π-Electron Ring-Current Effects in Multiple Adducts of $^3He@C_{60}$ and $^3He@C_{70}$: A ^3He NMR Study

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Dedicated to Professor Orville L. Chapman on the occasion of his 65th birthday

Abstract: Bis- to hexakisadducts of C_{60} (**1**–**6**) and mono- to tetrakisadducts of C_{70} (**7**–**13**) containing ^3He atoms (endohedral helium complexes) were prepared and studied by ^3He NMR spectroscopy to determine the influence of degree of functionalization and addition pattern on the chemical shift of the ^3He atom. In the series of C_{60} derivatives, which included the previously measured 6-6 monoadduct $^3He@C_{61}H_2$, the ^3He resonance was shifted considerably upfield relative to that of $^3He@C_{60}$ ($\delta = -6.36$) up to the bisadduct **1** ($\delta = -11.45$). The resonances of the higher adducts **3**–**6**, however, were shifted only slightly further upfield and all appeared in a rather narrow spectral range between $\delta = -11.84$ and -12.26. The absence of further substantial upfield shifts was rationalized in terms of the compensation of deshielding due to the functionalization-induced decrease in the diamagnetic π-electron ring currents that extend around the fullerene sphere by the shielding that results from the weaker pentagonal-ring paramagnetic currents and the increased number of localized benzenoid substructures in **3**–**6**. In contrast, all ^3He resonances of the C_{70} adducts are shifted downfield relative to the signal of $^3He@C_{70}$ ($\delta = -28.81$). A monotonic relationship exists between the chemical shift and the degree of functionalization, whereby the ^3He chemical shifts steadily decrease from monoadduct **7** ($\delta = -27.53$) to the isomeric tetrakisadducts **12** ($\delta = -21.09$) and **13** ($\delta = -20.68$). This deshielding was explained by the reduction of the strong diamagnetic ring currents extending along the polar corannulene perimeters as a result of the functionalization at α- and β-type polar bonds in **7**–**13**. In both series, the addition pattern was also found to have a distinct influence on the ^3He chemical shift.

Keywords
fullerenes · endohedral helium complexes · NMR spectroscopy · ring currents

Introduction

In their original publication describing the first experimental evidence for buckminsterfullerene, C_{60},[1] Kroto et al.[2] described this molecular carbon allotrope as aromatic, being covered on its inner and outer surface by a sea of π-electrons. Therefore, the NMR resonance of an atom inside the carbon sphere should have a remarkable chemical shift because of π-electron ring-current effects. London calculations by Elser and Haddon,[3] however, predicted C_{60} to be only weakly diamagnetic, and this was confirmed by measurements of the magnetic susceptibility of bulk C_{60}.[4] Nevertheless, substantial ring currents are present in C_{60}, as was revealed soon after by the specific changes in chemical shift of protons close to the surface in covalent fullerene adducts[5] and further computational studies by Haddon and co-workers.[6] These calculations, with a London approximation, suggested strong paramagnetic ring currents in the twelve pentagonal rings of C_{60} that almost exactly cancel out the diamagnetic currents extending around the fullerene sphere.[6] This theoretical description of compensating paramagnetic and diamagnetic ring currents in C_{60} and C_{70} is in agreement with the experimental findings that 1) C_{60} has a vanishingly small bulk magnetic susceptibility, 2) the measured magnetic susceptibility of C_{70}, with a higher hexagon-to-pentagon ratio, is larger than that of C_{60},[4] and 3) protons in adducts of C_{60} and C_{70} that are located close to the fullerene surface atop pentagons encounter large downfield shifts in the ^1H NMR spectrum.[5]

A deeper insight into fullerene magnetism was provided by Saunders et al., who incorporated ^3He into C_{60} and C_{70} to an extent sufficient for ^3He NMR experiments.[7] This work dramatically extended the initial mass spectrometric studies by Schwarz et al.,[8] in which neutral He atoms were incorporated into the fullerenes by collision between noble gas atoms and fullerene ions in the gas phase, followed by neutralization. Thus, almost ten years after Kroto et al. suggested the experiment,[2]

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the magnetic shielding environment inside the fullerene cavity could be probed experimentally. The measured ^{3}He NMR chemical shifts are $\delta = -6.36$ ($^3He@C_{60}$) and -28.81 ($^3He@C_{70}$) relative to the resonance of free ^{3}He dissolved in 1-methylnaphthalene.[7] The significantly higher shielding of the ^{3}He nucleus in $^3He@C_{70}$ was expected on the basis of the measured magnetic susceptibilities[4] and the ring-current calculations mentioned above.[6b] The ^{3}He chemical shifts measured for $^3He@C_{60}$ and $^3He@C_{70}$ represent the extremes for the fullerenes isolated and measured so far. The ^{3}He atoms inside the higher fullerene compounds, $^3He@C_{76}$, $^3He@C_{78}$, $^3He@C_{82}$, and $^3He@C_{84}$, display chemical shifts that lie between these two extremes.[9] Therefore, a simple correlation between the ^{3}He shielding and the overall number of carbon atoms or the hexagon-to-pentagon ratio does not exist in the fullerene family.

