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^{3}He NMR Spectra of Highly Reduced C_{60}

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Abstract: Two signals were observed in the ^{3}He NMR spectrum of $^3He@C_{60}H_{36}$. The major signal corresponds with the ^{3}He chemical shift calculated for a structure with $D_{3d'}$ symmetry. Copyright © 1996 Elsevier Science Ltd

The discovery[1,2] that ^{3}He can be introduced into C_{60} and C_{70} by heating at 620 °C with the helium at high pressure represents an important advance in the characterization of fullerene derivatives since the ^{3}He NMR spectrum of each product will yield a single sharp peak and no non-fullerene products or impurities give signals.[3] Bühl, Thiel and Schneider[4] have suggested that ^{3}He labeling and NMR, assisted by computational results dealing with ^{3}He chemical shifts, might provide new information concerning the nature of the highly reduced fullerene C_{60} formed either by dissolving metal reductions[5] or by transfer hydrogenation.[6] We report here the ^{3}He chemical shift values of $^3He@C_{60}H_{36}$ products prepared from both the Birch reduction of $^3He@C_{60}$ and transfer hydrogenation using dihydroanthracene as the source of hydrogen.

Samples of $^3He@C_{60}H_{36}$ were prepared by reduction of $^3He@C_{60}$ using a lithium/NH_3 medium.[5] Atmospheric Pressure Chemical Ionization (APCI), Chemical Ionization (CI) and Electron Impact (EI) mass spectral analyses of these samples show that $C_{60}H_{36}$ species are the main products of this reduction. In contrast to the report of Banks, et al.,[7] no evidence for either less-hydrogenated species or the parent fullerene was observed. Thus, mass spectra of the Birch reduction product taken immediately after work-up showed intense peaks for $C_{60}H_{36}$ only (EI: $M^+ = 756.4$, CI: $M-1 = 755.4$, APCI: $M-1 = 755.4$). However, we also find that a range of fullerene hydrides including $C_{60}H_{18}$ and $C_{60}H_{32}$ can be observed when the Birch product is exposed to air. Darwish et al. have reported similar results for mass spectral analyses of $C_{60}H_{36}$ formed by the Zn/HCl reduction of C_{60}.[8] The mass spectrum of a sample of $C_{60}H_{36}$ using EI conditions is displayed in Figure 1.

$^3He@C_{60}H_{36}$ from the transfer hydrogenation using dihydroanthracene was prepared by heating $^3He@C_{60}$ in the presence of dihydroanthracene as described by Rüchardt and his coworkers.[6] This reaction was carried out under conditions where $^3He@C_{60}H_{18}$ is also a component of the reaction mixture.

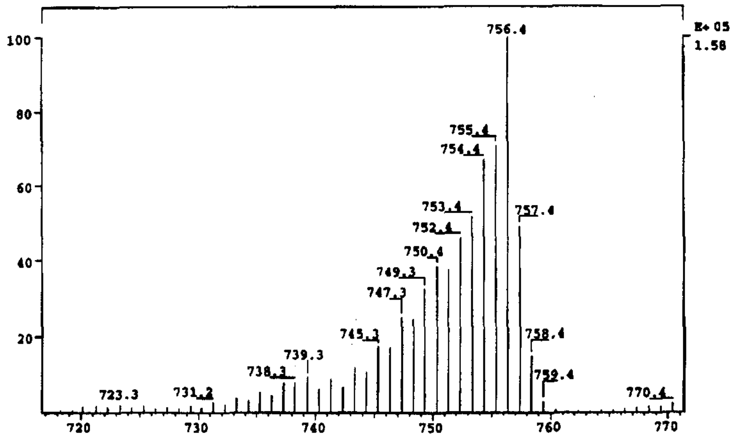


Figure 1. EI mass spectrum of the Birch reduction products of C_{60}.

The ^{3}He NMR spectrum of $^3He@C_{60}H_{36}$ from the Birch reduction exhibits two peaks at -7.7 and -7.8 ppm relative to dissolved ^{3}He gas. These peaks were also found in the ^{3}He NMR spectrum of the product mixture prepared using the dihydroanthracene reduction described by Rüchardt and his coworkers. A third absorption at -16.45 ppm was assigned to $^3He@C_{60}H_{18}$ by comparison with a nearly pure sample prepared via the Rüchardt procedure. The ^{3}He NMR spectrum of the dihydroanthracene reduction mixture is presented in Figure 2.

