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Reduction of C_{60} Using Anhydrous Hydrazine

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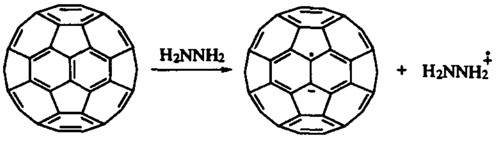
Abstract: Buckminsterfullerene (C_{60}) can be reduced by anhydrous hydrazine to yield a mixture of $C_{60}H_2$, $C_{60}H_4$ and other more highly reduced fullerenes. Copyright © 1996 Elsevier Science Ltd

The synthesis of fullerene hydrides is an area of considerable interest currently.[1-8] Henderson and Cahill showed that BH_3 in tetrahydrofuran could be used to convert C_{60} into $C_{60}H_2$.[1] This method was also used to form several of the $C_{60}H_4$ isomers.[6] Other reagents have also been used and these have been described in subsequent publications.[1-5,7,8] We now report that C_{60} can be reduced by anhydrous hydrazine in benzene to form the simple hydrogenated fullerenes $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$, and $C_{60}H_8$.[9]

In a typical experiment, a solution of anhydrous hydrazine in methanol was added to a solution of the fullerene in benzene and the resulting mixture was stirred under argon. The hydrazine reduction does not require the addition of the usual Cu^{2+} oxidizing agent. Sublimed C_{60} could also be reduced readily by anhydrous hydrazine, suggesting that the reaction is not initiated by an impurity in the C_{60}. Similarly, the reduction did not appear to be inhibited by the presence of Chelex, a reagent used to complex metal ions. C_{60} itself may be the oxidant, in which case diimide would probably be formed from the resulting hydrazine radical cation. In this regard, we observed that diimide gave about the same ratio of fullerene hydrides as the anhydrous hydrazine reagent.



The HPLC chromatogram for a typical reaction is presented in Figure 1. Analysis of the $C_{60}H_4$ isomers was achieved by both high field ^1H NMR spectroscopy and by ^3He NMR spectroscopy. The most stable[6,10,11] isomer **1** is found under the peak labeled C. A mixture of the remaining isomers elute as the group of peaks labeled B. Careful analysis by high field ^1H NMR spectroscopy revealed the presence of at least five, and possibly all, of the seven remaining isomers. The 500 MHz ^1H NMR spectrum of the $C_{60}H_4$ isomers (peaks labeled B) is presented in Figure 2.

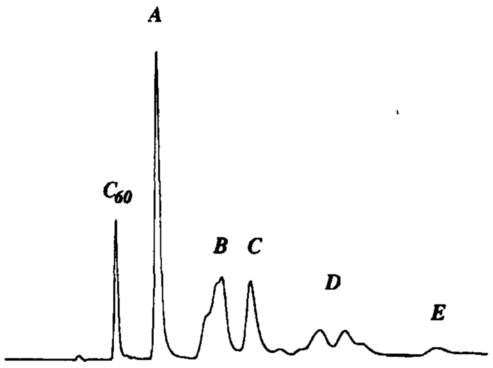


Figure 1. HPLC chromatogram for the hydrazine reduction of C_{60}. Conditions: Buckyclutcher I column (10 mm X 25 cm); Eluent: 70:30 toluene:hexane; Wavelength: 340 nm; Flow rate: 3.5 ml/min.; A = $C_{60}H_2$; B and C = $C_{60}H_4$; D = $C_{60}H_6$; E = $C_{60}H_8$.

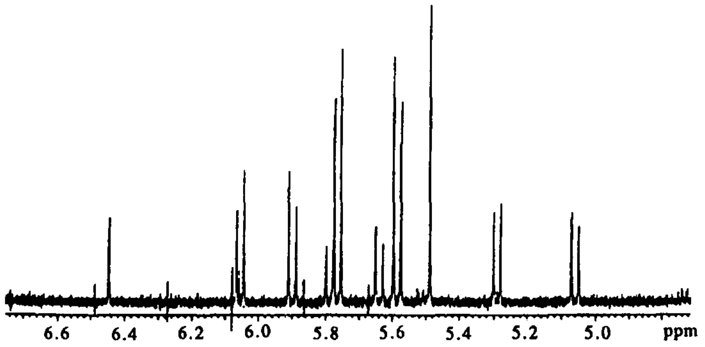
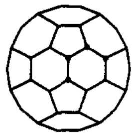


Figure 2. 500 MHz ^1H NMR spectrum of $C_{60}H_4$ isomers (peak B, Figure 1).



