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Reaction of Cyclopropa[b]naphthalene with $^3He@C_{60}$

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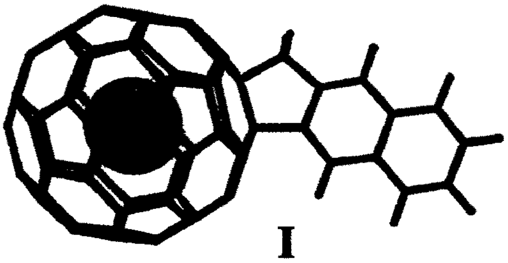
Abstract: The adduct (I) formed by the reaction of the diradical obtained by heating cyclopropa[b]naphthalene with ^3He-labeled C_{60} has been characterized. The corresponding ^1H, ^{13}C, and ^3He NMR spectra are reported.

Although the fullerenes react readily with a large number of reagents, complex mixtures of products are often produced and characterization can be a tedious process.[1] The recent discovery that ^3He can be introduced into C_{60} and C_{70} by heating with helium[2] and that the incorporation can be increased using high pressure[3] permits an important advance in the characterization of fullerene derivatives. In general, each product made from helium labeled fullerenes yields a single sharp peak in the ^3He NMR spectrum.[4] Non-fullerene products or impurities have no helium and do not give signals. We report here the addition of a 1,3-biradical[5]—generated by thermolysis of cyclopropa[b]naphthalene[6]—to the fullerene $^3He@C_{60}$ and the ^3HeNMR spectrum of this adduct I.[7]



I

A solution of the cycloproparene in anhydrous benzene was added dropwise in about 15 minutes to C_{60} in refluxing anhydrous benzene under an inert atmosphere. After approximately 2.5 hours, the reaction was terminated, and the product was isolated by column chromatography using silica gel, and was further purified by HPLC using a Regis Buckyclutcher^R column. The ^{1}H-NMR (250 MHz, $CS_2/CDCl_3$) spectrum exhibited signals at $\delta = 8.60$ (s, 1H); 8.23 (s, 1H); 8.04–7.97 (m, 2H); 7.64–7.52 (m, 2H); 5.35 (s, 2H) ppm. ^{13}C-NMR (75 MHz, INEPT experiment) revealed six methine signals at $\delta = 129.50$, 127.88, 126.71, 126.30, 125.57, 125.09 ppm; and one methylene signal at $\delta = 47.23$ ppm. The FDMS gave a strong peak at $m/e = 859.9$, and in *n*-hexane the product showed UV absorptions at 222, 254, 324, and 406 nm.

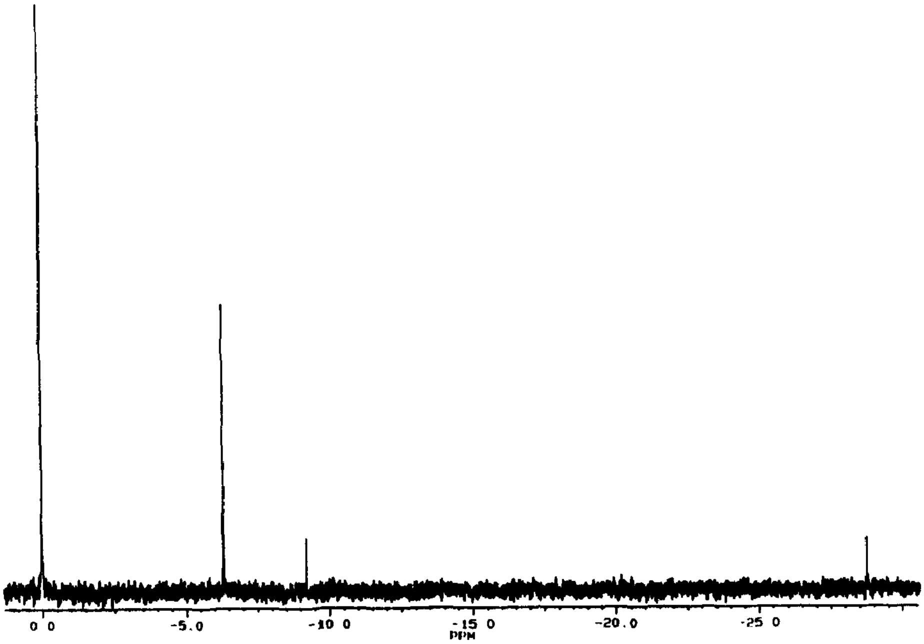


Figure 1. ^{3}He NMR spectrum (381 MHz) of I. A total of 30000 scans were accumulated (about 18 hours)

Fullerene extract (containing both C_{60} and C_{70}) was heated with ^{3}He at 2600 atmospheres at 620°C for 10 hours.[3] About 22 mg of the labeled fullerene was reacted with approximately 1 eq. of the cycloproparene using the conditions described above. The reaction product was concentrated, washed with a small amount of ether, and redissolved in a small volume of carbon disulfide. The resulting solution was filtered through a small plug of activated charcoal. No further purification was carried out. The solvent was evaporated and the solid was dissolved in a 4:1 mixture of 1-

methylnaphthalene/CD_2Cl_2 for NMR purposes, along with 1 mg of $Cr(acac)_3$ to speed up relaxation. About 1–1.5 mL of ^3He gas were bubbled through the solution in the NMR tube with a syringe. The corresponding ^3He NMR spectrum[13] is shown in **Figure 1**. Four signals are observed at 0.0 (^3He gas), −6.33 (C_{60}), −9.23 (cyclopropa[b]naphthalene-C_{60} adduct), and −28.76 ppm (C_{70}).

The ^3He NMR spectrum of He@C_{60} and He@C_{70} has been reported.[4] Formation of the C_{60} adduct results in an upfield shift of almost 3 ppm, suggesting that even though a double bond has been removed from the C_{60} skeleton, the product has a larger net ring current than the parent molecule. A similar shift has been observed for the adduct obtained from the reaction of He@C_{60} with azomethine ylide.[14] Thus far, all of the helium peaks we have measured in different derivatives of fullerenes have been at unique shifts and clearly resolvable.

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