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^{3}He NMR: A Powerful New Tool for Following Fullerene Chemistry

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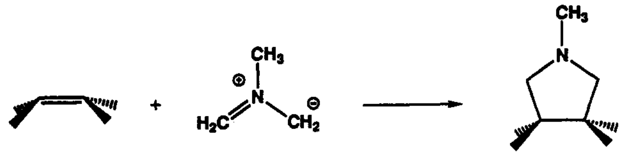
The fullerenes react readily with a variety of reagents.[1] Following their reactions with NMR spectroscopy has not been easy. While the ^{13}C NMR spectra of C_{60} and C_{70} are simple, spectra of reaction products are not, since the attachment of groups to the fullerene skeleton reduces the high symmetry. After chemical modification, the single resonance of C_{60} and the five peaks of C_{70} are replaced by many small peaks. It requires very long data acquisition times to obtain spectra of such products. The time can be decreased through the use of ^{13}C-enriched fullerenes. However, if several products are formed or, as is common, bis-adducts are produced, assigning the carbon peaks is difficult or impossible. It is necessary to carefully separate the reaction mixtures and examine each pure product. NMR of other nuclei on substituents of the fullerenes in reaction products can be useful. However, even with ^{1}H NMR there can be complications. Fullerenes tend to trap solvent in the lattice, and solvent protons can appear in the ^{1}H spectrum. Reagents and byproducts generally give proton signals as well. In order to obtain good ^{1}H NMR spectra of fullerene products, it is necessary to use thorough purification and drying procedures.

Continuing our studies of endohedral fullerene compounds of noble gases,[2] we have recently used high pressure and heating to introduce ^{3}He into C_{60} and C_{70}, increasing incorporation levels to around 0.15%.[3] We have used this material to obtain the first ^{3}He NMR spectra of helium compounds.[4] Each helium-labeled fullerene gives a single sharp peak. Line widths can be under 1 Hz. The large chemical shifts (C_{60}, –6.3 ppm; C_{70}, –28.8 ppm from dissolved ^{3}He as reference) show that there are substantial aromatic ring currents modifying the magnetic field experienced by the helium nucleus in the center of the fullerenes. We expected that altering the π-bonding structure of the fullerene through reaction would produce substantial shifts in the ^{3}He peak.

We have now verified this expectation. We have subjected a ^{3}He-labeled fullerene mixture (about 70% C_{60}, 30% C_{70}) to the reaction conditions recently reported by Maggini, Scorrano, and Prato[5] for the azomethine ylide addition to fullerenes to form *N*-methylpyrrolidines (Scheme 1). We heated 25 mg of the ^{3}He-labeled fullerene mixture with 2 equiv of *N*-methylglycine and 5 equiv of paraformaldehyde at reflux in benzene for 2 h. After removal of benzene, the reaction mixture was dissolved in CS_2 and filtered through a small plug of activated charcoal/silica gel. No other separation or purification of the reaction mixture was done. The ^{1}H NMR spectrum of the resulting material (C_6D_6/CS_2) shows a complex set of signals. The major peaks observed at δ 4.38 and 2.99 correspond to those reported for the product.[5] We believe that the additional signals correspond to bis-adducts of C_{60} and mono-adducts of C_{70}. The material used for ^{1}H NMR was recovered and redissolved in a 4:1 mixture of 1-methylnaphthalene/CD_2Cl_2 (a good solvent for fullerenes). About 1.0 mg of chromium acetylacetonate was added in order to decrease the relaxation time of the helium.

Scheme 1



After only a few hours of data acquisition (381 MHz),[6] we could clearly see peaks for $He@C_{60}$ and its pyrrolidine mono-adduct. The spectrum shown in Figure 1 was obtained after 36 h of accumulation (about 57 000 scans). Shifts given are with respect to dissolved ^{3}He at 0 ppm. The peaks at –6.4 and –28.8 correspond to $He@C_{60}$ and $He@C_{70}$, respectively.[3] We assign the peak at –9.4 to the mono-adduct reported.[5] We believe the smaller peaks at –10.9 and –12.3 to be due to bis-adducts of C_{60}. The peaks at –23.8 and –27.9 we believe to be mono-adducts of C_{70}. We show the ^{13}C NMR spectrum (125 MHz) of the fullerene region of the same sample for comparison (Figure 2). The large peak is C_{60}, and we assume that the smaller peaks are due to the mono-adduct of C_{60} and unreacted C_{70}. Peaks of the bis-adducts of C_{60} and the mono-adducts of C_{70} would be hidden by noise. There are also strong peaks (not shown) for the naphthalene carbons. Note the complexity of the ^{13}C spectrum as compared with the ^{3}He spectrum.

It is striking that addition to just one of the 30 double bonds of $^3He@C_{60}$ produced a 3 ppm shift of the helium upfield. At this point, even qualitative rationalization of the direction of these shifts would be speculative. It is interesting that the adducts of C_{70} shift downfield. We consider it very likely that other reaction products of the fullerenes will have distinguishable ^{3}He NMR peaks which will be correlatable with structure. The peak areas should be accurate indicators of relative amounts.

We expect that ^{3}He NMR spectroscopy will be an extremely useful tool for exploratory study of fullerene reactions. After a reaction on ^{3}He-labeled fullerenes is run, the ^{3}He spectrum of the reaction mixture will show whether the starting fullerene has been consumed as well as how many products have been formed and in what proportions, since each peak will correspond, in general, to a different compound. Separations can then be carried out (and followed using ^{3}He NMR), or further reactions can be performed on the mixture. There will be no extraneous peaks due to the reagents, non-fullerene products, the solvent, or their impurities. We anticipate that reactions which proceed via bond-

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(2) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993,** *259,* 1428.