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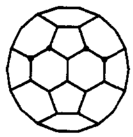

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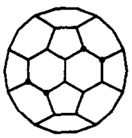

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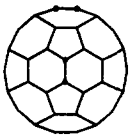

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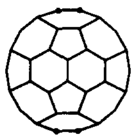

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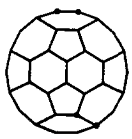

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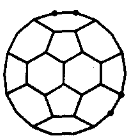

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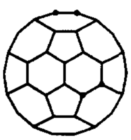

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The singlet at 6.45 ppm can be assigned readily to isomer **5**. Similarly, the singlet at 5.50 ppm, which is associated with the quartet centered at 5.18 ppm, can be assigned to isomer **4**. Each of the remaining five isomers would be expected to exhibit AB quartets. Although only three sets of AB quartets are clearly visible, high field ^1H NMR spectroscopy revealed the possible presence of the two remaining tetrahydrofullerene isomers, but in very small percentages. In addition, the 500 MHz and especially 750 MHz ^1H NMR spectra of the hydrogenated fullerenes $C_{60}H_2$ and $C_{60}H_4$ in solutions of C_6D_6:CS_2 revealed much unexpected fine structure that apparently results from the partial alignment of the molecules in the magnetic field.[12] A detailed analysis of these spectra will be delineated in a full paper.

^3He NMR spectra of $^3He@C_{60}H_4$ samples prepared from $^3He@C_{60}$ and purified by preparative HPLC are presented in Figures 3 and 4. Signals were observed at -9.3, -10.0, -10.9, -11.21, -12.42, and -12.48 ppm upfield from dissolved ^3He gas. Each isomer would be expected to yield a distinct peak in the ^3He NMR spectrum.[13,14] Although six of the eight possible isomers are clearly distinguishable, the remaining two isomers shown above are present in such low concentration that detection was not possible.[15]

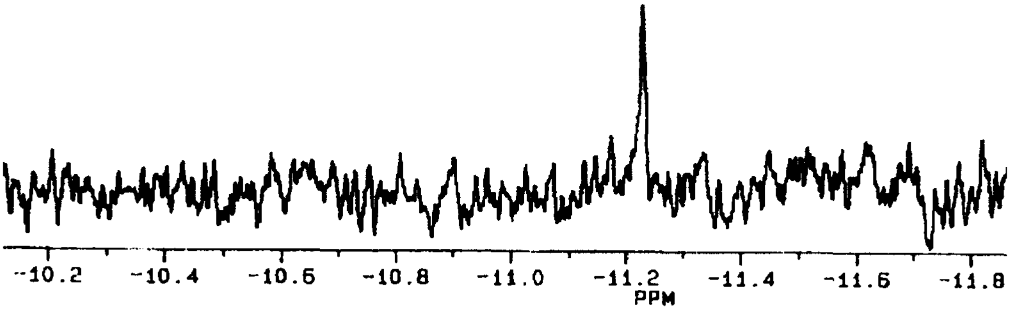

Figure 3. ^3He NMR spectrum of $^3He@$**1** (peak C, Figure 1) recorded in 1:1 C_6D_6:CS_2.

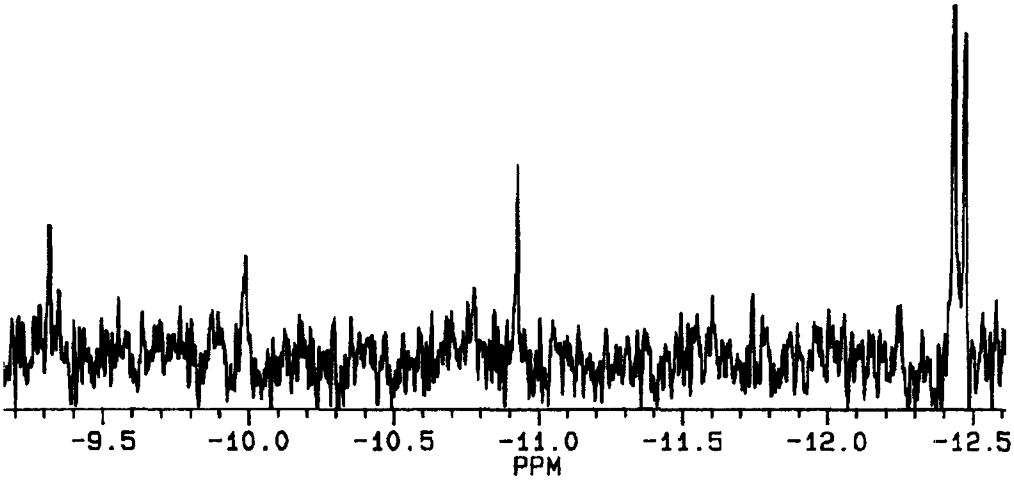

Figure 4. ^3He NMR spectrum of five $^3He@C_{60}H_4$ isomers (peak B, Figure 1) recorded in 1:1 C_6D_6:CS_2.

Acknowledgements

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