ORGANIC
LETTERS

2000
Vol. 2, No. 15
2241−2243

^{3}He NMR Study of ^{3}He@$C_{60}H_{6}$ and ^{3}He@$C_{70}H_{2-10}$

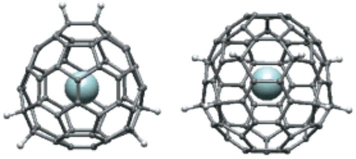
Guan-Wu Wang,[†] Brad R. Weedon,[‡] Mark S. Meier,[‡] Martin Saunders,*,[†] and R. James Cross[†]

*Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107 and
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055*

ms@gaus90.chem.yale.edu

Received May 26, 2000

ABSTRACT

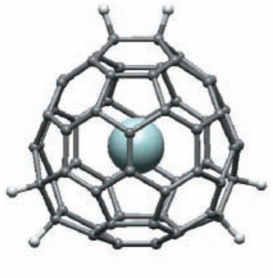


1 6

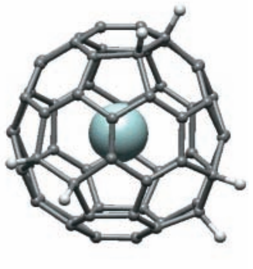
The ^{3}He NMR of ^{3}He@$C_{60}H_{6}$, ^{3}He@$C_{70}H_{2}$, ^{3}He@$C_{70}H_{4}$, ^{3}He@$C_{70}H_{8}$, and ^{3}He@$C_{70}H_{10}$ have been investigated. A new, unidentified $C_{60}H_{6}$ isomer has been found by using ^{3}He NMR. ^{3}He@$C_{70}H_{10}$ shows the most downfield-shifted ^{3}He NMR resonance among the neutral C_{70} derivatives.

Helium-3 NMR is an excellent tool for probing the magnetic field inside the cages of fullerenes and their derivatives.[1] ^{3}He-labeled C_{60},[2] C_{70},[2] C_{76},[2] and isomers of C_{78}[3] and C_{84}[3] show different chemical shifts with ^{3}He@C_{60} (−6.4 ppm relative to dissolved ^{3}He) and ^{3}He@C_{70} (−28.8 ppm) at the extremes. ^{3}He-labeled fullerene derivatives also have distinct ^{3}He NMR chemical shifts,[4] and the chemical shifts correlate with the degree of functionalization and addition pattern.[4c] ^{3}He NMR spectra of ^{3}He@$C_{60}H_{2}$ and ^{3}He@$C_{60}H_{4}$,[4b,5] as well as ^{3}He@$C_{60}H_{18}$ and ^{3}He@$C_{60}H_{36}$,[6] have been investigated before. In this paper, we present the ^{3}He NMR study of isomers of ^{3}He@$C_{60}H_{6}$ and those of ^{3}He@$C_{70}H_{2}$, ^{3}He@$C_{70}H_{4}$ ^{3}He@$C_{70}H_{8}$, and ^{3}He@$C_{70}H_{10}$.

The reaction of C_{60} with a Zn(Cu) couple in the presence of water affords a series of reduced fullerenes $C_{60}H_{n}$. Under appropriate reaction conditions, $C_{60}H_{6}$ isomers can be formed predominantly.[7] Here we are interested in the ^{3}He NMR chemical shifts of ^{3}He@$C_{60}H_{6}$ isomers. ^{3}He-labeled $C_{60}H_{6}$ isomers were synthesized by Zn(Cu) reduction of ^{3}He@C_{60} according to the reported procedure.[7] Two chromatographic bands (in a ratio of 6:1) from HPLC were separated by using a Regis Buckyclutcher I column. The first fraction consisted predominately of the major isomer 1,2,33,41,42,50-^{3}He@$C_{60}H_{6}$ (**1**), and the second fraction contained the minor isomer 1,2,18,22,23,36-^{3}He@$C_{60}H_{6}$ (**2**).[8]



1



2

[†] Yale University.

[‡] University of Kentucky.

(1) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong A. *Science* **1996**, *271*, 1693.

(2) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, A. L. *Nature* **1994**, *367*, 256.

(3) (a) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Billups, W. E.; Gesenberg, C.; Gonzalez, A.; Luo, W.; Haddon, R. C.; Diederich, F.; Herrmann, A. *J. Am. Chem. Soc.* **1995**, *117*, 9305. (b) Wang, G.-W.; Saunders, M.; Khong, A.; Cross, R. J. *J. Am. Chem. Soc*. **2000**, *122*, 3216.

