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Pyrolytic Syntheses of a C_{60} Derivative of Naphthalene and Some Congeners

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We recently characterized the C_{60} derivative of benzene (1) prepared by adding the fullerene to *o*-benzyne.[1] Fullerene derivatives of naphthalene result from analogous reactions with naphthynes. The 1,8-naphthyne is commonly generated by oxidation of the amino triazine **5**.[2] To date the derivatization by this procedure has proven inefficient. We were however able to prepare isolable quantities of a buckminsterfullerene derivative of naphthalene (**2**) in a simpler procedure, by pyrolytically decomposing 1,8-diiodonaphthalene (**4**) in the presence of C_{60} (Scheme 1).

Equimolar quantities of C_{60} (SES Research) and **4**[3] (50–100 mg of solids) were mixed in a Pyrex tube (10 cm × 0.8 cm (o.d.)). After evacuation to ~25 Torr and flame sealing, the mixture was heated to 500 °C in a furnace for 2 min, allowed to cool, shaken, and heated again for an additional 3 min.[4] The char was extracted with CS_2. Mass spectral analysis of the heterogeneous reaction mixtures showed that yields varied. From 1–14% of the C_{60} was converted to the mononaphthyne adduct, m/z = 846.[5] In addition to the monoadduct, compounds that corresponded to $[C_{60} + (C_{10}H_6)_n]^{-\bullet}$, where $2 \leq n \leq 10$, were also present. When 10 equiv of **4** was decomposed, the functionalized fullerenes represented up to 90% of the starting C_{60}. Comparable results were obtained by exposing one end of a tube to a gas/O_2 flame (Figure 1).

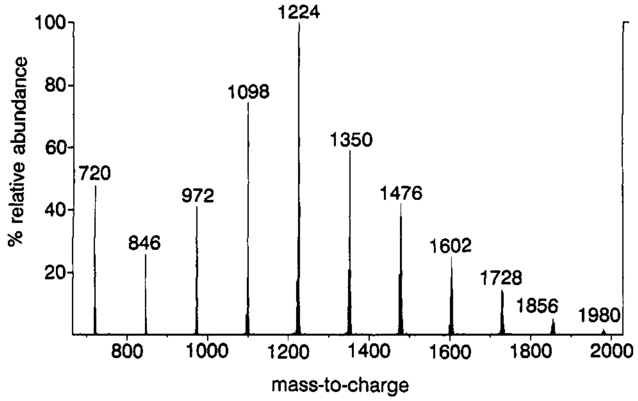
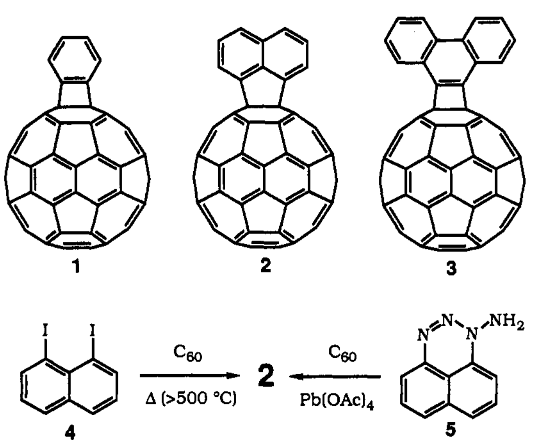


Figure 1. Negative ion desorption chemical ionization mass spectrum of the mixture resulting from the pyrolysis of 1,8-diiodonaphthalene in the presence of C_{60}.

Scheme 1



Milligram quantities of the mixtures were chromatographed on a semipreparative C_{18} column.[6] The ^{1}H-NMR spectrum[7] of the fraction corresponding to monoaddition of naphthyne contains an AA′BB′CC′ multiplet indicating that the 1,8 positions are attached to the fullerene: δ_A, 8.12 ppm; δ_B, 7.99 ppm; and δ_C, 7.83 ppm. The spectrum was simulated with coupling constants of J_{AB} = 0.8 Hz; J_{AC} = 7.2 Hz; and J_{BC} = 8.8 Hz. Compound **2** is yellow. The UV/vis spectrum in *n*-hexane showed absorptions at 325, 256, and 225 nm which are characteristic of fullerene derivatives.[1]

A structural comparison of a homologous series of addends to the pyracylene bonds of C_{60} would plainly address the subtle electrocyclic ring opening switch proposed by Diederich and co-workers.[8] The ^{13}C-NMR spectrum (Figure 2) shows 23 signals characteristic of a molecule with C_{2v} symmetry; the C_{60} molecule must be fused at the 6,6 ring juncture. The lone signal at 76.47 ppm is characteristic of quaternary bridgehead carbons.[9]

Fullerenes have been described as free radical traps.[10] We have established that a variety of aryl radical, or aryne, precursors effectively add to C_{60} under pyrolytic conditions.[11] For example, 9-bromophenanthrene, which has shown 9,10-phenanthryne reactivity above 300 °C,[12] provided a compound with m/z = 896 which may be formulated as **3** by analogy with the structures assigned to **1** and **2**.