Each covalent fullerene adduct with a ^{3}He atom inside measured so far gave a single sharp ^{3}He NMR resonance at a unique frequency.[10, 11] The ^{3}He resonances of C_{60} monoadducts appear upfield ($\Delta\delta = 1.7$ to 3.4, depending on the nature of the addend) of the resonance of $^3He@C_{60}$.[10] In contrast, the corresponding resonances of C_{70} monoadducts are shifted downfield ($\Delta\delta = 3.25$) from the signal of $^3He@C_{70}$.[11b]

We recently reported the synthesis of the series of C_{60} bis- to hexakisadducts **1**–**6** (Figure 1)[12] by regioselective tether-directed remote functionalization and of the series of C_{70} mono- to tetrakisadducts C_{70} **7-13** (Figure 2).[13] Systematic investigations of the changes in fullerene physical and chemical properties as a function of degree, pattern, and nature of the functionalization were conducted for a large series of multiple C_{60} adducts including **1**–**6**.[14] As part of these studies, it was observed that the ^{1}H NMR resonances of the CH_2 groups in the cyclohexene rings of **1**–**6** moved strongly upfield (by up to $\Delta\delta = 1$ ppm) with increasing degree of addition. With each addition to central 6-6 bonds of pyracyclene subunits in C_{60}, the paramagnetic π-electron ring currents in two pentagonal rings are interrupted, and this reduces the deshielding of protons located atop the carbon sphere. Furthermore, as more addends are attached, diamagnetic shielding by isolated benzenoid six-membered rings becomes increasingly important, and both effects can explain the observed upfield shifts of the ^{1}H resonances.

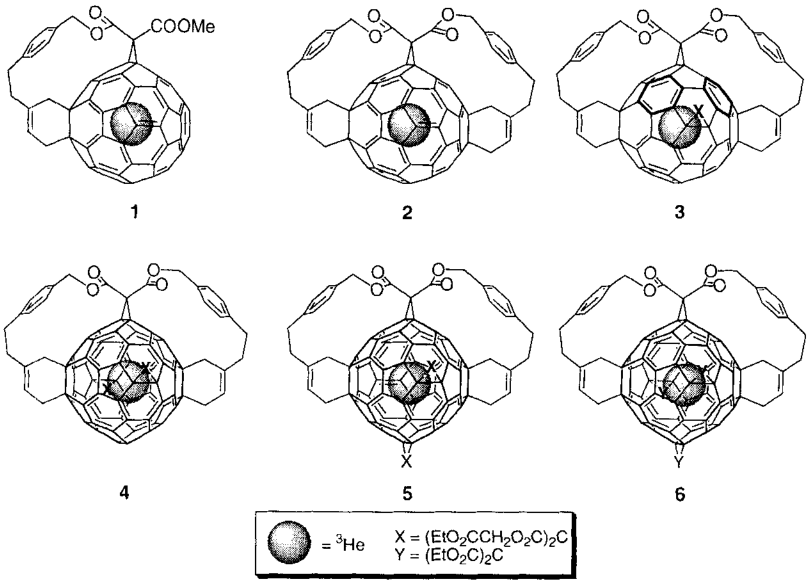


Figure 1. C_{60} multiple adducts **1**–**6** with ^{3}He atoms inside the cage. The two benzenoid substructures in **3** are highlighted in bold; **4** and **5** have four, and **6** has eight of these substructures (not highlighted).

As a consequence of their full exposure to the entire surrounding fullerene π-electron system, NMR resonances of ^{3}He atoms in covalent adducts should be very sensitive to changes in this system and the corresponding ring currents due to increasing functionalization. This sensitivity should differ from that of the NMR resonances of protons that are rigidly attached atop the fullerene surface and are exposed only to local anisotropic effects. Three influences of π-electron ring currents on the ^{3}He resonances were envisaged. Sequential additions to 6-6 bonds should weaken the paramagnetic ring currents in pentagonal rings and the diamagnetic ring currents that extend around the fullerene spheres.[6] Additionally the development of localized benzenoid rings with diamagnetic ring currents should influence the ^{3}He resonances in the higher adducts **3**–**6**. Based on these considerations, we initially expected a particularly strong shielding of the ^{3}He nucleus in hexakisadduct **6**, since the X-ray analysis of corresponding helium-free hexakisadducts[12b, 15] had revealed a residual π-chromophore consisting of eight localized benzenoid rings. Here, we report a systematic ^{3}He NMR study of the C_{60} and C_{70} adducts **1**–**13** and demonstrate that the ^{3}He NMR resonance is a powerful probe for exploring the magnetic properties and the importance of the various π-electron ring currents in higher adducts of fullerenes.

