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Two Helium Atoms Inside Fullerenes: Probing the Internal Magnetic Field in C_{60}^{6-} and C_{70}^{6-}

Tamar Sternfeld,[†] Roy E. Hoffman,[†] Martin Saunders,[‡] R. James Cross,[‡] M. S. Syamala,[‡] and Mordecai Rabinovitz*[,†]

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, and Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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Fullerenes are cage molecules, with cavities large enough to contain the noble gas atoms helium, neon, argon, krypton, and xenon.[1] Recently, it was shown that two helium atoms fit inside C_{70}.[2] The di-helium compound, $He_2@C_{70}$, was produced by our high-temperature high-pressure procedure for incorporating atoms, and its presence in a mixture containing both C_{70} and $He@C_{70}$ was detected by both ^3He NMR and MS. The ^3He NMR spectrum of this mixture contains two signals, where the chemical shift of $^3He_2@C_{70}$ is downfield relative to $^3He@C_{70}$ by $\Delta\delta = 0.014$ (Figure 1a). The ratio between the mono-helium compound, $He@C_{70}$, and the di-helium compound, $He_2@C_{70}$, was found to be 20:1. In contrast to the case of C_{70}, no $He_2@C_{60}$ was observed by ^3He NMR or MS.

^3He is an excellent NMR nucleus.[3] When a helium atom is inside a fullerene cage, the shift compared with the shift of a helium outside the fullerene informs us about the difference in magnetic field between the inside and the outside,[4,5] due to the diamagnetism of the fullerene. An upfield ^3He shift means that the magnetic field intensity is lower inside the fullerene and is associated with overall fullerene diamagnetism and aromaticity. On the other hand, a downfield shift would reflect paramagnetism. The reduction of C_{60} and C_{70} to their hexaanions strongly affects their internal magnetic field, by altering their aromatic character,[6] and produces remarkably large changes in their overall helium shifts.[7]

Because there is ample room in the cage, the helium atoms can move around. The chemical shift is a weighted average of the field at different positions sampled by the helium. When there are two helium atoms inside, their motion is restricted by repulsion keeping them roughly 1.5 Å apart and preventing them from getting to the center. Therefore, the ^3He chemical shift of a di-helium compound, as compared to that of a mono-helium compound, can be used as a probe of local magnetic field differences inside the fullerenes.

The purposes of this research are (i) to determine if C_{60} is able to accommodate two endohedral helium atoms, as C_{70} does, and (ii) to study the ^3He chemical shifts of endohedral mono- and di-helium atoms inside the reduced fullerenes.

A mixture of $He@C_{70}$ and $He_2@C_{70}$ was reduced by lithium metal in the presence of a trace of corannulene to their hexaanions.[7] The ^3He NMR spectrum contains two signals at $\delta = 8.198$ and $\delta = 8.044$, in the ratio of 10:1 (Figure 1b), which are assigned to $He@C_{70}^{6-}$ and $He_2@C_{70}^{6-}$, respectively. In the hexaanion, the chemical shift difference between the mono-helium and the di-helium signals is 10 times larger than that in the neutral state[2] and is reversed in sign (Figure 1). The increase in the chemical shift difference between these two ^3He peaks suggested that

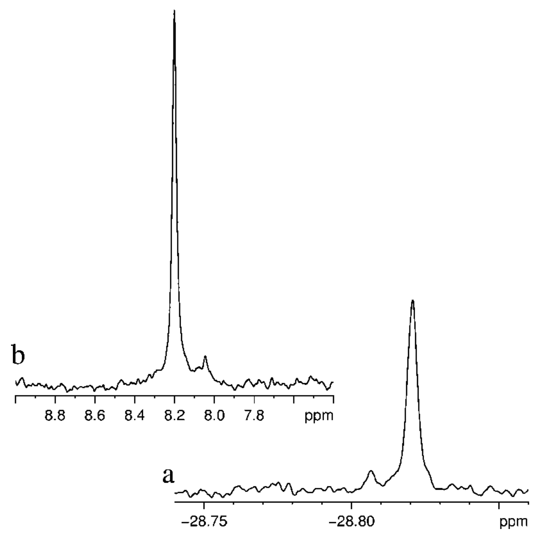

Figure 1. ^3He NMR spectra of the mixture of $^3He@C_{70}$ and $^3He_2@C_{70}$ (a) neutral species and (b) hexaanionic species.

