Probing Fullerene Aromaticity

The Inside Story of Fullerene Anions: A ^{3}He NMR Aromaticity Probe**

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A fundamental chemical question concerning the fullerenes involves their aromatic nature.[1] For many reasons, it is impossible to experimentally obtain anything that is similar to a resonance energy for a fullerene. We must therefore rely on information obtained from magnetic properties. Since fullerenes are borderless polycyclic conjugated systems with internal cavities, it is possible to study the diamagnetism from the inside. Incorporating ^{3}He inside a fullerene cage (endohedral) and measuring its NMR chemical shift compared with the shift of helium outside gives a direct measurement of the shielding of the magnetic field by the fullerene.[2,3] The magnetic field inside the fullerene is a consequence of diamagnetism and is related to the ring currents in the fullerene molecular orbitals.[4]

The aromaticity of C_{60} and C_{70} has been thoroughly investigated theoretically and experimentally. An interesting aspect of these investigations was the observation that the addition of electrons[5] drastically changes the magnetic properties of fullerenes. Reducing these fullerenes to their hexaanions inverted their aromatic character.[1]

^{3}He NMR chemical shifts have clearly shown the extraordinary changes that occur in the aromaticity of C_{60} and C_{70} upon reduction. While the ^{3}He chemical shift of He@C_{60} appears at $\delta = -6.4$ ppm, that of He@$C_{60}{}^{6-}$ is shifted to an extremely high field ($\delta = -49.5$ ppm), which exemplifies the much higher aromatic character of the $C_{60}{}^{6-}$ ion. On the other hand, the ^{3}He NMR of He@$C_{70}{}^{6-}$ is shifted to low field, when compared with the neutral state (δ(He@C_{70}) $= -28.8$; δ(He@

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C_{70}^{6-}) = 8.3 ppm), thus pointing a reduction in aromaticity.[6] Fullerenes can also host two endohedral helium atoms,[7] and the ratio of the amounts of $He_2@C_n$ and $He@C_n$ is highly dependent on the fullerene size. The chemical shift of the dihelium species is close to that of the monohelium species, and it can be shifted to either a slightly higher or lower field. The difference between the mono- and dihelium resonances can give an indication about the homogeneity and the direction of the magnetic-field gradient inside the fullerene, since the mono- and dihelium forms exhibit different magnetic properties resulting from a slight difference in the location of the helium atoms. In a previous report, we demonstrated that the reduction of fullerenes can affect the magnetic-field gradient inside the fullerene.[8]

Beside C_{60} and C_{70}, higher fullerenes (C_n, $n > 70$) can also be prepared using the Krätschmer–Huffman procedure.[9] Their separation[10] and characterization are very challenging, because of their relatively similar shape, and the multiplicity of the resulting ^{13}C NMR signals.[11] It has been shown previously that the ^{3}He NMR chemical shifts of higher fullerenes, $He@C_n$, lie between two extremes, that is, the low-field $^3He@C_{60}$ and the high-field $^3He@C_{70}$, which points to their "intermediate" aromatic character.[3c–d]

The higher fullerenes are able to accept a relatively large number of electrons into their π systems, in a manner similar to that of C_{60} and C_{70}. This behavior was demonstrated by their electrochemistry,[12] and explained by the availability of low-lying unoccupied molecular orbitals,[13] which results in high electron affinities.[14] Calculations suggest that the addition of electrons should change the magnetic properties of the higher fullerenes.[15]

The purpose of this research was to study the magnetic properties of the anions of higher fullerenes by ^{3}He NMR spectroscopy. The main objectives were: a) Monitoring the changes in the aromaticity of the higher fullerenes on reduction; b) comparing the aromaticity of the anions of higher fullerenes to establish whether it depends on their size and/or their symmetry/topology; c) examination of the chemical shifts of the mono- and dihelium species in higher fullerene anions.

