

Isolation and Characterization of Diels–Alder Adducts of C₆₀ with Anthracene and Cyclopentadiene

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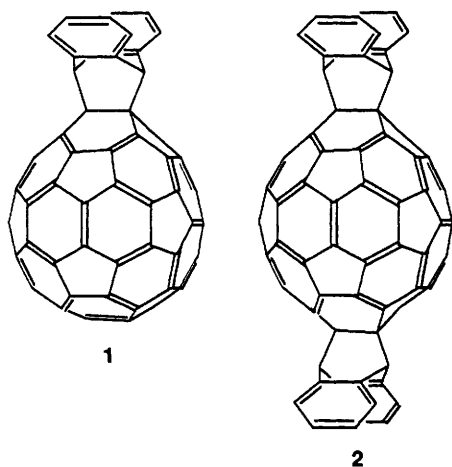
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The cycloadducts of C₆₀ and typical dienes have been isolated by HPLC, and the anthracene and cyclopentadiene adducts characterized by FAB mass and NMR spectroscopy.

Studies on fullerenes¹ have been extensive since the macroscopic synthesis of fullerenes was discovered in 1990.² It is important to study the chemical reactivity of fullerenes,^{3,4} in order to gain fundamental knowledge for the development of fullerene derivatives with interesting physical and chemical properties. This paper reports the syntheses, isolation and characterization of several cycloadducts of C₆₀ with anthracene, cyclopentadiene, 1,3-diphenylisobenzofuran and 2,3-dimethylbutadiene. Although Diels–Alder reactions of C₆₀ have been reported recently by some groups,^{5–7} they mentioned that mass spectral characterization of the adducts was hampered by fragmentation into component molecules. Rubin *et al.* also reported that the reaction products between

anthracene and C₆₀ could not be isolated and characterized.⁶ We have now found that the Diels–Alder adducts of C₆₀ with anthracene or cyclopentadiene can be characterized unequivocally by means of negative ion FAB mass and ¹H and ¹³C NMR spectroscopy.

The addition reaction of C₆₀ with anthracene is typical. A mixture of C₆₀ (18 mg), anthracene (5.4 mg) and benzene (5 ml) was refluxed for 12 h under nitrogen. After evaporation under reduced pressure below 50 °C, the products were separated by HPLC (LC 908, Japan Analytical Industry, Co., Ltd.) by using gel permeation columns (Jaigel 1H + 1H) and toluene as eluent, to give 5.6 mg (25%) of the mono-adduct C₆₀(C₁₄H₁₀) and 6.4 mg (24%) of di-adducts C₆₀(C₁₄H₁₀)₂.



The addition reaction was also conducted in toluene at 50, 80 and 110 °C to give the mono-adduct in 24, 17 and 8.5% yields respectively. Heating of the mono-adduct in toluene above 60 °C gave the component molecules. These findings mean that the reaction was reversible and that there was an equilibrium between addition and elimination reactions. The FAB mass spectra of mono- and di-adducts, using *m*-nitrobenzyl alcohol as a matrix and a Xe beam with an energy of 8 kV, gave weak molecular ion peaks at *m/z* 898 for $C_{60}(C_{14}H_{10})^-$ and *m/z* 1076 for $C_{60}(C_{14}H_{10})_2^-$, respectively, together with a strong signal at *m/z* 720 due to C_{60}^- . The mono-adduct has 3 and 21 resonances in the 1H and ^{13}C NMR spectra respectively.† 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 as for other adducts reported. The chemical shifts (δ_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 a diene adduct⁶ and benzyne adduct,⁴ which have the corresponding closed propellanic structure. Wudl *et al.* reported that $C_{61}Ph_2$ and $C_{61}H_2$ had the methanoannulene structures and that the chemical shifts of all the carbons in the C_{60} moiety appeared in the fulleroid region (δ_C 120–160).³ These facts strongly indicate that the anthracene adduct has a closed structure and not the isomeric open structure like bridged annulenes. The di-adduct, purified by HPLC, followed by repeated reprecipitation from CS_2 and hexane, exhibited 3 and 13 signals in 1H and ^{13}C NMR spectra, respectively.‡ The *trans*-polar D_{2h} structure 2 is proposed for the di-adduct.

Similarly, the reaction of C_{60} with cyclopentadiene (1 : 1.5 molar ratio) was conducted in toluene at a room temperature,

† NMR spectral data: 1H NMR (270 MHz, $CDCl_3$) δ 5.81 (2H, s, bridgehead CH), 7.46–7.49, 7.76–7.79 (4H and 4H, AA'BB', *o*-phenylene). ^{13}C NMR [68 MHz, $CDCl_3$ – CS_2 (1 : 1) with 0.02 M Cr(acac)₃ (acac = pentanedionato) as a relaxation agent] δ_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 δ_C 145.20 and 145.26 were unresolved.

‡ NMR spectral data: 1H NMR ($CDCl_3$) δ 6.10 (4H, s, bridgehead CH), 7.50–7.53, 7.84–7.87 (8H and 8H, AA'BB', *o*-phenylene). ^{13}C NMR [$CDCl_3$ – CS_2 (1 : 3)] δ_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). The carbon abundances are shown in parentheses.

