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Use of Naphthalene as a Solvent for Selective Formation of the 1:1 Diels-Alder Adduct of C_{60} with Anthracene

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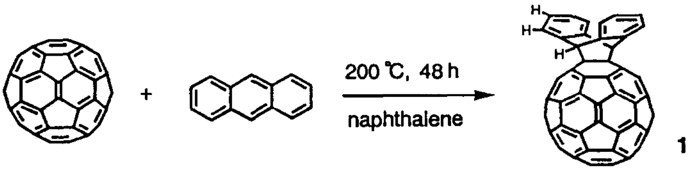
Abstract: A reaction of C_{60} with an equimolar amount of anthracene in refluxing naphthalene gives the 1:1 Diels-Alder adduct in 67% yield based on consumed C_{60}: the adduct was fully characterized by IR, UV-vis, ^{1}H and ^{13}C NMR, and MS spectroscopy, and exhibited reversible reduction waves at the potential 0.11 to 0.19 V more negative and an irreversible oxidation peak at the potential 0.11 V less positive than those of C_{60} itself.

The dienophilic nature of the specific bond connecting the two five-membered rings of the π-conjugated surface of C_{60} has been well demonstrated by [4+2] reactions of C_{60} towards several dienes, such as cyclopentadiene,[1] anthracene,[1] isobenzofuran,[2] orthoquinodimethane,[3] and its equivalent.[4] Among these, the reaction of C_{60} with an excessive amount of anthracene in refluxing *o*-dichlorobenzene has been simply reported to give the poly-adduct "$C_{60}(C_{14}H_{10})_n$",[1,5] but to date there has been no report on the formation and properties of the 1:1 adduct of C_{60} and anthracene with a well-defined structure. Here we report the successful use of naphthalene as a high-boiling solvent to give selectively the 1:1 adduct, which is fully characterized spectroscopically and by electrochemical means. The use of a simple hydrocarbon solvent rather than a halogenated one is desirable when consideration is made on the effect of contamination by the remaining high-boiling solvent upon possible further reaction on the produced C_{60} derivatives.

As a typical procedure, C_{60} (40 mg, 0.055 mmole), anthracene (12 mg, 0.067 mmol), and naphthalene (2.0 g) were mixed well by grinding in a mortar, and sealed together with a small magnetic stirring bar in a Pyrex glass tube under vacuum. The mixture was heated with stirring at 200 °C for 2 days.[6] The reaction mixture was thoroughly washed with pentane, by application of ultrasonic agitation, to remove naphthalene and unchanged anthracene. The residue was separated by the use of medium pressure liquid chromatography



(hexane-toluene (9:1) / silica gel) to give unchanged C_{60} (17 mg, 42%) and the [4+2] adduct **1**[7] as a dark brown powder (19 mg, 39%).[8] The structure of **1** was determined based on the spectral data as follows.

As shown in Fig. 1, the ^1H NMR of the product exhibited typical A_2B_2 quartets at δ 7.73 and 7.43 and a singlet at δ 5.76 which are both about 0.4 ppm downfield shifted as compared with corresponding signals in triptycene, reflecting the deshielding effect characteristic of the fulleroid π-system.[9] The ^{13}C NMR spectrum showed two signals for the proton-bearing aromatic carbons (δ 127.251, 125.761) and seventeen signals in the aromatic region (δ 155.450, 147.435, 146.320, 146.068, 145.289, 145.266, 145.243, 145.226, 144.517, 142.859, 142.447, 142.149, 141.912, 141.507, 141.491, 139.826, 136.946) together with one signal for an aliphatic quaternary carbon (δ 72.442) and one signal for a methine carbon (δ 58.377) (Fig. 1). Since the structure **1** has two planes of symmetry, the signals for the sixty carbons in the original C_{60} sphere are classified into thirteen four-carbon signals (marked by closed circles; all sp^2-carbons) and four two-carbon signals (marked by open circles; three sp^2- and one sp^3-carbons).[10] These signals are all observed together with additional four-carbon signals of the *ipso*-, α-, and β-carbons of the phenyl rings and two-carbon signal of the methine carbon as described above, thus strongly supporting the assigned structure.

