

Synthesis, Purification, and Characterization of the 1 : 1 Addition Product of C₆₀ and Anthracene

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A cleanly separated Diels–Alder product of C₆₀, a 1 : 1 adduct of anthracene, has been synthesized and characterized by thermogravimetric analysis, and NMR, UV–VIS, IR and mass spectroscopies.

In a relatively short period of time, buckminsterfullerene-based materials have been shown to possess numerous interesting properties including superconductivity,¹ ferromagnetism² and nonlinear optical behaviour.³ Fullerene-based derivatives are also expected to produce materials that may exhibit similar novel physical properties. Functionalizing C₆₀ results in derivatives that add a 'handle' to the spherical molecule, which could also hinder its rapid rotation in the solid state.⁴ The characterization of fullerene derivatives has been hampered by the formation of multiply-substituted, and difficult to separate byproducts. Recently, several cycloadditions to C₆₀ have been reported that have been stabilized against retro-Diels–Alder reactions.^{5–7} C₆₀ reportedly reacts with anthracene^{5,8,9} forming insoluble brown precipitates and uncharacterized multiply-substituted products. We find that the retro-Diels–Alder reaction of C₆₀(anthracene) is very facile, resulting in the adducts being relatively unstable. Herein, we report the synthesis, purification, and characterization of a 1 : 1 adduct of C₆₀ and anthracene prepared by use of a Diels–Alder reaction. The increased solubility of this adduct (with respect to the parent C₆₀ molecule) in common organic solvents is expected to facilitate crystallization with organic donors creating a new class of charge transfer salts with novel electronic and magnetic properties.

C₆₀(anthracene) was prepared by the reaction of 10 equiv. of anthracene (Aldrich, 99%) with 1 equiv. of C₆₀ (Strem Chemicals, purified with Norit-A–silica gel, toluene, chrom-

atography¹⁰) in refluxing toluene for three days. The initial purple colour of the solution, due to unreacted C₆₀, became red as the reaction proceeded. When fewer equivalents of anthracene were used, the equilibrium shifted towards the starting materials resulting in lower product yields.

Purification was accomplished by use of column chromatography (4' silica gel column) with carbon disulfide as eluent. The first fraction was purple and identified as unreacted C₆₀ by IR and UV–VIS spectroscopies. The golden second fraction, the desired 1 : 1 C₆₀(anthracene) adduct, was cleanly separated from both the unreacted fullerene and a pinkish-tan coloured third fraction. ¹H NMR data indicated that this third fraction is a multiple-adduct whose characterization is not yet completed. The 1 : 1 adduct remained stable for several weeks when stored in a freezer (–10 °C). The doubly chromatographed C₆₀(anthracene) product was produced in 13% yield. (Calcd. for C₇₄H₁₀: C, 98.9; H, 1.11. Found: C, 98.0; H, 1.3%). The slightly low carbon content is attributed to incomplete burning of the fullerene.¹¹ Refluxing purified C₆₀(anthracene) in toluene for several days resulted in product degradation forming neutral C₆₀ and anthracene *via* a retro-Diels–Alder reaction.

The ¹H NMR spectrum of C₆₀(anthracene) is shown in Fig. 1. The resonances from the A and B protons exhibit A₂B₂ coupling and are centred at δ 7.83 and 7.52, respectively. The integrated intensity of the A, B and X resonances is in the expected ratio of 2 : 2 : 1. The A proton resonance is shifted

