (1,  $\text{CH}_2$ ), 56.43(2, CH), 75.17(2), 137.28(2), 137.56(2, CH), 137.70(2), 139.68(2), 139.90 (2), 141.64(2), 141.71(2), 141.84(2), 141.89 (2), 141.93(2), 142.42(2), 142.44(2), 142.48 (2), 142.81(1), 142.88(1), 144.27(2), 144.45 (2), 145.17(3), 145.20(2), 145.23(2), 145.24 (1), 145.26(2), 145.68(2), 145.86(2), 145.96 (2), 146.09(2), 146.19(4), 146.98(2), 155.29 (2), 157.03(2). The signals at  $\delta_c$  145.17 and 146.19 were unresolved.
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- $^{13}\text{C}$  NMR ( $\text{CDCl}_3\text{-CS}_2(1:1)$  / 0.02 M  $\text{Cr}(\text{acac})_3$ )  $\delta_c$  64.07(1), 80.11(2), 138.94(4), 141.26(4), 142.03(4), 142.23(4), 142.76(2), 143.13(4), 143.35(4), 143.64(4), 143.67(4), 144.28(2), 144.57(4), 144.67(4), 144.74(6), 145.22(8). The signals at  $\delta_c$  144.74 and 145.22 were unresolved. The signal intensity at  $\delta_c$  64.07 decreased with a short pulse interval (<1.5 sec), which is interpreted in terms of the relaxation prolonged by the chlorine atoms. Similar measurements in  $\text{C}_6\text{D}_6\text{-CS}_2$  (4:1) revealed that no signal was buried in the solvent  $\text{CDCl}_3$  signals.
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