Results and Discussion

1. Experimental Considerations: The endohedral compounds $^3He@C_{60}$ and $^3He@C_{70}$ were prepared from pure C_{60} and C_{70} by published procedures.[16] The incorporation level of ^{3}He was around 0.15%. Subsequently, **1**–**6** and **7**–**13** (Figures 1 and 2) were synthesized as previously reported for the corresponding derivatives without incorporated helium.[12, 13] The ^{3}He NMR measurements at 20 °C were performed by dissolving **1**–**6** and **7**–**13** in 1-methylnaphthalene/CD_2Cl_2 (3/1) containing chromium(III) acetylacetonate as a relaxation agent.[17] Tables 1 and 2 list the chemical shifts of the ^{3}He in compounds **1**–**13** relative to dissolved free ^{3}He. Also shown for comparison are the resonances of $^3He@C_{60}$ and $^3He@C_{70}$, as well as of the known 6-6 adduct $^3He@C_{61}H_2$.[11b] The ^{3}He NMR spectra of **1**–**6** and **7**–**13** are depicted in Figure 3. The minor impurities seen in the ^{3}He NMR spectra of the C_{60} bis- and trisadducts **1** and **2** are attributed to oxidation products arising from $^1O_2$ ene reaction at their cyclohexene rings,[12c] since the formation of $^1O_2$ is efficiently sensitized by the fullerene derivatives.[18] In contrast, the C_{60} tetrakis- through hexakisadducts **3**–**6** gave a single ^{3}He NMR resonance which is consistent with their reduced ability to photosensitize the formation of $^1O_2$.[12c] Small, unidentified impurity peaks are observed in the spectra of the C_{70} adducts **7**–**10** and **13**.