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(5) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993,** *115,* 9798.

(6) The ^{3}He NMR spectrum was obtained with a Bruker AM-500 spectrometer. An external 20-W amplifier was used to produce 381-MHz pulses. A 500-MHz probe was modified to tune at 381 MHz. A pulse width of 15 μs (60°) and a pulse delay of 1 s were used. The digital resolution of the spectrum shown in Figure 1 is 0.925 Hz/point.

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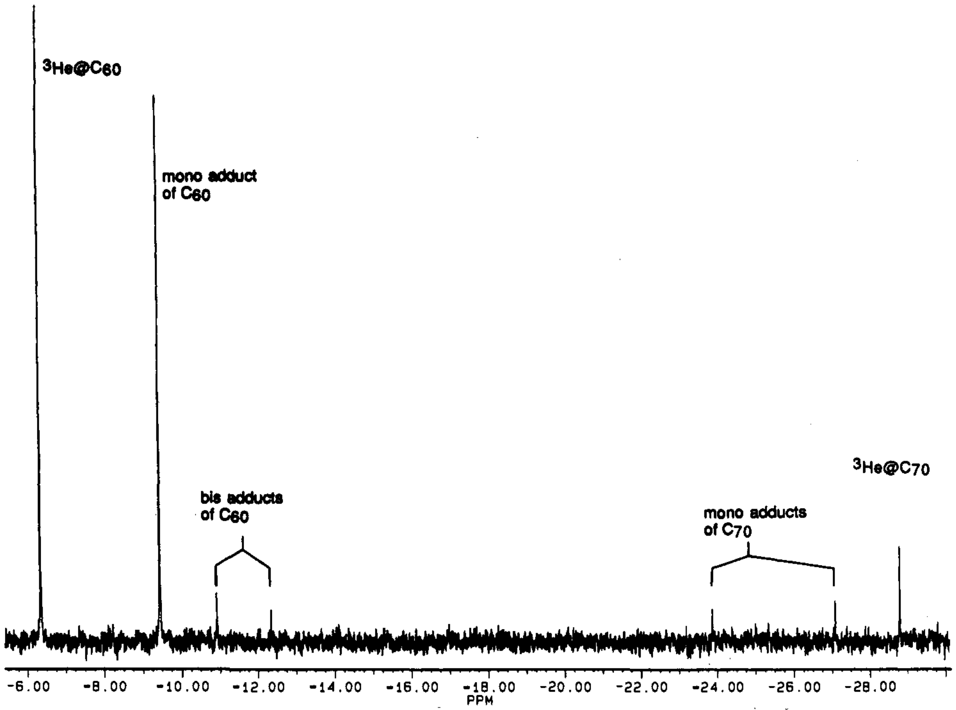

Figure 1. ^{3}He NMR spectrum (381 MHz) of the product of addition of azomethine ylide to a ^{3}He-labeled C_{60}–C_{70} mixture. Another spectrum was acquired after 1.5 mL of ^{3}He was bubbled through the sample in the NMR tube with a syringe to create a reference peak.

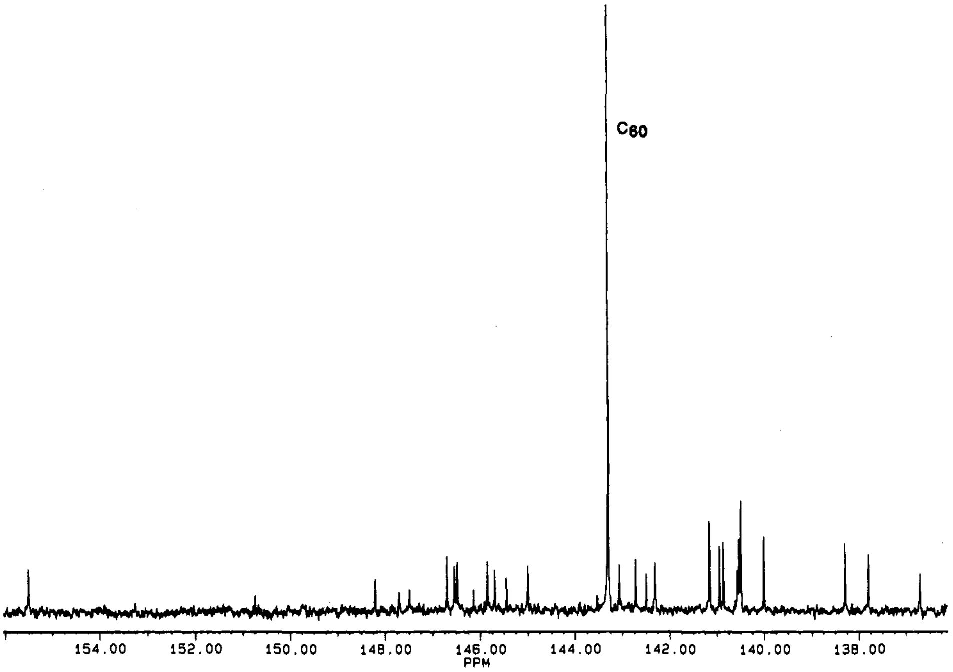

Figure 2. ^{13}C NMR spectrum (125.77 MHz) of the same sample as in Figure 1. The large peak corresponds to unreacted C_{60}.

opened intermediates (temporarily forming "windows" in the fullerene cage) will result in escape of the helium and can be followed by the decrease of the helium peak of that compound or the growth of the peak for free helium in a sealed NMR tube.

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