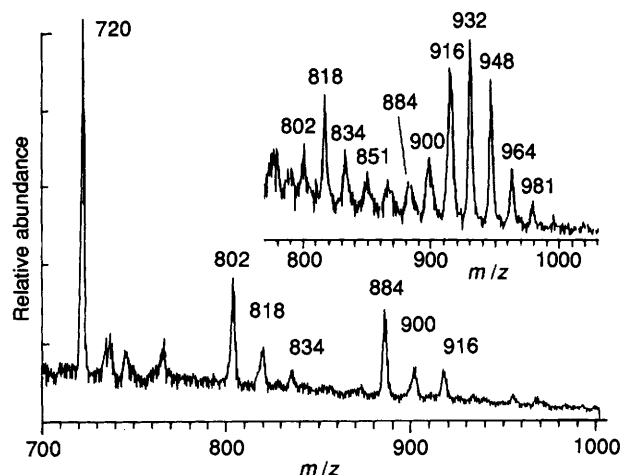


Fig. 1 Negative ion FAB mass spectrum of the crude mixture for the addition reaction of C_{60} and 2,3-dimethylbutadiene. Inset: FAB mass spectrum of a series of autoxidized products from the di-adduct.

and the adducts were purified by HPLC. This system gave mono- and di-adducts in 68 and 28% yields, respectively. These products gave molecular ion peaks at *m/z* 786 and 852, respectively, in the FAB mass spectra. The mono-adduct showed 4 and 35 signals in the 1H and ^{13}C NMR spectra, respectively.§ The C_s structure explains these data satisfactorily.⁸ The adduct has a closed structure in the C_{60} sphere; the position of addition to the C_{60} moiety cannot be determined by means of ^{13}C NMR spectrum alone. The 1H NMR spectrum of the di-adduct was very complicated. The appearance of at least 10 1H resonances in the aliphatic region (δ 1–5) suggests that the second cyclopentadiene can add to the pendant cyclopentene moiety as well as to the C_{60} moiety.

Although the above products could be isolated by HPLC, the cycloadduct between C_{60} and 1,3-diphenylisobenzofuran (DPIF) or 2,3-dimethylbutadiene (DMBD) could not be isolated because of the facile retro-Diels-Alder reaction of the former product⁷ and because of the autoxidation of the latter product. The addition reaction of DPIF with C_{60} occurred smoothly at 0 °C in toluene and the mass spectra measured immediately after the removal of the solvent indicated the presence of the mono-adduct at *m/z* 990. However, the mono-adduct in toluene gradually decomposed to the component molecules at room temperature. This decomposition seems to be facilitated by steric repulsion due to the bulky phenyl groups.

After the reaction of C_{60} and DMBD (molar ratio 1 : 10) in toluene at 70 °C, followed by the removal of the solvent, the mass spectrum of the residue was measured immediately. It showed peaks corresponding to the mono- and di-adducts at *m/z* 802 and 884 respectively (Fig. 1). Both signals were accompanied by two signals at *m/z* corresponding to $M + 16$ and $M + 32$. The generation of the accompanying products was suppressed under nitrogen atmosphere, and their relative abundance increased in the air. Therefore, the new products were concluded to be air-oxidized products. The mass spectra of the final products exposed in the air exhibited two series of several peaks due to C_{60} (DMBD)_{*n*}O_{*m*} (*n* = 1, 2; *m* = 1–6). The inset of Fig. 1 shows the peaks of molecular ions of

§ NMR spectral data: 1H NMR [$CDCl_3$ – CS_2 (1 : 3)] δ 2.52 (1H, d of t, *J* 9.3, 1.5 Hz, CH_AH_B), 3.43 (1H, br d, *J* 9.3 Hz, CH_AH_B), 4.48 (2H, m, bridgehead CH), 7.05 (2H, m, vinyl CH). ^{13}C NMR [$CDCl_3$ – CS_2 (1 : 3)] δ_C 45.07(CH_2), 56.43(CH), 75.17, 137.28, 137.56(CH), 137.70, 139.68, 139.90, 141.64, 141.74, 141.84, 141.89, 141.93, 142.42, 142.44, 142.48, 142.81, 142.88, 144.27, 144.45, 145.17, 145.20, 145.23, 145.24, 145.26, 145.68, 145.86, 145.96, 146.09, 146.19, 146.98, 155.29, 157.03. The signals at δ_C 145.17 and 146.19 were unresolved.

$C_{60}(DMBD)_2O_m$. Tandem MS-MS measurements of the parent ions at m/z 818 due to $C_{60}(DMBD)O$ gave the fragment peaks at m/z 736 and 82 ascribable to $C_{60}O$ and DMBD respectively. This fact indicates that the autoxidation occurred on the C_{60} moiety.¶

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¶ *Note added in proof*: A very recent report on the mono-adduct of C_{60} and anthracene is consistent with our results. See J. A. Schlueter, J. M. Seaman, S. Taha, H. Cohen, K. R. Lykke, H. H. Wang and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 972.

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