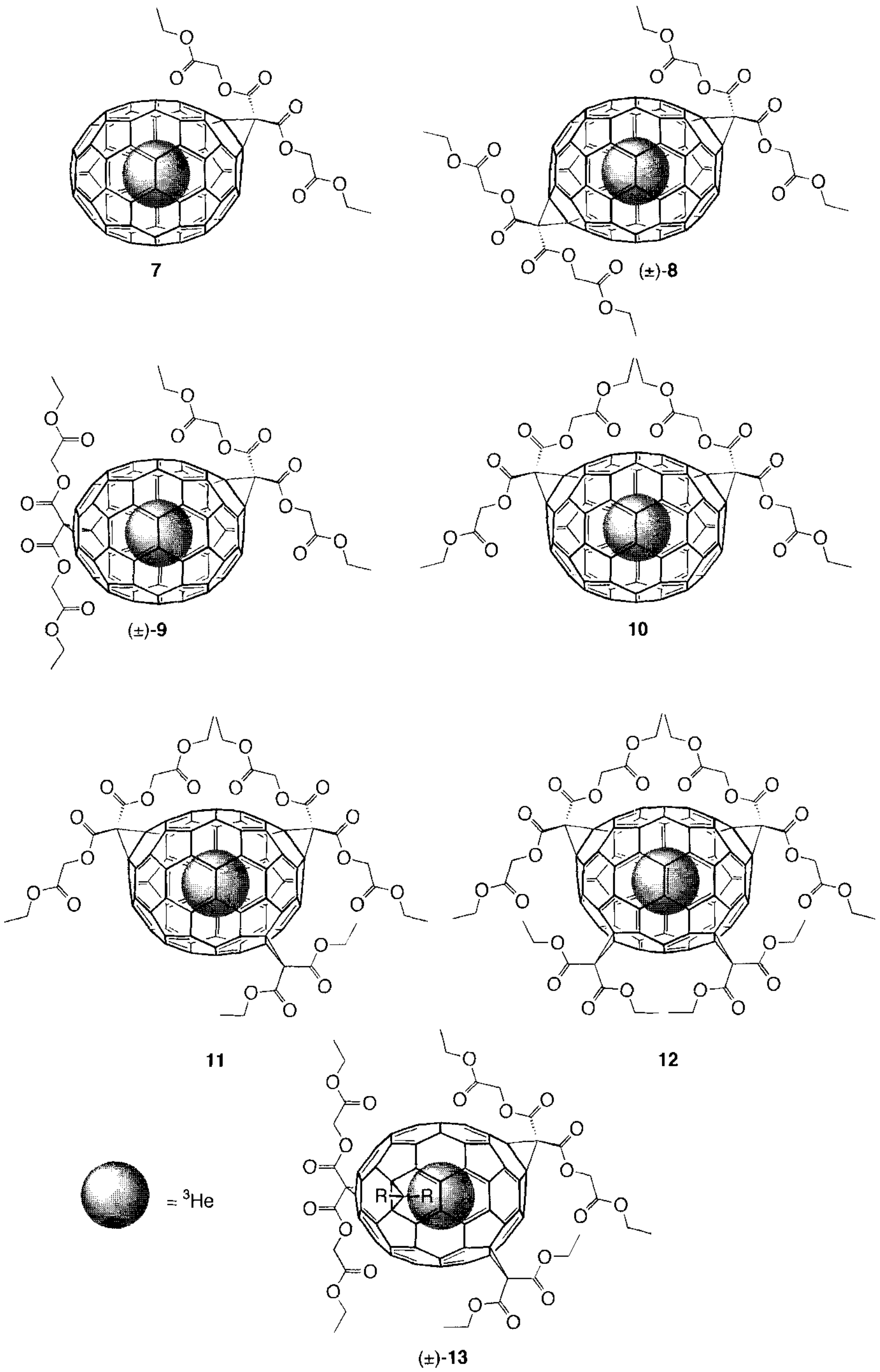


Figure 2. C_{70} mono and higher adducts **7**-**13** with ^{3}He atoms inside the cage. R = COOEt.

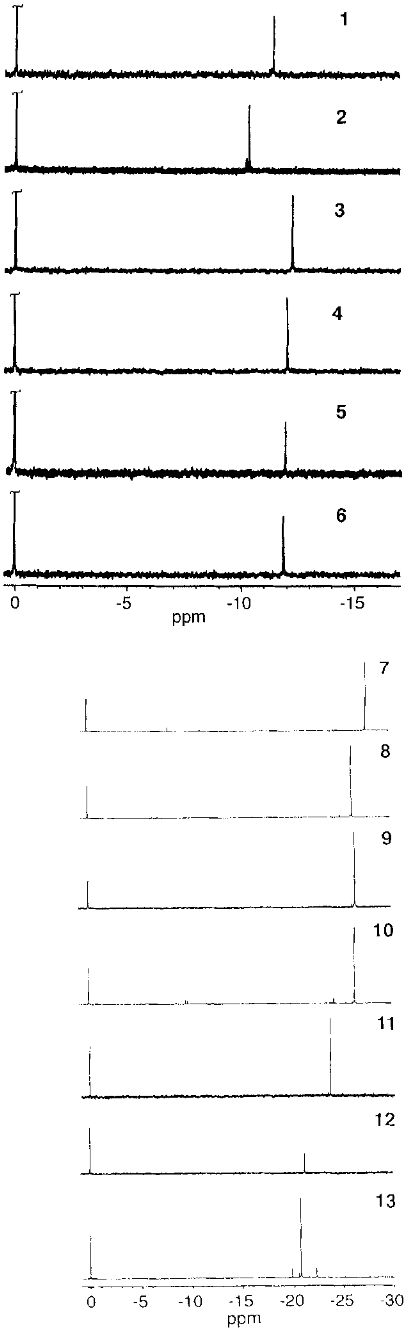


Figure 3. ^{3}He NMR spectra (1-methylnaphthalene/CD_2Cl_2, 3/1) of C_{60} adducts **1**-**6** (above) and C_{70} adducts **7**-**13** (below). Chemical shifts are relative to dissolved free ^{3}He.

Table 1. ^{3}He NMR chemical shifts (1-methylnaphthalene/CD_2Cl_2, 3/1) for the C_{60} adducts **1**-**6** in comparison to those of $^3He@C_{60}$ and $^3He@C_{61}H_2$. Chemical shifts are relative to dissolved free ^{3}He.

Compound	Symmetry	Degree of functionalization	$\delta(^3He)$	$\Delta\delta(^3He)$ rel. to $^3He@C_{60}$	Ref.
$^3He@C_{60}$	I_h	–	−6.36	0.00	[11b]
$^3He@C_{61}H_2$	C_{2v}	mono	−8.11	−1.75	[11b]
1	C_s	bis	−11.45	−5.09	
2	C_{2v}	tris	−10.35	−3.99	
3	C_s	tetrakis	−12.26	−5.90	
4	C_{2v}	pentakis	−12.04	−5.68	
5	C_s	pentakis	−11.84	−5.48	
6	C_{2v}	hexakis	−11.89	−5.53	

Table 2. ^{3}He NMR chemical shifts (1-methylnaphthalene/CD_2Cl_2, 3/1) for the C_{70} adducts **7**-**13** in comparison to $^3He@C_{70}$. Chemical shifts are relative to dissolved free ^{3}He.