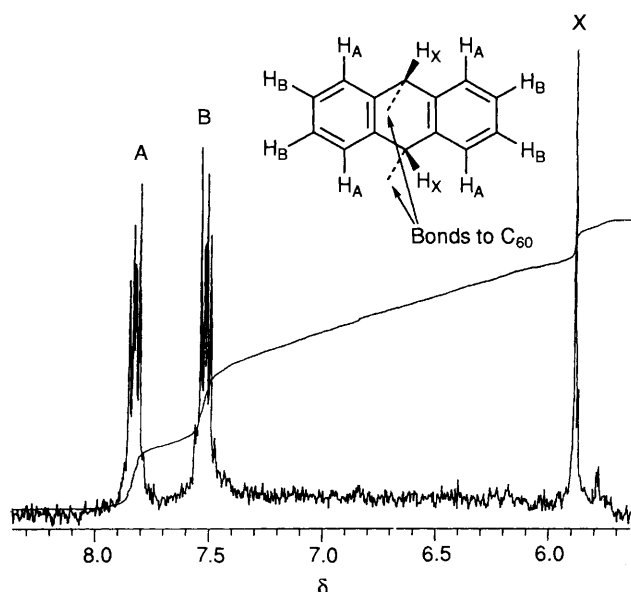


Fig. 1 ^1H NMR of C_{60} (anthracene) in CD_2Cl_2

upfield from the δ 7.91 observed in neutral anthracene,¹² while the B proton resonance is shifted downfield from δ 7.39. As a comparison, the monobenzyne adduct of C_{60} also shows A_2B_2 coupling,⁷ but both resonances are shifted downfield by about 0.2 ppm with respect to this anthracene adduct. This shift is probably due to the closer proximity of the benzyne protons to the electron-withdrawing buckyball. The 9,10-protons (X) give rise to a single resonance at δ 5.89, significantly upfield from the corresponding resonance (δ 8.31) in anthracene. The alkyl proton resonance of triptycene (δ 5.30),¹³ which also has an aromatic group bridging the anthracene 9,10-positions, is slightly upfield from that observed in the C_{60} (anthracene) adduct. The resonances characteristic of neutral anthracene protons are not observed in the NMR spectrum confirming that this material is a cleanly separated adduct, not just a mixture of C_{60} and anthracene. Based on the symmetrical nature of the ^1H NMR spectrum of C_{60} (anthracene), it is postulated that the anthracene unit adds across the reactive 6–6 ring junction.

Thermal gravimetric analysis (TGA) of C_{60} (anthracene) was performed by increasing the temperature at a rate of $20\text{ }^\circ\text{C min}^{-1}$ with $5\text{ }^\circ\text{C}$ resolution (Fig. 2). A 19.97% weight loss occurred (transition onset at $120\text{ }^\circ\text{C}$ and midpoint at $194\text{ }^\circ\text{C}$). This compares favourably with the 19.84% weight loss expected for the removal of the single anthracene unit from the 1:1 adduct. The transition temperature is $40\text{ }^\circ\text{C}$ higher than the sublimation point observed for neutral anthracene under identical conditions, confirming that the two moieties are bound to one another.

UV-VIS spectroscopy has been used to characterize the 1:1 adduct further. The absorbances observed for C_{60} ¹⁴ [$\lambda_{\text{max}}/\text{nm}$ 213 ($10^{-3}\text{ } \epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ 126.5), 256, (166.6), 328 (53.2) and 404 (2.80)] and anthracene¹⁵ [$\lambda_{\text{max}}/\text{nm}$ 217 ($10^{-3}\text{ } \epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ 1.2), 245 (48.4), 323 (2.5), 339 (5.2), 356 (7.9) and 375 (7.7)] agree with the literature values. C_{60} (anthracene) [$\lambda_{\text{max}}/\text{nm}$ 209 ($10^{-3}\text{ } \epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ 138.1), 255 (115.5), 311 (32.4) and 433 (3.8)] shows a significant decrease in the intensity of the bands near 255 and 320 nm. This hypsochromic effect contrasts with that reported for H_2C_{61} ¹⁶ and $\text{C}_{60}\text{Ph}_{12}$,¹⁷ which exhibit no significant change in electronic structure from the parent fullerene. The bathochromic shift of the weak visible band from 404 to 433 nm is similar to that observed in the monobenzyne adduct of C_{60} .⁷ The bands characteristic of anthracene are not observed in the C_{60} (anthracene) product, confirming that the aromatic system of the anthracene moiety has been broken, and that no unreacted anthracene remains in the product.

