

Synthesis and ^3He NMR Studies of C_{60} and C_{70} Epoxide, Cyclopropane, and Annulene Derivatives Containing Endohedral Helium[†]

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The entrapment of atoms in the cavities of fullerenes has stimulated considerable theoretical study and has begun to provide unique and valuable materials.¹ Recently we have achieved ca. 0.15% incorporation of helium into C_{60} and C_{70} at high temperature and pressure.^{2–4} Fullerenes doped with ^3He should immediately find widespread application as NMR probes of reactivity, as just a single, sharp peak is expected for each component of a reaction mixture.^{5,6} We now describe the transformations of $^3\text{He}@C_{60}$ (**1**) and $^3\text{He}@C_{70}$ (**2**) to their monofunctional derivatives **3–6** and **7–10**, respectively, as well as ^3He NMR analysis of the products (Figure 1).

The syntheses of **3–10** exploited protocols we developed previously for the “empty” parent compounds.^{7–9} He-labeled and unlabeled fullerenes could react at different rates, but we currently assume that helium incorporation levels in the reactants and products are comparable. Effects on rates or equilibria, if any, might be considered analogous to isotope effects.⁴ The endohedral-helium products coeluted with the corresponding empty compounds in flash chromatography and HPLC. As we reported earlier,^{2–4} the standard preparation of C_{60} and C_{70} affords modest incorporation of helium (about 1 molecule in 880 000), suggesting that undetectably small quantities of **3–10** were in fact generated in our prior studies.

[†] This paper is dedicated to Professor Jerome A. Berson on the occasion of his 70th birthday.

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Oxygenated fullerene derivatives are the focus of intensive current effort.¹⁰ The prototypical epoxide C_{60}O , a constituent of fullerene soot,¹¹ was first isolated, synthesized in controlled fashion, and characterized at Penn and Exxon.⁷ The epoxide structure, with oxygen bridging a 6,6 ring junction, was originally deduced via ^{13}C NMR⁷ and recently confirmed by X-ray analysis of an organometallic derivative.¹² Oxygenation of 25 mg of doped fullerene soot (containing ca. 0.15 mol % ^3He) afforded 3 mg of monoepoxide containing $^3\text{He}@C_{60}\text{O}$ (**3**). The ^3He chemical shift of **3** proved to be -8.24 ppm.

Both direct carbene additions and dipolar cycloadditions of alkyl and aryl diazo compounds readily furnish fullerene derivatives.^{10,13} Reaction of C_{60} with 1 equiv of diazomethane generates the 6,6-monopyrazoline adduct,¹⁴ progenitor of both the parent 6,6-bridged cyclopropane (methanofullerene)⁸ and 6,5-bridged annulene (homofullerene).¹⁴ Following similar treatment of ^3He -labeled soot (25 mg, 4:1 $\text{C}_{60}/\text{C}_{70}$), the ^3He NMR spectrum revealed the presence of pyrazoline **4** (-9.29 ppm) accompanied by unreacted **1** and **2**. Upon heating of the sample in the NMR tube at 80°C for 2 h, the ^3He resonance at $\delta -9.29$ was replaced by a signal at $\delta -6.62$, assigned to the bridged annulene **5** by analogy with thermolysis of the empty pyrazoline.¹⁴

Annulene **5** and the isomeric cyclopropane **6** were then prepared via photolysis⁸ of a second sample of ^3He -labeled pyrazoline. Reversed-phase HPLC furnished the endohedral helium species, each admixed with the corresponding hydrocarbon; the ^3He chemical shift for **6** was -8.11 ppm.

We turned next to a set of four C_{71}H_2 isomers which we recently characterized as a pair of cyclopropanes and a pair of annulenes.⁹ Following addition of 1 equiv of diazomethane to a 4:1 mixture of ^3He -doped C_{70} and C_{60} (100 mg), flash chromatography afforded a mixture of three C_{71} -derived monopyrazolines (10:1 toluene/hexane eluant). Half of the latter solution was photolyzed, and the remainder was heated at reflux for 10 min, furnishing a mixture of cyclopropanes (6 mg) and a mixture of annulenes (7 mg), respectively, after normal-phase HPLC. The ^3He chemical shifts of the major cyclopropane **7** and the minor cyclopropane **8** were -28.14 and -25.56 ppm; the helium annulenes resonated at -27.46 (major isomer **9**) and -27.82 ppm (minor isomer **10**).