Compound	Symmetry	Degree of functionalization	$\delta(^3He)$	$\Delta\delta(^3He)$ rel. to $^3He@C_{70}$	Ref.
$^3He@C_{70}$	D_{5h}	–	−28.81	0.00	[11b]
7	C_s	mono	−27.53	1.28	
8	C_2	bis	−26.12	2.69	
9	C_2	bis	−26.44	2.37	
10	C_{2v}	bis	−26.27	2.54	
11	C_s	tris	−23.64	5.17	
12	C_{2v}	tetrakis	−21.09	7.72	
13	C_2	tetrakis	−20.68	8.13	

2. ^3He NMR results for the C_{60} multiple adducts 1–6. The ^3He NMR resonances of multiple adducts **1**–**6** (Table 1) together with those of $^3He@C_{60}$ and $^3He@C_{61}H_2$ were plotted against the degree of functionalization (Figure 4). The resonances of monoadduct $^3He@C_{61}H_2$ ($\delta = -8.11$) and bisadduct **1** ($\delta = -11.45$) showed strongly enhanced shielding with respect to the $^3He@C_{60}$ signal ($\delta = -6.36$), as was expected from literature data.[10, 11, 19] However, the shielding of the ^3He resonances is not substantially enhanced by further functionalization. The resonance of tetrakisadduct **3** ($\delta = -12.26$) displays the largest shielding, whereas those of the two pentakisadducts **4** ($\delta = -12.04$) and **5** ($\delta = -11.84$) and of hexakisadduct **6** ($\delta = -11.89$) appear at comparable chemical shifts, in the range of the ^3He resonance of bisadduct **1**. This experimental result was initially quite surprising since we had expected strong shielding of the ^3He atoms, particularly in the higher adducts, due to the vanishing of the paramagnetic ring currents of the pentagons[6, 20] and the development of localized benzenoid rings with strong diamagnetic ring currents. As mentioned above, the π-chromophore in hexakisadduct **6** contains a total of eight localized benzenoid rings connected by biphenyl-type bonds.[15]

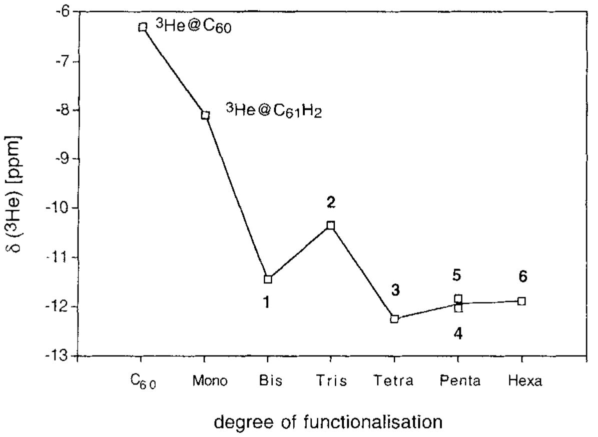
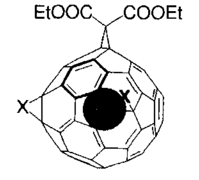


Figure 4. ^3He NMR chemical shifts of $^3He@C_{60}$ [7,11 b], $^3He@C_{61}H_2$ [11 b], and the C_{60} multiple adducts **1**–**6** plotted against the degree of functionalization.

An interpretation of these experimental results needed to take into consideration that the chemical shifts in ^3He@fullerenes are not only determined by π-electron ring-current effects.[6, 21] Bühl et al.[22] performed ab initio calculations on the fully hydrogenated fullerene derivatives $^3He@C_{60}H_{60}$ and $^3He@C_{70}H_{70}$ and found a prominent local contribution arising from the σ-electron framework of about $\Delta\delta = -5.2$ ppm.[22, 23] However, the local contributions resulting from σ-bond anisotropy should be roughly constant over a series of fullerene derivatives such as **1**–**6** and therefore, changes in ^3He NMR chemical shift should reflect mainly the different contributions of the various π-electron ring currents. This should also apply to the C_{70} adducts discussed in Section 2.3. We therefore propose that the enhanced shielding upon changing from $^3He@C_{60}$ to bisadduct **1**, in which full π-electron conjugation in four pentagons is destroyed, results mainly from the weakening of the paramagnetic ring currents in these rings. In the higher adducts **3**–**6**, however, the deshielding due to the functionalization-induced reduction in the diamagnetic ring currents that extend all around the fullerene sphere balances out the shielding due to the decrease in pentagonal ring currents and the increased number of localized benzenoid rings. As a result of this compensating effect, the ^3He resonances in **3**–**6** appear at very similar chemical shifts. This is in contrast to the ^1H NMR data, which show a monotonic upfield shift of the cyclohexene CH_2 protons in the series **1**–**6**.[14a] As compared to ^3He atoms at the center of the cage, protons located in a defined position atop the fullerene surface are more strongly influenced by local changes in pentagonal and (benzenoid) hexagonal-ring currents and less by changes in the diamagnetic ring currents extending around the entire C_{60} sphere. Although the latter have been calculated to be rather small in their local strength, they nevertheless have a significant effect on the resonance of ^3He atoms inside the cage due to the large area they enclose. These extended ring currents have been conceptually correlated with aromatic character,[6, 21] and, hence, higher functionalization can be viewed as destroying the aromaticity of the fullerene.