reduction of endohedral C_{60} might make the observation of di-helium inside C_{60} feasible. Reduction of C_{60} containing ^3He was conducted by the same method as described above. ^3He NMR measurements gave the following results: In addition to the signal already known for $^3He@C_{60}^{6-}$ at $\delta = -49.266$,[7] another signal, about 1% intensity as compared to the main signal, appeared downfield by $\Delta\delta = 0.093$ (Figure 2). The "new" signal consistently appeared in several experiments at different temperatures and was assigned to $He_2@C_{60}^{6-}$. For the first time, two helium atoms inside C_{60} could be observed. The spectrum indicates a ratio of 1:200 for $He_2@C_{60}$ and $He@C_{60}$, respectively. The smaller amount of $He_2@C_{60}$, relative to $He_2@C_{70}$, probably results from the smaller cavity of C_{60}, thus accommodating two helium atoms less readily.[8] The observation of the di-helium chemical shift only in the reduced endohedral C_{60} suggests that the chemical shift of $He_2@C_{60}$ is very close to that of $He@C_{60}$, and therefore cannot be observed by ^3He NMR spectroscopy. It follows that in the reduced fullerenes, the difference between the signals of the di-helium and the mono-helium, of both endohedral C_{70} and C_{60}, becomes significantly larger than the differences between them in the neutral fullerenes (Table 1), thus suggesting larger magnetic field differences.

In C_{60}, the two helium atoms can reside along any axis inside the fullerene and rapidly attain any location ca. 0.75 Å from the center. Therefore, their chemical shift would represent the average field at 0.75 Å from the center of the symmetrical C_{60}. The neutral C_{60} has a net low aromatic character.[5,6] Its calculated magnetic field over most of the volume is uniform;[9] thus it is not surprising that

* To whom correspondence should be addressed. E-mail: mordecai@vms.huji.ac.il.
† The Hebrew University of Jerusalem.
‡ Yale University.

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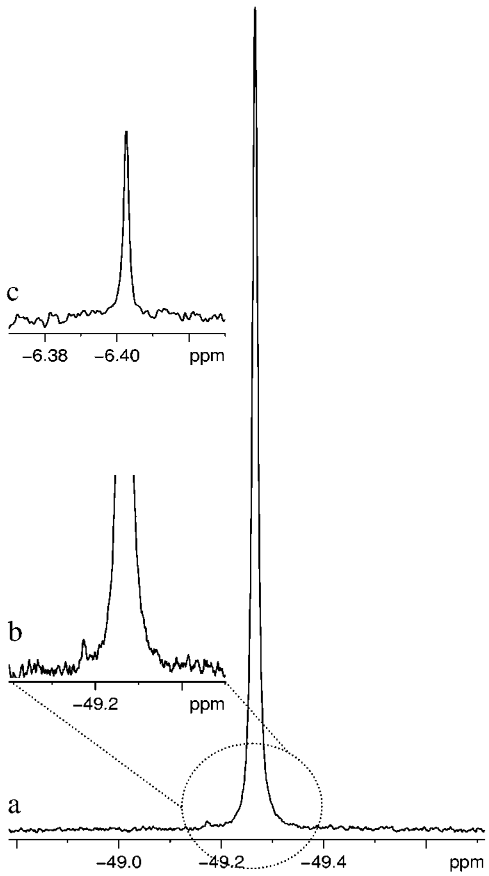

Figure 2. ^{3}He NMR spectra of the mixture of $^3He@C_{60}$ and $^3He_2@C_{60}$. (a) and (b) are the hexaanionic species. (b) Zoom on the di-helium signal. (c) The neutral species, where the di-helium signal was not observed.