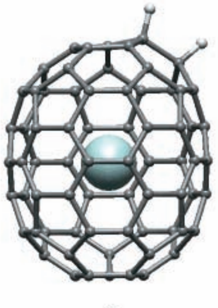
(4) Examples see: (a) Smith, A. B., III; Strongin, R. M.; Brard, L.; Romanow, W. J.; Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J. *J. Am. Chem. Soc*. **1994**, *116*, 10831. (b) Cross, R. J.; Jiménez-Vázquez, H. A.; Lu, Q.; Saunders, M.; Schuster, D. I.; Wilson, S. R.; Zhao, H. *J. Am. Chem. Soc*. **1996**, *118*, 11454. (c) Rüttimann, M.; Haldimann, R. F.; Isaacs, L.; Diederich, F.; Khong, A.; Jiménez-Vázquez, H. A.; Cross, R. J.; Saunders, M. *Chem. Eur. J*. **1997**, *3*, 1071.

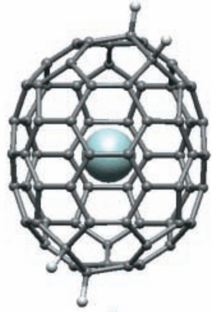
(5) Billups, W. E.; Luo, W.; Gonzalez, A.; Arguello, D.; Alemany, L. B.; Marriott, T.; Saunders, M.; Jiménez-Vázquez, H. A.; Khong A. *Tetrahedron Lett*. **1997**, *38*, 171.

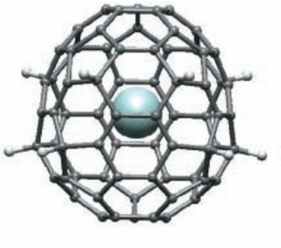
10.1021/ol006116h CCC: $19.00

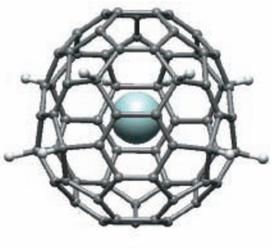
While the ^{3}He NMR spectrum[9] of the second fraction showed a single peak at -16.35 ppm due to **2**, that of the first fraction had three resonances at -12.73, -14.24, and -15.31 ppm in a ratio of 1:3:10. We were puzzled by this result, since we were expecting a single ^{3}He resonance due to **1**. After the ^{3}He NMR measurement, the first fraction was analyzed on the same Buckyclutcher I column. UV$-$vis detection at 310 nm revealed that 9% of the mixture had changed to 1,2,33,50-$C_{60}H_4$ due to the decomposition of $C_{60}H_6$ over time. This allows us to safely assign the resonance at -12.73 ppm to be 1,2,33,50-^{3}He@$C_{60}H_4$,[4b,5] and the relative intensity (7%) of the resonance at -12.73 ppm among the ^{3}He resonances agrees well with the HPLC result (9%). The ^{3}He NMR of a repurified sample from the first fraction by HPLC was taken again; it showed only two peaks at -14.24 and -15.31 ppm in the same 3:10 ratio. This result indicates that a new reduced fullerene, which has not been isolated before, has been found in the first fraction. Careful HPLC examination indeed reveals that an unidentified product exists in the first fraction. On the Buckyclutcher column, the unknown product elutes on the backside of **1** (without showing a shoulder) and before **2**. The failure to observe this unidentified product in the previous work[7] was due to the aggressive shaving of the backside of the first fraction and the frontside of the second fraction during the HPLC separation. Further analysis on a 10 mm × 250 mm Cosmosil Buckyprep column using toluene as the eluent clearly showed that a new peak at 6.6 min appeared besides the major peak for **1** at 6.0 min. On the basis of the above observations, we assign the most intense resonance at -15.31 ppm to be **1**. The ^{3}He NMR chemical shifts of ^{3}He@$C_{60}H_2$, ^{3}He@$C_{60}H_4$, **1**, and **2** strikingly have almost the same chemical shifts as do the corresponding isomers of ^{3}He@C_{60}(DMA)$_n$.[10] The second most abundant ^{3}He@C_{60}(DMA)$_3$ isomer shows a ^{3}He resonance at -14.21 ppm. Therefore, the unidentified compound at -14.24 ppm is most likely another $C_{60}H_6$ isomer.