A contribution of benzenoid ring diamagnetic ring currents to the shielding of the ^3He atom becomes apparent in the comparison of the ^3He NMR resonances in the two different trisadducts *trans-1,e,e*-**2** ($\delta = -10.35$) and *e,e,e*-**14** ($\delta = -12.0$).[19, 24] Based on the higher shielding seen in cyclohexene-fused C_{60} monoadducts compared with cyclopropane-fused derivatives,[10] a higher upfield shift of the resonance of doubly cyclohexene-fused **2** could be expected. However, **14** possesses a diamagnetically shielding benzenoid substructure which is absent in **2**, and this difference could well explain the upfield shift of the ^3He resonance in **14**.



14

● = ^3He X = $(EtO_2C)_2C$

The large difference in ^3He NMR chemical shift ($\Delta\delta = 1.65$) between the trisadducts **2** and **14** nicely illustrates the influence of the nature of the addition pattern on the chemical shift of ^3He atoms inside C_{60} adducts.

3. ^3He NMR results for the C_{70} adducts 7–13: The plot of the ^3He NMR resonances of the C_{70} adducts **7**–**13** (Table 2) against the degree of functionalization (Figure 5) differs strikingly from

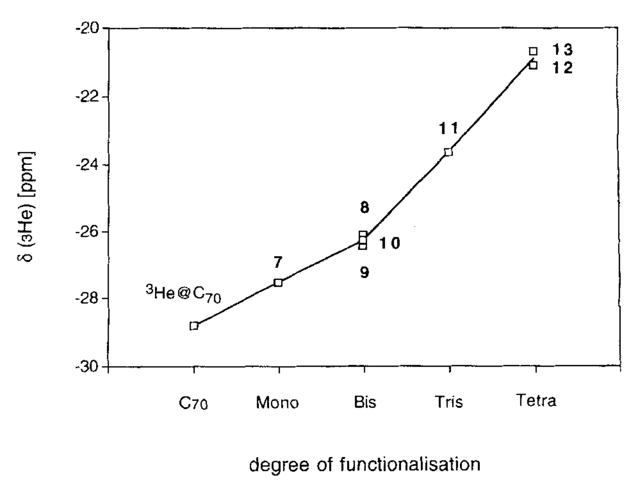


Figure 5. ^3He NMR chemical shifts of $^3He@C_{70}$ [7,11 b] and the C_{70} adducts **7**–**13** plotted against the degree of functionalization.

that obtained for the C_{60} adducts (Figure 4). Firstly, as expected from the results reported for C_{70} monoadducts,[11b] all adduct resonances are shifted downfield relative to $^3He@C_{70}$. Secondly, a monotonic relationship exists between chemical shift and degree of functionalization. The ^3He chemical shifts steadily decrease from monoadduct **7** ($\delta = -27.53$) to the isomeric tetrakisadducts **12** ($\delta = -21.09$) and **13** ($\delta = -20.68$).

The addends in **7**–**13** are located exclusively near the poles at 6-6 bonds at the centers of pyracyclene subunits, which had previously been defined as α- and β-type (Figure 6).[25] This functionalization destroys the paramagnetic ring currents of the pentagons in the polar region but leaves the diamagnetic ring current associated with the biphenyl-type equatorial belt of C_{70} intact. Based on these considerations, increased shielding of the ^3He resonances would be expected with increasing functionalization in the series **7**–**13**. In their London calculations of ring currents in C_{70}, Pasquarello et al. found rather strong diamagnetic ring currents extending along the polar corannulene perimeters (Figure 6).[6b] Since the area enclosed by these currents is large, a substantial contribution to the total magnetic susceptibility of C_{70} can be expected.[6b] These ring currents are destroyed upon functionalization at α- and β-type bonds, and we propose this effect to be the origin of the deshielding of the ^3He atoms in all C_{70} adducts measured so far.

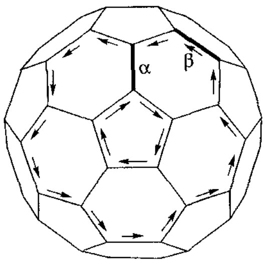


Figure 6. View above the pole of C_{70} depicting α- and β-type bonds and showing the paramagnetic ring current in the polar pentagon and the diamagnetic ring current extending along the polar corannulene perimeter, as revealed in London calculations by Pasquarello et al [6b].