Table 1. ^{3}He NMR Chemical Shifts of Endohedral Mono- and Di-helium Fullerenes and Fullerene Hexaanions

	$\delta\ ^3He@C_n$[a]	$\delta\ ^3He_2@C_n$[a]	$\Delta\delta$[b]
C_{60}	−6.403	−6.403[c]	0
C_{60}^{6-}	−49.266	−49.173	−0.093
C_{70}[d]	−28.821	−28.807	−0.014
C_{70}^{6-}	+8.198	+8.044	+0.154

[a] In ppm, relative to ^{3}He in THF-d_8. [b] ($\delta^3He@C_n$)−($\delta^3He_2@C_n$). [c] Most probably, the $^3He_2$ peak is under the main peak; see text. [d] Consistent with results reported in ref 2.

$He_2@C_{60}$ seems to have approximately the same ^{3}He chemical shift as $He@C_{60}$. Reduction of C_{60} to its hexaanion renders it highly aromatic[5−7] and decreases the internal magnetic field. The downfield shift of ^{3}He in $He_2@C_{60}^{6-}$ relative to the $He@C_{60}^{6-}$ (Table 1) is in line with calculations. Theoretical calculations by Schleyer and Hommes[10] found that in C_{60}^{6-}, the magnetic field intensity is most strongly reduced in the center, with a predicted helium shift of $\delta = -56$, but becomes less strongly reduced as one moves away from the center. Moving toward a five-membered ring, $\delta = -56.2$ at 0.5 Å and $\delta = -52.7$ at 1 Å. Moving toward a six-membered ring, the corresponding values are $\delta = -55.8$ and $\delta = -48.6$. If one assumes random orientation of the pair of heliums, the averaged peak in the di-helium species would be predicted to go downfield in accordance with the observation (Table 1). Another possibility is that the orientations of the pair of heliums toward the five- and six-membered rings are slightly different in energy. This would perturb the equilibrium between the two orientations and alter the shift. It might be difficult to calculate this energy difference with a high enough accuracy to make a prediction.

C_{70} has a much higher aromatic character than does C_{60}.[5−7] The two helium atoms are constrained to reside toward the narrow poles of the cavity, and there is apparently a small gradient in the magnitude of the magnetic field, along the 5-fold axis. The chemical shift of the two helium atoms, which are constrained to be away from each other, and therefore from the center, is slightly shifted downfield; therefore, the magnetic field intensity is evidently lower at the center.[9]

The reduction of C_{70} to its hexaanion clearly increases the magnetic field intensity gradient along the longer axis and reverses it. This means that in C_{70}^{6-}, which is perhaps anti-aromatic in character,[5−7] the magnetic field gradient is in the opposite direction than in C_{70}, and it decreases from the center toward the poles.[11]

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(8) The diameter of C_{60} is 7.0 Å, and those of C_{70} are 6.9 Å, axial, and 7.8 Å, longitudinal (McKenzie, D. R.; Davis, C. A.; Cockayene, D. J. H.; Muller, D. A.; Vassallo, A. M. *Nature* **1992**, *355*, 622−624). The van der Waals radius of a helium atom is 1.5 Å. Another example of the significant difference in the population of endohedral atom in C_{60} and C_{70}, probably as a result of their different size, is the smaller yield of $Xe@C_{60}$ as compared to $Xe@C_{70}$, where xenon is the biggest noble gas that was inserted into fullerene. See ref 1.
(9) The magnetic field inside C_{60} is practically uniform throughout the interior cavity until one comes quite close to the walls, where there would be local effects. In C_{70} it is nearly homogeneous. This is based on the calculation of $He@C_{60}$ and $He@C_{70}$ with correspondingly displaced helium atoms. See ref 5a and Bühl, M.; Wüllen, C. V. *Chem. Phys. Lett.* **1995**, *247*, 63−68.
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