Recently, we have reported the Zn(Cu) reduction of C_{70} and have isolated a series of hydrogenated C_{70} species.[10b,11] A mixture containing ^{3}He@$C_{70}H_2$, ^{3}He@$C_{70}H_4$, and ^{3}He@$C_{70}H_8$ was prepared by the reported procedure[11] using ^{3}He@C_{70} instead of C_{70}. The ^{3}He NMR of this mixture showed resonances at -28.81, -27.18, -25.33, and -17.84 ppm. The resonance at -28.81 ppm is due to ^{3}He@C_{70}.[2] The mixture was separated on a Buckyclutcher HPLC column.[11] The individual separated bands with known identities were subject to ^{3}He NMR measurements. 1,2-^{3}He@$C_{70}H_2$ (**3**) has a ^{3}He chemical shift at -27.18 ppm, and the major isomer of ^{3}He@$C_{70}H_4$, 1,2,56,57-^{3}He@$C_{70}H_4$ (**4**), has a resonance at -25.33 ppm. The band containing ^{3}He@$C_{70}H_4$ minor isomers (the two peaks at 16.96 and 18.43 min in Figure 2 of ref 11) has two ^{3}He resonances with near same intensity at -24.77 and -23.76 ppm, which are too weak to be seen in the crude mixture. As many as five minor isomers of $C_{70}H_4$ have been isolated, and one of the most abundant is 1,2,67,68-$C_{70}H_4$.[11] It is obvious that one of the above two ^{3}He resonances is from 1,2,67,68-^{3}He@$C_{70}H_4$. The ^{3}He resonance of 7,19,23,27,33,37,44,53-^{3}He@$C_{70}H_8$ (**5**) is at -17.84 ppm. Compound **5** shifts downfield compared to **3**, **4**, and ^{3}He@$C_{70}H_4$ minors. This can be understood by the fact that **5** has a very different structure. All hydrogens are added near the equatorial belt of **5** in a 1,4-pattern mode, while the other compounds have hydrogens added to double bonds near the poles in a 1,2-addition pattern. The resulting structure of **5** produces a quite different magnetic environment inside the cage compared to other C_{70} derivatives.


3


4


5


6

^{3}He@$C_{70}H_{10}$ was synthesized by the reported method, and three isomers have been observed.[7b] The major isomer, 7,8,-19,26,33,37,45,49,53,63-^{3}He@$C_{70}H_{10}$ (**6**), was isolated by HPLC.[12] Compound **6** shows a ^{3}He chemical shift at -17.17 ppm, only slightly further downfield shifted relative to **5**, because the two additional hydrogens of **6** are also added to the equatorial belt, and the whole structure of **6** is almost the same as that of **5**.

In summary, the ^{3}He NMR spectra of ^{3}He@$C_{60}H_6$ and ^{3}He@$C_{70}H_{2-10}$ have been measured. ^{3}He NMR is a powerful tool to probe the magnetic field inside the fullerene cages. ^{3}He NMR can be used to follow a reaction and help identify

---

(6) Billups, W. E.; Gonzalez, A.; Gesenberg, C.; Luo, W.; Marriott, T.; Alemany, L. B.; Saunders, M.; Jiménez-Vázquez, H. A.; Khong A. *Tetrahedron Lett.* **1997**, *38*, 175.

(7) (a) Meier, M. S.; Weedon, B. R.; Spielmann, H. P. *J. Am. Chem. Soc.* **1996**, *118*, 11682. (b) Bergosh, R. G.; Meier, M. S.; Cooke, J. A. L.; Spielmann, H. P.; Weedon, B. R. *J. Org. Chem.* **1997**, *62*, 7667.

(8) The numbering system is due to Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813.

(9) All ^{3}He NMR spectra were taken at 381 MHz frequency. Compounds were dissolved in 3:1 1-methynaphthlene/CD_2Cl_2, and 1 mg of Cr(acac)$_3$ was added as the relaxation reagent. ^{3}He was dissolved in the solution as the reference.

(10) Wang, G.-W.; Saunders, M.; Cross, R. J. *J. Am. Chem. Soc.*, submitted.

(11) Spielmann, H. P.; Wang, G.-W.; Meier, M. S.; Weedon, B. R. *J. Org. Chem.* **1998**, *63*, 9865.

(12) Spielmann, H. P.; Weedon, B. R.; Meier, M. S. *J. Org. Chem.* **2000**, *65*, 2755.

new products. From everything which has been found so far, we conclude that observation of a single helium resonance strongly implies that the sample is composed of a single pure substance, and multiple resonances demonstrate a mixture with intensities proportional to amounts. Separation procedures can be readily followed with ^{3}He NMR. A previously unidentified $C_{60}H_6$ isomer has been found by using ^{3}He NMR. The ^{3}He chemical shift of $^3He@C_{70}H_{10}$ (**6**) is the most downfield-shifted one among neutral C_{70} derivatives studied so far.

Acknowledgment. The financial support from National Science Foundation (CHE9610215 and CHE 9816339) is greatly appreciated.

OL006116H