A mixture of ^{3}He-labeled fullerenes that contained mainly C_{70}, C_{76}, C_{78}, and C_{84} was separated by HPLC, depending on their molecular weight.[16] C_{76} was separated as one isomer,[10a] but C_{78} and C_{84} were separated as mixtures of isomers. The three isomers of C_{78} (C_{2v} (2)[17],C'_{2v} (3)[17] and D_3) were separated into two fractions (C_{78}-A and C_{78}-B), each of which contained a mixture of two isomers in unequal ratios (Figure 1). Unfortunately, a similar separation was not possible for the different isomers of C_{84}. The separation process was followed by measuring the ^{3}He NMR spectra of the mixture before separation, and those of each fraction obtained. [18] The ^{3}He chemical shifts of the neutral fullerenes (Table 1) are in good agreement with previously reported results.[3c–d] Most of the fullerenes showed a small ^{3}He NMR signal which is due to the $^3He_2@C_n$ species, in addition to the major ^{3}He NMR signal (Table 1).

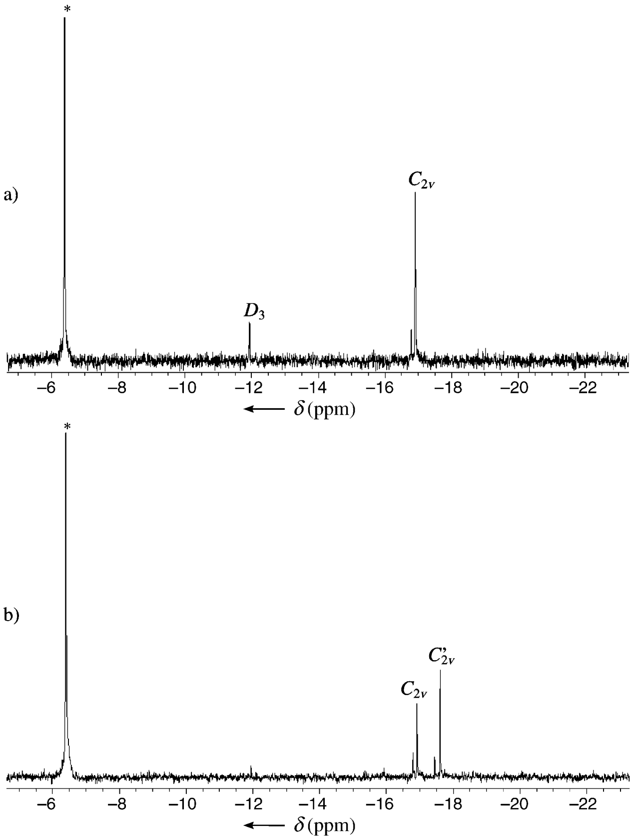

Figure 1. ^{3}He NMR spectra (methylnaphthalene/CD_2Cl_2) of the two fractions of C_{78} containing the three isomers. a) Fraction C_{78}-A; b) fraction C_{78}-B. * = $^3He@C_{60}$ (internal reference).

Table 1: ^{3}He NMR chemical shifts (in ppm) of $He@C_n$, $He@C_n^{6-}$ and the dihelium species (in parentheses).

	Neutral[a]	Anion	Δ[d]
$He@C_{60}$	−6.40	−49.27 [b], (−49.17)[c]	−42.87
$He@C_{70}$	−28.82, (−28.81)	+8.20[b], (+8.04)[c]	+37.02
$He@C_{76}$	−18.75, (−18.61)	−20.62, (−20.55)	−1.87
$He@C_{78}$-C_{2v}	−16.91, (−16.79)	−10.02	+6.89
$He@C_{78}$-D_3	−11.94	−32.39, (−32.54)	−20.45
$He@C_{78}$-C'_{2v}	−17.60, (−17.45)	−13.50, (−13.61)	+4.1
$He@C_{84}$ (mixture of isomers)	−7.53, (−7.57), −8.40, (−8.43), −8.99, −9.64, (−9.68)	−22.12, (−22.06), −22.80, (−22.76)	≈ −12

[a] Mostly consistent with data reported in refs. [3] and [7a], see text. [b] Taken from ref. [6]. [c] Taken from ref. [8]. [d] $\delta(He@C_n^{6-})-\delta(He@C_n)$.

