# Helium and Lithium NMR Chemical Shifts of Endohedral Fullerene Compounds: An ab Initio Study

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Are fullerenes aromatic? This question, which has elicited vigorous discussion, was raised in the very first description of the structure of $C_{60}$, published by Osawa in 1970.[1] He wondered if $C_{60}$ would constitute a novel, three-dimensional, aromatic system. Very recently, Haddon concluded that "$C_{60}$ is of ambiguous aromatic character." [2]

While quantitative estimates of aromatic stabilization energies are difficult to obtain, the magnetic criteria of aromaticity (e.g., chemical shifts and magnetic susceptibilities) provide insights in many other systems and are applicable to the fullerenes.[3] Although ring current effects on the chemical shifts of protons attached to exohedral substituents have already been noted,[4] substituted fullerenes are by necessity missing one or more of the double bonds.[5] The endohedral noble gas compounds[6,7] preserve the complete fullerene bonding and, in the case of $^3$He,[7] have allowed measurement of the magnetic field in the very center of the structure. The $^3$He NMR chemical shifts of He@$C_{60}$ and He@$C_{70}$, −6.3 and −28.8 ppm,[7] respectively, were found to differ appreciably from those predicted by Haddon et al.[3]

A preliminary ab initio (GIAO-SCF) calculation was able to reproduce the experimental $\delta$(He) value of He@$C_{60}$ within ca. 2 ppm.[8] We now report a more detailed GIAO-SCF study calling attention to effects of cage geometries and He mobility on the computed He chemical shifts. Interesting comparisons are provided by the predicted $\delta$(Li) values of the isoelectronic $Li^+$@$C_{60}$ and $Li^+$@$C_{70}$.

The computed[9,10] NMR chemical shifts of endohedral guest atoms and ions are summarized in Table 1. If one places a He atom in the center of icosahedral, 3-21G optimized $C_{60}$, a $\delta(^3He)$ value of ca. −13 ppm is computed (employing tzp basis for He and dz for C), which deviates somewhat from the experimental value, −6.3 ppm.[7,11] Using the MP2/TZP optimized $C_{60}$ geometry[12] rather than the SCF/3-21G one affords a $\delta$(He) value of −8.7 ppm, which is in better agreement with experiment. The computed He chemical shift is surprisingly sensitive to the lengths of CC bonds 3.5 Å away! In particular, the degree of bond alternation seems critical: While the two CC bond lengths in $C_{60}$ differ appreciably at SCF levels (3-21G: 1.367/1.453 Å), a trend toward bond equalization is apparent in the MNDO (1.400/1.474 Å),[13] in the gas-phase electron diffraction [1.401(10)/1.458(6) Å],[14] and in the MP2/TZP (1.406/1.446 Å)[12] geometries. This structural trend is paralleled by a decrease of the computed endohedral He shielding ($\delta \approx -13$, −12, −11, and −9 ppm, respectively, in the same sequence, see Table 1). For the "idealized" geometry with equal CC bond lengths of 1.4 Å (as employed by Haddon in his London HMO calculations[3]), a value of ca. −4 ppm is computed (Table 1).

It has been estimated that "the $^3$He atom senses the magnetic field only inside a sphere of less than 1 Å diameter at the center" of $C_{60}$.[7] The field within this sphere appears to be very homogeneous, as displacement of the He out of the center (by 0.5 Å along one 5-fold axis) leaves the computed $\delta$(He) virtually unchanged (Table 1).

According to Haddon's predictions,[3] the hexaanion of $C_{60}$ should be highly aromatic and should possess only diamagnetic ring currents. In complete accord with this prediction, $\delta(^3He)$ $\approx -58$ ppm is computed for He@$C_{60}^{6-}$ (Table 1).[15] Interestingly, the $C_{60}$ carbons are calculated to be deshielded by ca. 25 ppm with respect to the neutral complex, despite bearing partial

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(9) NMR chemical shifts have been computed employing the direct implementation of the GIAO-SCF method (Häser, M.; Ahlrichs, R.; Baron, H. P.; Weiss, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455) using the following contracted Huzinaga (Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta: Edmonton, 1971) basis sets. He: tzp, (5s)[3s], one polarization function ($\alpha_d = 1.0$). Li: II, (9s)[5s], three polarization functions ($\alpha_p = 0.19$, 0.75, and 3.0, cf.: Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principles and Progress Vol. 23*; Springer Verlag: Berlin, Heidelberg, 1990; p 165). C: dz (8s4p)[4s2p]. Relative He chemical shifts are reported with respect to free He ($\sigma = 59.9$); $\delta$(Li) is referenced to Li$(OH_2)_4^+$ [$S_4$ symmetry, 6-31G* optimized, $\sigma(Li) = 91.7$ with basis II on Li and DZ on O and H], a model for the experimental standard, aqueous LiBr.