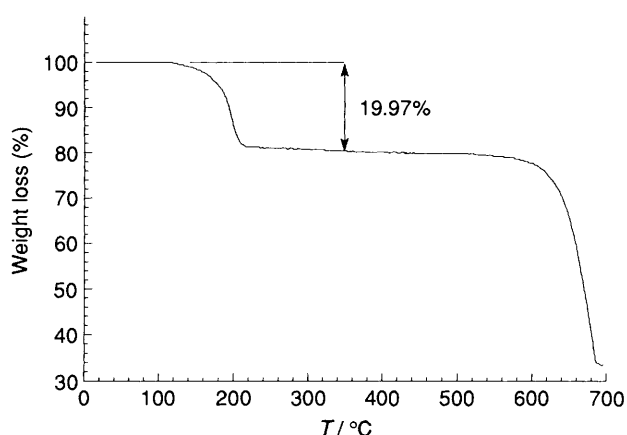


Fig. 2 Thermal gravimetric analysis (TGA) of C_{60} (anthracene)

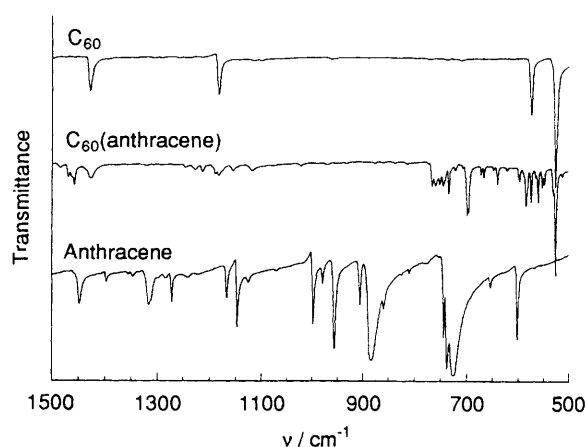


Fig. 3 Comparison of the infrared spectra of C_{60} , anthracene, and C_{60} (anthracene) determined in KBr pellets

The IR spectrum of C_{60} shows four characteristic vibrational frequencies at 528, 577, 1183 and 1429 cm^{-1} .^{18–20} The most intense absorptions of neutral anthracene occur at 475, 464, 602, 725, 738, 744, 884, 957, 998 and 1147 cm^{-1} , while for C_{60} (anthracene) they occur at 527, 531, 553, 561, 575, 585, 698, 735, 746 and 767 cm^{-1} . The C_{60} (anthracene) bands at 527, 575, 1183 and 1428 cm^{-1} are attributed to the fullerene moiety. The anthracene moiety is probably responsible for the bands near 750 cm^{-1} , which may be associated with 1,2-disubstituted benzene group modes, and the 698 cm^{-1} absorption is due to a *cis*-alkene-type vibration. A comparison of these spectra is shown in Figure 3. Thus, the IR data support the assumption that the aromatic anthracene unit is radically altered while the fullerene unit is essentially unchanged upon the formation of C_{60} (anthracene).

A weak parent peak (m/z 898) has been observed in the laser desorption–time of flight mass spectrometry (TOFMS) of C_{60} (anthracene) by use of *ca.* 50 ps 532 nm laser pulses. The C_{60} (m/z 720), anthracene (m/z 178) and another C_{60} (anthracene) fragment (m/z 822) are much more intense than the parent. These results are similar to the findings of Rubin⁵ and confirm that this complex undergoes facile fragmentation into its anthracene and C_{60} substituents.

Preliminary experiments indicate that C_{60} reacts with a number of dienes through Diels–Alder reactions and it is expected that this will lead to a new class of compounds that may exhibit interesting electronic and magnetic properties after doping with electron donor or acceptor molecules. Doping C_{60} (anthracene) by use of alkali metal vapour reactions, as reported for C_{60} ,¹ will be hampered by the relatively low thermal decomposition temperature of this

adduct. This difficulty may be overcome by use of solution phase techniques,²¹ which allow the use of lower reaction temperatures. The increased solubility of this adduct in common solvents (such as tetrahydrofuran) promises to facilitate electrocrystallization and cocrystallization techniques, which may be used to synthesize novel C₆₀(anthracene) charge-transfer salts not possible with the less soluble C₆₀.

Dr David French is acknowledged for his assistance in obtaining the NMR spectrum and Karen Crippen (Institute of Gas Technology) for TGA results. We also thank Mr Joseph Gregar for his custom fabrication of necessary glassware. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN). This work was sponsored by the Office of Basic Energy Sciences, Division of Materials Sciences, US Department of Energy, under Contracts W-31-109-ENG-38. H. C. is a member of the chemistry staff at Roosevelt University. J. M. S. and S. T. are undergraduate research participants from Mount Holyoke College and Stanford University, respectively, sponsored by the Argonne Division of Educational Programs.

Received, 2nd March 1993; Com. 3/01232H

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