In a more detailed analysis, addition to α- or β-type bonds has a significantly different effect on the NMR signal of the ^3He atom. A similar observation was previously made by Smith et al.[11b] Monoadduct **7** ($\delta = -27.53$) resulting from addition to an α-type bond shows a downfield shift of $\Delta\delta = 1.28$ relative to $^3He@C_{70}$. Addition to a second α-type bond at the opposite pole causes a further downfield shift of $\Delta\delta = 1.41$ (**8**), 1.09 (**9**), and 1.26 (**10**). Further cyclopropanation of bisadducts **9** and **10** occurs at β-type bonds.[13] This leads to a significantly larger downfield shift of 2.63 upon passing from bisadduct **10** ($\delta = -26.27$) to trisadduct **11** ($\delta - 23.64$). Similarly, addition to a β-type bond upon passing from trisadduct **11** to tetrakisadduct **12** ($\delta - 21.09$) leads to a deshielding of $\Delta\delta = 2.55$. These data suggest that the deshielding resulting from addition to either α- or β-type bonds at one pole is nearly independent of the degree of functionalization at the other, opposite one. Based on the data in Table 2, incremental values for the deshielding of the ^3He atom by cyclopropanation of C_{70} can be assigned which amount to about $\Delta\delta = 1.3$ for addition to an α-type bond and about $\Delta\delta = 2.7$ for addition to a β-type bond.

Finally, the ^3He resonances in the three isomeric C_{70} bisadducts **8**–**10** differ significantly, by as much as $\Delta\delta = 0.32$. An even larger difference ($\Delta\delta = 0.41$) exists between the resonances of the isomeric tetrakisadducts **12** and **13**. While these data reveal a distinct influence of the addition pattern on the shielding of ^3He atoms, this effect is, however, one order of magnitude smaller than the effects produced by differences in the degree of functionalization.

Conclusions

A strikingly different influence of the degree of functionalization on the ^3He chemical shift was observed by ^3He NMR spectroscopy for covalent multiple adducts of $^3He@C_{60}$ and $^3He@C_{70}$. In the series of C_{60} derivatives **1**–**7**, which included monoadduct $^3He@C_{61}H_2$ for comparison, all resonances are shielded relative to $^3He@C_{60}$. However, large changes in chemical shift are only observed up to the stage of bisadduct **1**. The resonances of the higher adducts **3**–**6** are not substantially further shifted upfield and all appear in a rather narrow spectral range. In sharp contrast, all ^3He resonances in the C_{70} adducts are shifted downfield relative to $^3He@C_{70}$, and a monotonic relationship exists between chemical shift and degree of functionalization, in that the ^3He atoms become steadily deshielded with increasing number of addends. Attempts to rationalize these observations are based on theoretical work, in particular by Haddon and co-workers,[6] who have shown that the magnetic properties of the fullerenes can be explained by the existence of paramagnetic ring currents in the pentagonal rings and diamagnetic ring currents extending around the fullerene spheres. In addition, the ^3He resonance in the higher adducts of C_{60} should be influenced by the diamagnetic ring currents of the localized benzenoid substructures that develop with increasing functionalization of the residual fullerene π chromophore. In contrast to protons located close to the fullerene surface, ^3He atoms at the center of the cage are exposed to the magnetic influence of the entire fullerene chromophore and thus to all existing π-electron ring currents. Therefore, they represent a unique experimental probe for the existence and magnitude of these ring currents. This study revealed in particular the strong influence of functionalization on the diamagnetic ring currents that extend around the entire fullerene sphere. Despite an increasing degree of addition in the higher C_{60} adducts **3**–**6**, the ^3He NMR chemical shifts remain nearly constant due to the balancing out of the deshielding resulting from the destruction of these ring currents and the shielding resulting from the vanishing paramagnetic pentagonal ring currents and the increasing number of benzenoid rings with diamagnetic ring currents. In the series of C_{70} derivatives formed by addition to α- or β-type bonds, strong evidence was obtained that the disruption of the diamagnetic ring currents extending along the polar corannulene perimeters is the major factor determining the observed deshielding of the ^3He resonances. A fruitful interplay between theory and experiment has in the past guided the interpretation of the ^3He NMR spectra of pure fullerenes and their lower adducts with ^3He atoms inside the cage.[10, 11] We are confident that theoretical calculations will also further substantiate and fine-tune the explanations proposed for the surprising experimental findings reported in this paper.

Experimental Section

Compounds **1**–**6** [12c] and **7**–**13** [13] were synthesized according to the reported procedures. ^3He NMR analyses of all samples were performed with a Bruker 500 MHz spectrometer. The samples were dissolved in 1-methylnaphthalene/CD_2Cl_2 (3/1). CD_2Cl_2 was the lock solvent. About 1 mg of Cr(acac)$_3$ was added as an external relaxation agent. Approximately 0.25 mL of ^{3}He gas was introduced into the liquid samples in a NMR tube of 5 mm diameter. The referenced samples were loaded into a ^{3}He probe made by the Nalorac company. Data acquisition was carried out for at least 8 h. This corresponds to about 12000 to 17000 scans.