(10) Geometry optimizations of neutral and anionic fullerenes have been carried out using TURBOMOLE (Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *154*, 165) employing the following standard basis sets (in parentheses, cf.: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986): $C_{60}$, $I_h$ (3-21G); $C_{70}$, $D_{5h}$ (3-21G); $C_{60}^{6-}$, $I_h$, (6-31+G). The optimized geometrical parameters are in line with those obtained by others at comparable levels of theory; cf.: Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 423 ($C_{60}$); **1991**, *180*, 451 ($C_{70}$). Hutter, J.; Lüthi, H. P. *Int. J. Quantum Chem.* **1993**, *46*, 81 ($C_{60}^{6-}$). For the endohedral He and $Li^+$ complexes, the geometries of the free fullerenes have been employed.

(11) In the experiments, dissolved He is used as standard. The same chemical shifts are obtained when gaseous helium is the reference, provided that a correction is made for the magnetic susceptibility of the solvent (ref 7; see also: Seydoux, R.; Diehl, P.; Mazitov, R. K.; Jokisaari, J. *J. Magn. Reson. A* **1993**, *101*, 78). Thus, by comparing experimental and theoretical values we assumed that solvent effects are similar for the chemical shifts of free and of endohedral He.

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(15) Accordingly, the computed (direct IGLO, cf.: Meier, U.; van Wüllen, C.; Schindler, M. *J. Comput. Chem.* **1992**, *13*, 551) increase of the diamagnetic susceptibility $\chi_g$ is extremely large when going from He@$C_{60}$ to He@$C_{60}^{6-}$, ca. −920 ppm cgs [II(He), DZ(C) basis]. Our preliminary estimates of the diamagnetic susceptibility exaltations are −94 and −386 ppm cgs for He@$C_{60}$ and He@$C_{70}$, respectively. For the use of magnetic susceptibilities as criteria for aromaticity, see, e.g.: Dauben, H. P.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811. Dauben, H. P.; Wilson, J. D.; Laity, J. L. In *Nonbenzoid Aromaticity, Vol. 2*; Snyder, J., Ed.; Academic Press: New York, 1971. For computations of magnetic properties of $C_{60}$ and $C_{70}$, see also ref 9 (Häser et al.) and, e.g.: Fowler, P. W.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Chem. Phys. Lett.* **1991**, *179*, 174.

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**Table 1.** Computed (GIAO-SCF)[a] Chemical Shifts[b] of Endohedral He and $Li^+$ Fullerene Complexes

| compd | fullerene geometry[c] | symmetry | δ(He) | δ(Li) | exptl[d] |
|---|---|---|---|---|---|
| He@$C_{60}$ | 3-21G | $I_h$ | −12.9 | | |
| He@$C_{60}$ | MNDO[e] | $I_h$ | −11.7 | | |
| He@$C_{60}$ | electron diffraction[f] | $I_h$ | −10.6 | | |
| He@$C_{60}$ | MP2/TZP[g] | $I_h$ | −8.7 | | −6.3 |
| He@$C_{60}$ | MP2/TZP, He displaced[h] | $C_{5v}$ | −9.0 | | |
| He@$C_{60}$ | idealized[i] | $I_h$ | −3.8 | | |
| He@$C_{60}^{6-}$ | 6-31+G | $I_h$ | −58.3 | | |
| He@$C_{70}$ | 3-21G | $D_{5h}$ | −24.0 | | −28.8 |
| He@$C_{70}$ | X-ray[j] | $D_{5h}$ | −24.3 | | |
| He@$C_{70}$ | 3-21G, He displaced[k] | $C_{5v}$ | −23.9 | | |
| He@$C_{70}$ | 3-21G, He displaced[l] | $C_{2v}$ | −24.1 | | |
| $Li^+$@$C_{60}$ | MP2/TZP | $I_h$ | | −14.5 | |
| $Li^+$@$C_{60}$ | MP2/TZP, Li displaced[m] | $C_{5v}$ | | −15.3 | |
| $Li^+$@$C_{70}$ | 3-21G | $D_{5h}$ | | −29.7 | |

[a] Employing tzp(He),II(Li),dz(C) basis. [b] In parts per million, relative to He and $Li(OH_2)_4^+$, respectively. [c] Source of fullerene cage geometry. [d] Reference 7. [e] From reference 13. [f] From reference 14. [g] From reference 12. [h] By 0.5 Å along $C_5$ axis. [i] Equal CC bond lengths of 1.4 Å employed. [j] From reference 17. [k] By 1.0 Å along $C_5$ axis. [l] By 0.5 Å toward an equatorial six-membered ring. [m] By 1.4 Å along $C_5$ axis.