Each fullerene fraction (2–5 mg) was reduced with lithium metal in [D_8]THF, in the presence of a trace of corannulene[6] and $^3He@C_{60}$ as an internal reference. The reduction process was followed by observing the solution color (up to the point that a green color was observed, which is indicative of the corannulene monoanion), and by measuring ^{3}He NMR spectra. The ^{3}He NMR data of all of the fullerene anions ($He@C_{76}^{6-}$, $He@C_{78}^{6-}$, and $He@C_{84}^{6-}$) together with those of $He@C_{60}^{6-}$ and $He@C_{70}^{6-}$ are summarized in Table 1, and compared with the chemical shifts of the neutral species.

The ^{3}He NMR spectra of the two fractions of C_{78}, together with the ^{13}C NMR spectra, make it possible to assign the ^{3}He signals of the different isomers. In the first fraction of C_{78}^{6-} (C_{78}-A), two signals were observed in the ^{3}He NMR spectrum; a major peak at −32.39 ppm and a smaller peak at −10.02 ppm (Figure 2). These two peaks were assigned as the anions of the isomers C_{78}-D_3 and C_{78}-C_{2v}, respectively. The signals in the spectrum of fraction C_{78}-B were observed at −10.02 ppm (the same as in fraction C_{78}-A: C_{2v}-isomer) and at −13.5 ppm, which was assigned to the isomer C_{78}-C'_{2v}.

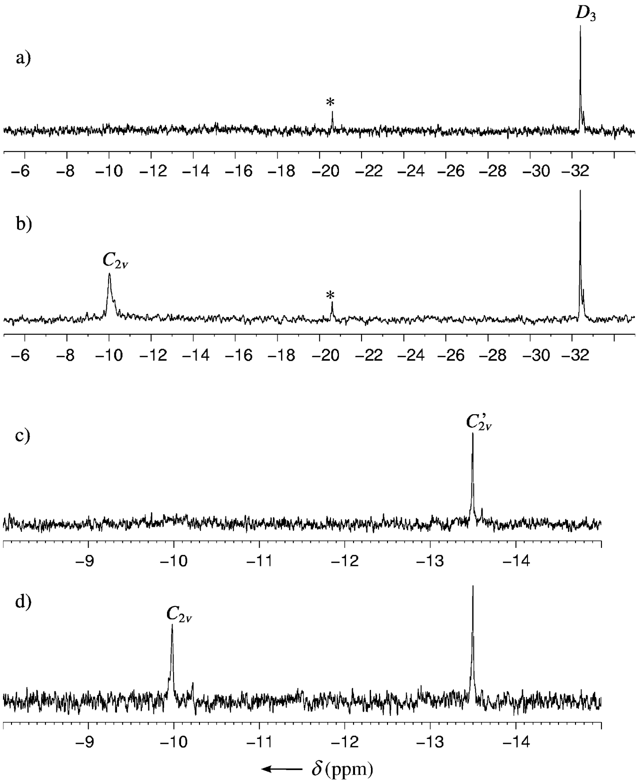

Figure 2. ^{3}He NMR spectra ([D_8]THF) of the two fractions of C_{78}^{6-} as a function of reduction time. a) the reduced fraction C_{78}-A; b) the same fraction after an additional 20 min reduction; c) the reduced fraction C_{78}-B; d) the same fraction after an additional 20 min reduction. * = a trace of ^{3}He@C_{76}^{6-}.

The assignment of the different isomers of C_{78} was based on the ^{13}C NMR spectrum of the reduced fractions. The ^{13}C NMR spectra of the reduced fraction C_{78}-A, was the same (at both 170 K and 298 K) as in our previous study of C_{78}^{6-}, which included the C_{2v} and D_3 isomers.[19] The ^{13}C NMR spectrum of fraction C_{78}-B did not contain the absorption of the D_3 isomer at 298 K, and a different ^{13}C NMR spectrum appeared at 170 K. This led us to conclude that the C'_{2v} isomer is the major form present in this fraction, and that the minor form is the C_{2v} isomer.[20]