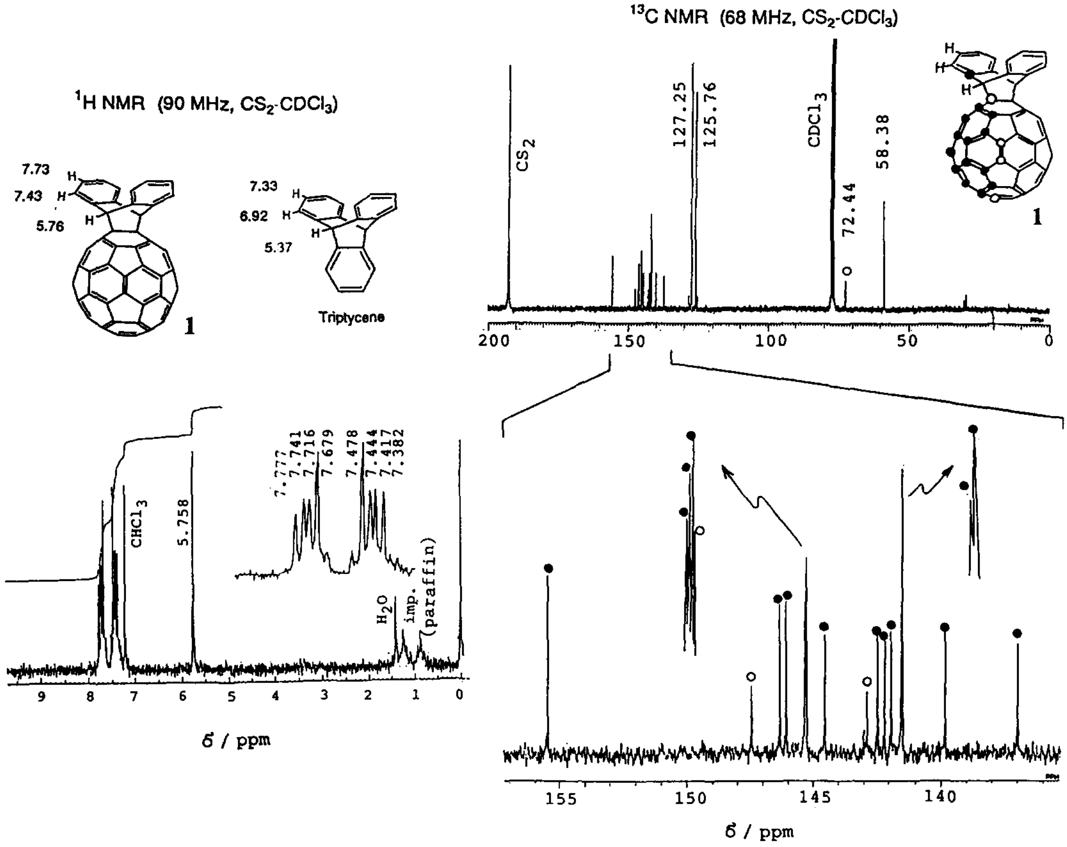


Fig. 1. ^1H and ^{13}C NMR spectra of the adduct **1**.

In the FAB MS spectrum, the peak for $C_{74}H_{10}$+H was very weak, but strong peaks for C_{60} and $C_{14}H_{10}$ were observed indicating the occurrence of retro [4+2] cleavage.

In spite of loss of full conjugation and formation of two saturated carbons on the original C_{60} surface, the electronic spectrum of the adduct **1** exhibited UV absorptions similar to those of C_{60} and the visible absorption which extends over to 703 nm as shown in Fig. 2.

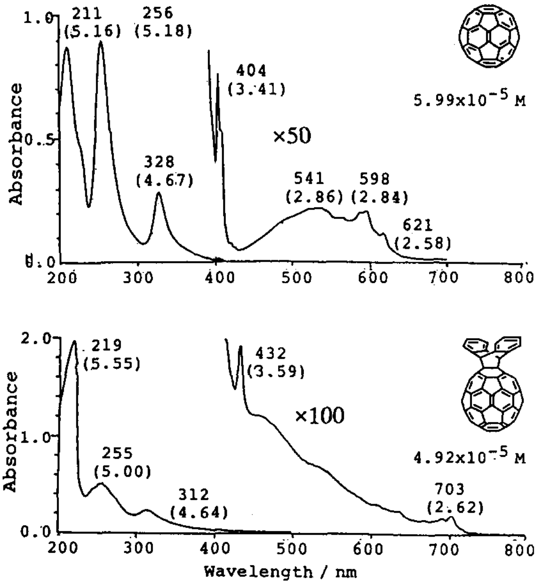


Fig. 2. UV-Vis spectra of C_{60} and the adduct **1** in cyclohexane.