negative charges. The same trend has been noted experimentally for δ($^{13}C$) of $C_{60}$ polyanions which are deshielded up to 14 ppm relative to neutral $C_{60}$.[16]

Compared to $C_{60}$, the 3-21G structure of $C_{70}$ performs slightly better: the computed chemical shift of an encapsulated $^3He$ atom, −24 ppm, deviates less than 5 ppm from the experimental value, −28.8 ppm.[7] Practically the same result, −24 ppm, is obtained when the experimental (X-ray) $C_{70}$ geometry[17] is employed (Table 1). The bond alternation in the equatorial six-membered rings is already quite small at SCF levels [3-21G, 1.403 and 1.414 Å; cf. X-ray, 1.407(7) and 1.430(4) Å, respectively[17]]. Unfortunately, no MP2 optimized structure of $C_{70}$ has been reported to date. As for He@$C_{60}$, the exact position of the He atom in the $C_{70}$ cage hardly affects δ(He): displacements along the 5-fold (by 1.0 Å) and 2-fold axes (by 0.5 Å toward an equatorial six-membered ring) afford changes in the computed δ(He) of only +0.1 and −0.1 ppm, respectively. As expected, the computed He atomic charge (employing Mulliken population analysis) is 0 in both He@$C_{60}$ and He@$C_{70}$. Thus, the substantial difference in δ(He) for both molecules is qualitatively consistent with the proposed ring current models.[3] The quantitative, i.e., numerical, differences between our results and Haddon's London HMO calculations[3] may be due in part to the use of idealized geometries in the latter (see above). Also, σ-effects, which are not accounted for in the Hückel approach, may affect the endohedral shieldings: For the fully hydrogenated He@$C_{60}H_{60}$ ($I_h$ symmetry) and He@$C_{70}H_{70}$ ($D_{5h}$), δ(He) chemical shifts of −5.2 and −5.4 ppm, respectively, are computed (3-21G geometries).

$^7Li$ chemical shifts are a useful probe of ring current effects in organolithium compounds.[18] Since $Li^+$ is isoelectronic with He, we were interested in the δ(Li) values of $Li^+$@$C_{60}$ and $Li^+$@$C_{70}$. Placing $Li^+$ in the centers of the $C_{60}$ and $C_{70}$ cages affords GIAO-SCF chemical shifts of −14.5 and −29.9 ppm, respectively. Moving $Li^+$ out of the center in $C_{60}$ (by 1.4 Å along a 5-fold axis as suggested by LDF calculations[19]) affects δ(Li) only slightly, i.e., by less than 1 ppm (Table 1). The computed upfield shift of $Li^+$ in $C_{60}$ ($\delta \approx -15$ ppm) is substantial and is comparable to that of $Li^+$ sandwiched between two cyclopentadienyl anions ($\delta = -13.1$ ppm[18a]). The calculated upfield shift of $Li^+$ in the $C_{70}$ cage is even larger, suggesting that $^7Li$ NMR could readily distinguish between exo- and endohedral $Li^+$–fullerene complexes. For both He and $Li^+$ in $C_{70}$, notable chemical shift anisotropies of $\Delta\sigma \approx -12$ ppm are predicted.[20]

In summary, experimental $^3He$ NMR chemical shifts of He@$C_{60}$ and He@$C_{70}$ are reproduced reasonably well at the GIAO-SCF/tzp(He)/dz(C) level, employing MP2/TZP and 3-21G geometries, respectively. The computed δ($^3He$) values are quite sensitive to changes in the host fullerene structure,[21] but not to the exact position of the He atom near the center of the cage. Qualitatively similar results are predicted for δ($^7Li$) in the isostructural $Li^+$@$C_{60}$ and $Li^+$@$C_{70}$ complexes. Ring currents and their directly observable effects upon chemical shieldings[22] are important diagnostic indicators of aromaticity. Our findings support earlier conclusions that $C_{60}$ is aromatic, but only to a modest extent. The aromaticity in $C_{70}$ and especially in $C_{60}^{6-}$ are greater, judging from the magnetic criteria. Clearly, chemical shifts of endohedral guests will be highly significant for the higher fullerenes, as well as for fullerene derivatives,[23] which are currently being investigated.

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(21) Geometry dependencies of chemical shifts are quite common; usually, the paramagnetic contributions are responsible since energy differences between occupied and virtual orbitals are involved which often are sensitive to geometrical changes; cf. ref 9 (Kutzelnigg et al.). Geometry effects on magnetic properties have been noted for benzene: e.g., the computed out-of-plane component of the proton shielding is increased by ca. 0.7 ppm in going from benzene to the hypothetical cyclohexatriene; cf. ref 22.

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