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(4) The C_{60}-*p*-xylylene copolymer was prepared pyrolytically. See: Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977–3978.

(5) The mass spectra of the reaction mixtures were recorded by electron attachment desorption chemical ionization mass spectrometry (DCI-MS). A 1-μL aliquot of the CS_2-soluble fraction was placed on the rhenium wire filament of a direct evaporation probe and allowed to dry. The probe was then introduced into the source of a Finnigan Triple Stage Quadrupole (TSQ) 700 mass spectrometer and the sample was thermally desorbed by resistive heating, typically at a rate of 20 °C/s. Desorbed molecules were ionized by electron attachment in an ammonia chemical ionization plasma with an ammonia pressure of 7000 mTorr, uncorrected. See: von Ardenne, M.; Steinfelder, K.; Tummler, R. *Elekronenanlagerungsmassenspektrometric Organischer Substanzen*; Springer-Verlag: Berlin, 1971. Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953–6963. Dillard, J. G. *Chem. Rev.* **1973**, *73*, 589–643.

(6) A Vydac 201TP, 5-μm, C_{18}, 250 × 10-mm i.d. column protected by a C_{18} guard column was used in the HPLC separations. Isocratic elution was achieved on a Perkin-Elmer Series 400 liquid chromatograph at a flow rate of 2 mL/min with a 55:45 mixture of Fischer HPLC-grade acetonitrile and Baker chloroform. The reaction mixture was dissolved in CS_2 and filtered with a nylon 66, 0.45-μm membrane filter, and the brown solution was injected using a Rheodyne Model 7120 injector. Elution was monitored by ultraviolet absorption at 254 nm with an Altex mercury vapor detector.

(7) ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian VXR 500 and VXR 600 NMR spectrometers, respectively. The UV/vis spectrum was recorded with a Hewlett-Packard 8451A diode array spectrometer.

(8) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M. M.; Anz, S. J.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548–551. Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231–1250.

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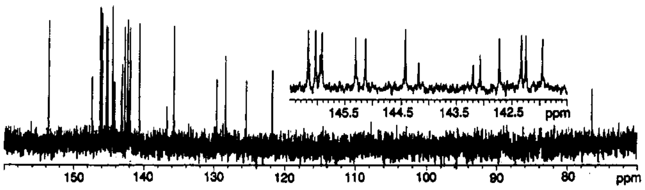

Figure 2. The ^{13}C-NMR spectrum of the mononaphthyne adduct of C_{60} in 3:1 CS_2/CD_2Cl_2 with 0.04 M $Cr(acac)_3$ as a relaxation agent. The sample was enriched with about 25% of material that was prepared from ^{13}C-enriched C_{60} (SES Research, ~5% ^{13}C). ^{13}C NMR ppm: 153.59; 147.37; 146.17; 146.04; 145.96; 145.92; 145.31; 145.13; 144.42; 144.19; 143.20, 142.72, 142.34, 142.24, 141.95, 140.66, 136.73, 135.73, 129.57 (CH), 128.34, 125.41 (CH), 121.77 (CH), 76.47. Peak at 143.06 ppm represents a few percent of C_{60}.

It is known that large η^2 addends to C_{60} tend to occupy the octahedral pyracylene sites.[13] The sixth addition was a saturation point in the benzyne reaction[1] as well as in the addition of cyclopentadienes[14] and carbenes (Ar_2C).[15] A C_{60} decorated with six 1,8-naphthyne units at these traditional positions could not accommodate sterically a seventh addend. Ten groups can reasonably be fitted if, at 500 °C, the pyracylene bonds that terminate opposing corannulene caps of the C_{60} molecule serve as addition sites. Wudl and co-workers showed that the reaction of C_{60} with Grignard reagents was terminated after ten additions.[16]

As the number of naphthyne additions to C_{60} increases, the successive clusters of ions deviate increasingly, on the low side, from the theoretical isotope distributions. This can be accounted for by H_2 losses. Naphthynes crowning corannulene pyracylene sites may lose H_2, thus forming 2,2′-binaphthyne connections between adjacent addends.

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