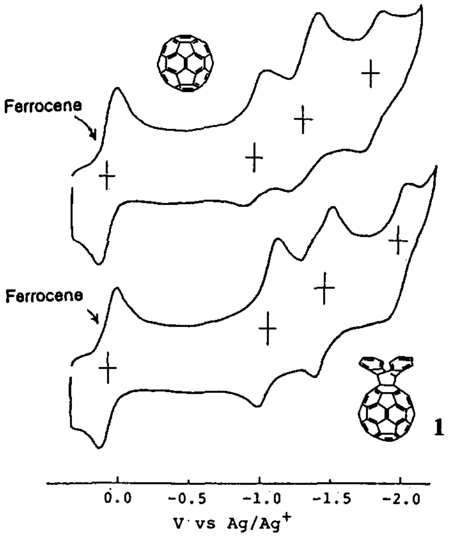


Fig. 3. Cyclic voltammogram of C_{60} and the adduct **1** in dichloromethane: sample, 3×10^{-4} M; supporting electrolyte ($Bu_4N^+BF_4^-$), 5×10^{-2} M; scan rate, 0.1 V s^{-1}.

The cyclic voltammogram of **1** (Fig. 3) also demonstrated the redox behavior similar to that of C_{60} in CH_2Cl_2 with $Bu_4N^+BF_4^-$ as a supporting electrolyte at 25 °C. Three reversible reduction waves were observed at -1.15, -1.54, and -2.06 V vs Fc (ferrocene) / Fc^+, which are cathodically shifted by only 0.11 to 0.19 V as compared with those of C_{60} taken under the same conditions (-1.04, -1.40, and -1.87 V).[11] These results imply that the π-conjugated system in **1** still retains considerably high electron affinity comparable to C_{60} and also to the "fulleroid" $C_{61}(C_6H_5)_2$.[9a]

In contrast, the oxidation potential of **1** measured in benzonitrile with $Bu_4N^+BF_4^-$ as a supporting electrolyte (irreversible; E_{pa} +1.28 V vs Fc / Fc^+) was found to be lowered by 0.11 V as compared with that of C_{60} obtained under the same conditions (E_{pa} +1.39 V).[12] It might be concluded that this ease of oxidation is due to the intramolecular through-space supply of π-electron from the benzene rings which are rigidly held in the close proximity to the spherical conjugated surface.[13]

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REFERENCES AND NOTES

1. Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. in *Fullerenes Synthesis, Properties, and Chemistry of Large Carbon Clusters*; Hammond, G. S.; Kuck, V. J. Eds.; American Chemical Society: Washington DC, 1992; pp.161-175. Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561-1562.
2. Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594-1595.
3. Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem.* **1993**, *105*, 95-97 ; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78-80.
4. Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344-345.
5. A product from the reaction of C_{60} with anthracene is also mentioned simply as "an insoluble brown precipitate" in ref. 4 without any further description.
6. The reaction was also carried out by heating in a usual flask equipped with a reflux condenser under nitrogen atmosphere to give essentially the same result.
7. **1**; mp >300°C. IR (KBr) ν 3021, 2918, 1458, 1428, 1213, 1188, 1182, 1155, 766, 760, 752, 746, 735, 698, 672, 641, 598, 585, 575, 581, 549, 526 cm^{-1}. Anal. Calcd for $C_{74}H_{10}$: C, 98.88; H, 1.12. Found: C, 98.23; H, 0.90.
8. This yield is for the reaction using C_{60} as a mixture containing 8% of C_{70}. When purified C_{60} was used, the yield was somewhat low (24%) probably due to the lower solubility of the purer material.
9. a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186-1188. b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *J. Am. Chem. Soc.* **1992**, *114*, 7300-7301.
10. The distinction between the signals for the carbons marked by open and closed circles was made by comparison of the peak height and peak width in the expanded spectra shown as the insets in Fig. 1.
11. Literature data; -0.92, -1.32, and -1.81 V vs Fc / Fc^+ with the same supporting electrolyte as in the present study: Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050-1051.
12. Literature data; +1.30 V vs Fc / Fc^+ in benzonitrile using $Bu_4N^+PF_6^-$ as a supporting electrolyte: Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773-7774.
13. Although this lowering of oxidation potential might also be interpreted as due to splitting of the original five-fold degenerate HOMO of C_{60}, such effect should be small since no such decrease was observed for other derivative of C_{60} such as the 1:1 adduct with phenylchlorocarbene: K. Komatsu, A. Kagayama, Y. Murata, N. Sugita, and T. S. M. Wan, submitted for publication in *Chem. Lett.*

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