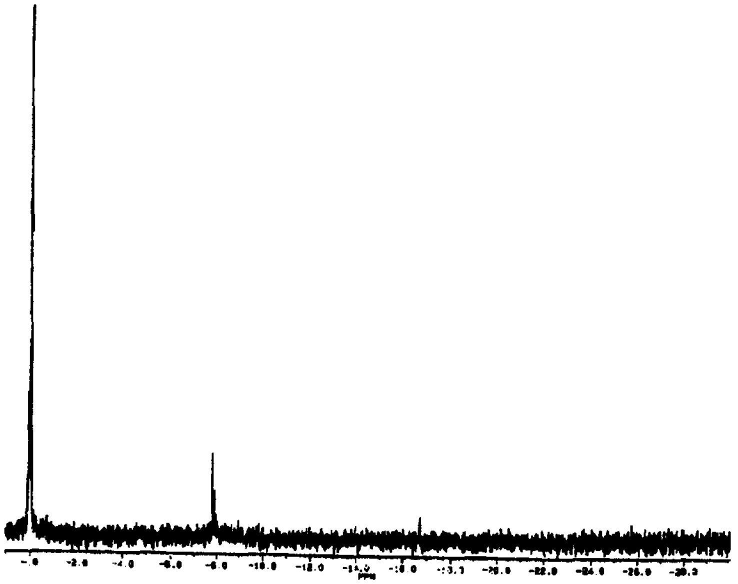
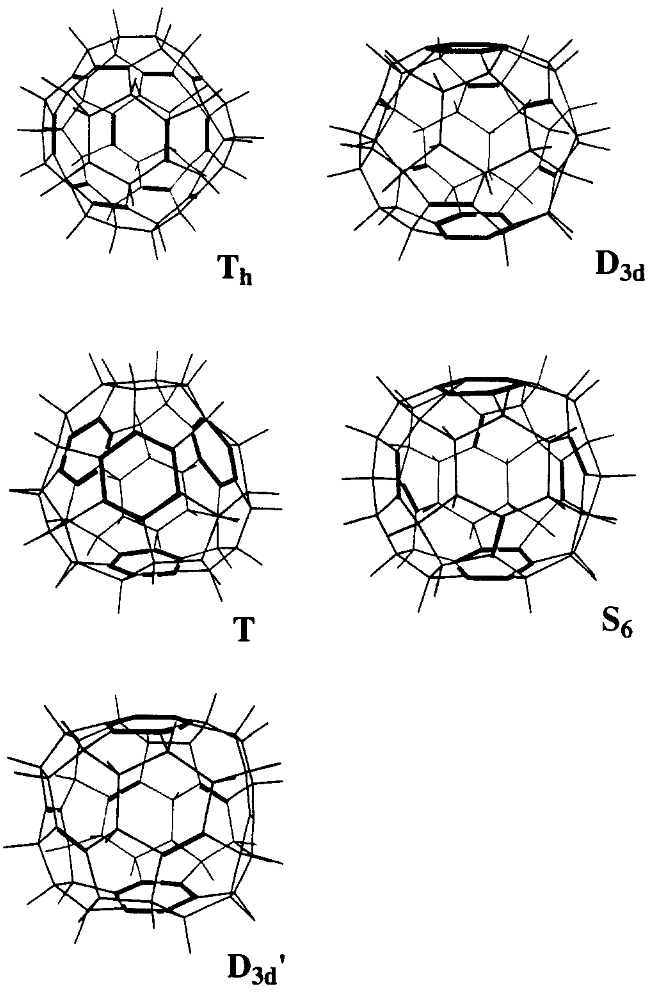


Figure 2. ^{3}He NMR spectrum of a mixture of $^3He@C_{60}H_{36}$ and $^3He@C_{60}H_{18}$

The computed endohedral NMR chemical shifts reported by Bühl, Thiel and Schneider[4] for selected isomers of $^3He@C_{60}H_{36}$ (Figure 3) are -10.8 (*T*), -7.7 ($D_{3d'}$), -6.1 (S_6), -3.4 (T_h) and -5.6 ppm (D_{3d}). Comparison of these values with the experimental chemical shifts would seem to support the $D_{3d'}$ isomer as the most reasonable candidate. The less intense signal appearing at -7.8 ppm may represent a structure not considered by Bühl, Thiel and Schneider. Although the *T* form has the lowest energy of all the isomers studied,[9-12] the computed chemical shift for this isomer is 3.1 ppm upfield from the nearest observed signal. The T_h isomer which was originally proposed on the basis of a rational Birch reduction mechanism can probably be eliminated as a possible candidate since the calculated chemical shift for this isomer is 4.3 ppm downfield from the observed value.



T_h

D_{3d}

T

S_6

D_{3d}'

Figure 3. Five isomers of $C_{60}H_{36}$.

Acknowledgments

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References

1. Saunders, M.; Jiménez-Vásquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993** *259* 1428.
2. Saunders, M.; Jiménez-Vásquez, H. A.; Cross, R. J.; Mroczkowski, S.; Gross, M. L.; Giblin, D. E.; Poreda, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 2193.
3. Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256.
4. Bühl, M.; Thiel, W.; Schneider, U. *J. Am. Chem. Soc.* **1995**, *117*, 4623.
5. Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.
6. (a) Rüchardt, C.; Gerst, M.; Ebenhoch, J.; Beckhaus, H.; Campbell, E. E. B.; Tellgmann, R.; Schwarz, H.; Weiske, T.; Pitter, S. *Angew. Chem. Int. Ed. Engl.* **1993**, *32* , 584. (b) Gerst, M.; Beckhaus, H.; Rüchardt, C.; Campbell, E. E. B.; Tellgmann, R. *Tetrahedron Letters* **1993**, *34*, 7729.
7. Banks, M. R.; Dale, M. J.; Gosney, I.; Hodgson, P. K. G.; Jennings, R. C. K.; Jones, A. C.; Lecoultre, J.; Langridge-Smith, P. R. R.; Maier, J. P.; Scrivens, J. H.; Smith, M. J. C.; Smyth, C. J.; Taylor, A. T.; Thorburn, P.; Webster, A. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1149.
8. Darwish, A. D.; Abdul-Sada, A. K.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc. Perkin Trans. 2* **1995**, 2359.
9. Dunlap, B. I.; Brenner, D. W.; Mintmire, J. W.; Mowrey, R. C.; White, C. T. *J. Phys. Chem.* **1991**, *95*, 5763.
10. Austin, S. J.; Batten, R. C.; Fowler, P. W.; Redmond, D. B.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1993**, 1383.
11. Attalla, M. I.; Vassallo, A. M.; Tattam, B. N.; Hanna, J. V. *J. Phys. Chem.* **1993**, *97*, 6329.
12. Book, L. D.; Scuseria, G. E. *J. Phys. Chem.* **1994**, *98*, 4283.

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