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[1] E. Osawa, *Kagaku (Kyoto)* **1970**, *25*, 854–863.

[2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature (London)* **1985**, *318*, 162–163.

[3] V. Elser, R. C. Haddon, *Nature (London)* **1987**, *325*, 792–794.

[4] R. C. Haddon, L. F. Schneemeyer, J. V. Waszczak, S. H. Glarum, R. Tycko, G. Dabbagh, A. R. Kortan, A. J. Muller, A. M. Mujsce, M. J. Rosseinsky, S. M. Zahurak, A. V. Makhija, F. A. Thiel, K. Raghavachari, E. Cockayne, V. Elser, *Nature (London)* **1991**, *350*, 46–47; R. S. Ruoff, D. Beach, J. Cuomo, T. McGuire, R. L. Whetten, F. Diederich, *J. Phys. Chem.* **1991**, *95*, 3457–3459.

[5] a) T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, *J. Am. Chem. Soc.* **1992**, *114*, 7301–7302; b) L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231–1250; c) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt, R. C. King, *J. Am. Chem. Soc.* **1995**, *117*, 5492–5502.

[6] a) A. Pasquarello, M. Schlüter, R. C. Haddon, *Science* **1992**, *257*, 1660–1661; b) A. Pasquarello, M. Schlüter, R. C. Haddon, *Phys. Rev. A* **1993**, *47*, 1783 1789.

[7] M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, F. A. L. Anet, *Nature (London)* **1994**, *367*, 256–258.

[8] T. Weiske, T. Wong, W. Krätschmer, J. K. Terlouw, H. Schwarz, *Angew. Chem.* **1992**, *104*, 242–244; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 183–185, and references cited therein.

[9] M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, W. E. Billups, C. Gesenberg, A. Gonzalez, W. Luo, R. C. Haddon, F. Diederich, A. Herrmann, *J. Am. Chem. Soc.* **1995**, *117*, 9305–9308.

[10] M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, A. Khong, *Science* **1996**, *271*, 1693–1697.

[11] a) M. Saunders, H. A. Jiménez-Vázquez, B. W. Bangerter, R. J. Cross, S. Mroczkowski, D. I. Freedberg, F. A. L. Anet, *J. Am. Chem. Soc.* **1994**, *116*, 3621–3622; b) A. B. Smith III, R. M. Strongin, L. Brard, W. J. Romanow, M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, *J. Am. Chem. Soc.* **1994**, *116*, 10831–10832.

[12] a) L. Isaacs, R. F. Haldimann, F. Diederich, *Angew. Chem.* **1994**, *106*, 2434–2437; *Angew. Chem Int. Ed. Engl.* **1994**, *33*, 2339–2342; b) L. Isaacs, P. Seiler, F. Diederich, *ibid.* **1995**, *107*, 1636–1639 and **1995**, *34*, 1466–1469; c) L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317–342.

[13] A. Herrmann, M. Rüttimann, C. Thilgen, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1673–1704.

[14] a) F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343–371; b) C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *ibid.* **1995**, *78*, 1334–1344.

[15] a) P. Seiler, L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1996**, *79*, 1047–1058; b) P. J. Fagen, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, *113*, 9408–9409; c) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755–1757; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607–1609; d) B. Kräutler, J. Maynollo, *ibid.* **1995**, *107*, 69–70 and **1995**, *34*, 87–88.

[16] M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, M. L. Gross, D. E. Giblin, R. J. Poreda, *J. Am. Chem. Soc.* **1994**, *116*, 2193–2194.

[17] M. L. Martin, J.-J. Delpuech, G. J. Martin, *Practical NMR Spectroscopy*, Heyden, London, **1980**, pp. 404–405.

[18] Y.-Z. An, G. A. Ellis, A. L. Viado, Y. Rubin, *J. Org. Chem.* **1995**, *60*, 6353–6361.

[19] R. J. Cross, H. A. Jiménez-Vázquez, Q. Lu, M. Saunders, D. I. Schuster, S. R. Wilson, H. Zhao, *J. Am. Chem. Soc.* **1996**, *118*, 11454–11459.

[20] R. Zanasi, P. W. Fowler, *Chem. Phys. Lett.* **1995**, *238*, 270–280.

[21] J. Cioslowski, *J. Am. Chem. Soc.* **1994**, *116*, 3619–3620.

[22] M. Bühl, W. Thiel, H. Jiao, P. von R. Schleyer, M. Saunders, F. A. L. Anet, *J. Am. Chem. Soc.* **1994**, *116*, 6005–6006.

[23] R. C. Haddon, *Nature (London)* **1995**, *378*, 249–255.

[24] For nomenclature, see A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem.* **1994**, *106*, 453–455; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437–438.

[25] A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, W. H. Müller, *Helv. Chim. Acta* **1994**, *77*, 1689–1705.