In general, the ^3He chemical shifts of fullerene derivatives containing helium reflect the influence of the magnetic fields induced by ring currents around the π orbitals;¹⁵ the ring currents in turn can be correlated with the aromatic character of the fullerenes.^{16–19} The ^3He chemical shifts for **1–10** and $\Delta\delta$ values for **3–6** and **7–10** (relative to **1** and **2**, respectively) are tabulated in Figure 1.

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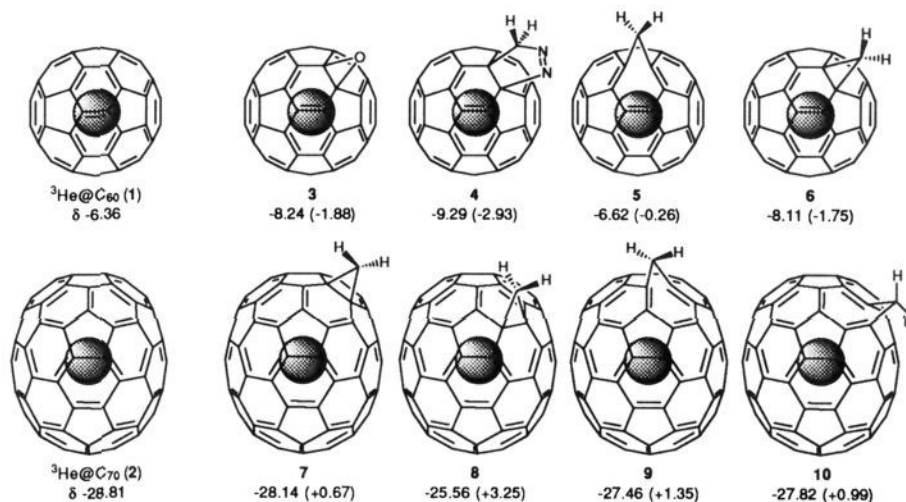
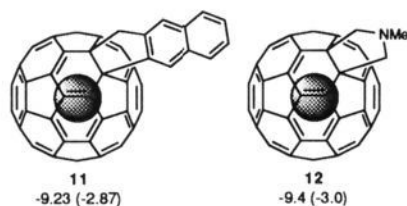


Figure 1. Structures and ^3He NMR chemical shifts (ppm) for 1–10. $\Delta\delta$ values for 3–6 and 7–10 (relative to 1 and 2, respectively) are given in parentheses.

The chemical shift of $^3\text{He}@C_{70}$ (2, -28.81 ppm) reveals a large net diamagnetic ring current⁴ (cf., gaseous ^3He , 0 ppm) which is diminished slightly in derivatives 7–10 ($\Delta\delta$ $+0.67$ to $+3.25$). In contrast, the chemical shifts of $^3\text{He}@C_{60}$ and 3–6 (-6.36 to -9.29 ppm) reflect the more modest aromaticity now ascribed to C_{60} .^{4,19} The limited available data do suggest an empirical correlation of ^3He δ values with structure for $^3\text{He}@C_{60}$ derivatives. For 11 and 12, cyclopentanoid and pyrrolidine derivatives of $^3\text{He}@C_{60}$, we previously reported chemical shifts



of -9.23^6 and -9.4^5 ppm, very similar to the -9.29 ppm shift for the pyrazoline 4. All three structures contain five-membered rings fused to a 6,6 ring junction. Other four- and five-membered ring derivatives show similar shifts.²⁰ The smallest

$\Delta\delta$ value derives from annulene 5 (-6.62 ppm, $\Delta\delta$ -0.26), which also embodies the smallest perturbation of the C_{60} π system. The 6,6-epoxide 3 and cyclopropane 6 give rise to similar ^3He chemical shifts (-8.24 and -8.11 ppm), intermediate between those observed for 5 and for 4, 11 and 12. One might interpret this as a homoconjugative phenomenon wherein the contributions of the cyclopropane-type orbitals in 3 and 6 are similar to those of double bonds but smaller in magnitude. The latter results complement earlier UV-vis studies which suggested that the unique electronic structures of the parent fullerenes are more fully expressed in 6,5-annulene derivatives than in 6,6 cyclopropanes and epoxides.^{7–9,13} Interestingly, variations in electronegativities of substituent atoms seem to exert little effect on the ^3He chemical shifts.

We will report in due course on further studies designed to explicate theoretical and empirical correlations of chemical shift with structure in helium derivatives of fullerenes.

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Supplementary Material Available: ^3He NMR spectra of 3–10 (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(20) Unpublished results of Dr. Hugo A. Jiménez-Vázquez (Yale University).