By measuring the ^{3}He NMR spectra of both fractions as a function of reduction time, it can be seen that the signal of the C_{2v} isomer appears soon after the two other signals were observed (Figure 2). This means that a longer reduction time is needed for this isomer, even though it constitutes the larger component of the mixture (in fraction C_{78}-A), as was shown from the spectrum of the neutral isomers. This phenomenon was also observed by measuring the ^{13}C NMR spectra.[19]

Two major signals for He@C_{84}^{6-} were observed, one at −22.12 ppm and the other at −22.80 ppm, and one major signal appeared for ^{3}He@C_{76}^{6-} at −20.62 ppm. The ^{3}He NMR chemical shifts of all of the anions of the higher fullerenes are between two extremes: the high-field shift of He@C_{60}^{6-}, and the low-field shift of He@C_{70}^{6-}. Thus, an "aromaticity scale" of the fullerene anions can be suggested: $C_{60}^{6-} > C_{78}^{6-}(D_3) > C_{84}^{6-}$(two isomers) $> C_{76}^{6-} > C_{78}^{6-}(C'_{2v}) > C_{78}^{6-}(C_{2v}) > C_{70}^{6-}$.[21] The magnetic properties of the fullerene anions are in line with the magnetic susceptibility calculations.[15]

Comparison between the ^{3}He NMR chemical shifts of the neutral fullerenes and their anions (Table 1) shows that the changes in the chemical shifts are different from one fullerene to another. While the ^{3}He signals of C_{78}-D_3, C_{84}, and C_{76} are shifted to higher field as a result of their reduction, the two isomers of C_{78}-C_{2v} are shifted to lower field. These changes point to an increase or decrease, respectively, in the aromaticity of the fullerenes. These two opposite trends were observed in the reduction of C_{60} and C_{70}, but in a much more dramatic manner.

The magnetic properties of fullerenes and their anions are not simply related to the number of carbon atoms or the number of electrons in the π system. This is demonstrated by the three C_{78} isomers, which behave quite differently. The aromatic character of C_{78}-D_3 increases, when reduced, thus C_{78}^{6-}-D_3 is highly aromatic. However, the aromaticity of the two C_{2v} isomers decreases as a result of the reduction, and their anions show lower aromatic character than the anion of the D_3 isomer (the C_{2v} isomer shows lower aromaticity than C'_{2v}).

The He_2@C_n^{6-} signal was also observed in most of the ^{3}He NMR spectra. As for the neutral compounds, these minor signals appear at a slightly higher or lower field than the major signals (Table 1). In most of the "highly aromatic" fullerene anions, which show a high-field ^{3}He chemical shift (C_{60}^{6-}, C_{84}^{6-}, C_{76}^{6-}), the ^{3}He$_2$@C_n^{6-} resonance is shifted to a lower field, compared with the monohelium compound ^{3}He@C_n^{6-}. On the other hand, when the monohelium signal is shifted to a low field (C_{70}^{6-}, C_{78}^{6-}-C_{2v}), the signal for the dihelium compound is shifted to higher field. This can be explained by the direction of the magnetic-field gradient inside the fullerene. In most of the highly aromatic fullerene anions, the aromaticity is at its highest close to the fullerene center (as indicated by the chemical shift of the monohelium compound). An opposite behavior is observed for the "less aromatic" fullerene anions.[8]

The differences in the aromaticity of the isomers of reduced C_{78} are not only visible from the ^{3}He chemical shifts, but are also demonstrated kinetically.[22] The two isomers of C_{78}^{6-}-D_3 and C'_{2v}, which are found to be more aromatic than C_{78}^{6-}-C_{2v}, also have a faster reduction rate.[23] This can indicate the presence of a more stable transition state, which is affected by their aromaticity.[24]

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[20] This obvious assignment makes it also possible to assign the ^{3}He NMR chemical shifts of the neutral isomers of He@C_{78}.

[21] The assignment as hexaanions is based on DFT calculations, see ref. [19].

[22] The neutral compounds are not soluble in THF, and the C_{2v} isomer was found in larger quantities than the D_3 isomer.

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