Analysis of Isomers of the Higher Fullerenes by ^{3}He NMR Spectroscopy

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Abstract: The high-pressure, high-temperature ^{3}He labeling procedure previously used with C_{60} and C_{70} was applied to mixtures of isomers of the higher fullerenes C_{76}, C_{78}, and C_{84}. Sufficient helium was introduced inside them to allow helium NMR spectra to be obtained. Each isomer yields a single, sharp, characteristic NMR peak resolved from the others. Our results show that there are more isomers of these fullerenes than previously reported. Three C_{78} isomers and three C_{84} isomers have been described, but we have shown that there are at least five C_{78} isomers and nine C_{84} isomers.

Introduction

Discovery of fullerenes larger than C_{60} (**1**) and C_{70} (**2**) as products of the Krätschmer–Huffman preparation has stimulated much effort to predict and determine the structures and properties of these molecules. According to Euler's theorem,

1   **2**
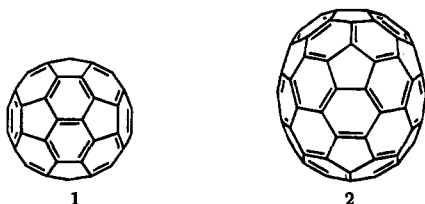
if these higher fullerenes are constructed with five- and six-membered rings as are C_{60} and C_{70}, they must each have twelve five-membered rings. The hypothesis that adjacent five-membered rings within a fullerene cage would produce structures of higher energy has led to the proposal of the "isolated pentagon rule" (IPR).[1] Within the constraints of this rule, there are two C_{76} (although only one has been predicted to have a closed shell structure), five C_{78}, nine C_{82}, and twenty-four C_{84} possible fullerene isomers. Up to now, experimental evidence has been presented for one C_{76}, three C_{78}, one C_{82}, and three C_{84} isomers.[2] It has been assumed that the other isomers are not formed or are formed in small amounts. Since the isomers of a given fullerene have similar shapes, it is expected that their separation by chromatographic methods would be difficult. Each isomer should have a distinct CMR spectrum with a number of signals dictated by the symmetry of the molecule, lower symmetry leading to more peaks and weaker individual intensities. Isomers present in small amounts would be hard to detect from the CMR of such mixtures.

We have recently shown that it is possible to introduce noble gas atoms inside fullerene molecules by heating them in the presence of the gas.[3] Using high pressure, sufficient ^{3}He can be incorporated so that helium NMR spectra can be obtained.[4] The labeled fullerenes ^{3}He@C_{60} and ^{3}He@C_{70} yielded peaks at -6.4 and -28.8 ppm (upfield of dissolved ^{3}He).[5] We have attributed these chemical shifts to the magnetic fields inside the fullerenes. These unique magnetic fields can be ascribed to ring currents in the π-systems of the fullerenes. Since the peaks can be as narrow as 1 Hz at half-width under optimum conditions, the relative shifts can be measured to ± 0.003 ppm. Reactions carried out on the labeled fullerenes produce changes in the π-structure, modifying the chemical shift of the helium inside. So far, each of the many products we have analyzed has yielded a characteristic helium peak resolved from all the others.[6] In mixtures, a single, sharp peak is obtained for each fullerene species present, with the intensities or areas of the peaks indicating their relative amounts. Helium NMR is thus a powerful method for following chemical transformations of fullerenes. This also makes ^{3}He NMR particularly useful for analyzing mixtures of isomers of the higher fullerenes.

The helium NMR chemical shift of ^{3}He@C_n is related to the magnetic susceptibilities of the fullerenes. Both properties were studied by Elser and Haddon in C_{60} and C_{70} with calculations involving the London approach.[7] Although the London theory does not provide a rigorous account of the magnetic properties,

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the calculations qualitatively predicted the experimental results.[8] The diamagnetic (Larmor) and paramagnetic (Van Vleck) terms almost cancel in C_{60},[8a,9] while for C_{70} the Larmor term was found to be dominant, predicting a substantial upfield shift of the helium. Elser and Haddon also proposed that the five-membered rings are responsible for the quenching of the diamagnetism in the fullerenes. As the number of five-membered rings remains fixed at twelve, the magnitude of the paramagnetic contribution would be expected to be proportional to the ratio of six- to five-membered rings. Because this ratio is larger in C_{70}, it was expected to show a larger diamagnetism. In larger fullerenes then, the magnetic susceptibility would approach that of graphite.[7a,8]

Further calculations carried out on C_{60} and C_{70} using the London approach showed that, even though the total magnetic susceptibility of C_{60} is very small, there are ring currents.[9] In C_{60}, the currents could be dissected into two types of contributions: (a) strong paramagnetic currents within all pentagons, and (b) diamagnetic currents flowing in all other parts of the molecule. The diamagnetic currents are of lesser magnitude, but cover a larger area. The net result is an almost complete cancellation of the ring current contribution to the magnetic susceptibility of C_{60}. Estimates of the shielding experienced by a probe inside the fullerene were also carried out. For C_{60}, a deshielding of less than 1 ppm was predicted. In C_{70}, paramagnetic currents in the pentagons were found, although the paramagnetic currents in the pentagons away from the poles were substantially weaker. The overall effect is that the diamagnetic currents are dominant. A probe located at the center of the fullerene would be substantially shielded. It should be noted that the five-membered rings around the "belt" in C_{70} have different bonding and probably less radialene character than those of C_{60}. The six-membered rings in this area are also different.

The goals of the work we present here were the following: (1) to find out whether the higher fullerenes C_{76}, C_{78}, and C_{84} incorporate ^{3}He under the same conditions in which C_{60} and C_{70} do; (2) to study the ^{3}He NMR spectra of these higher fullerenes, trying to assign signals to known isomers; and (3) to compare theoretical predictions with the experimental results.
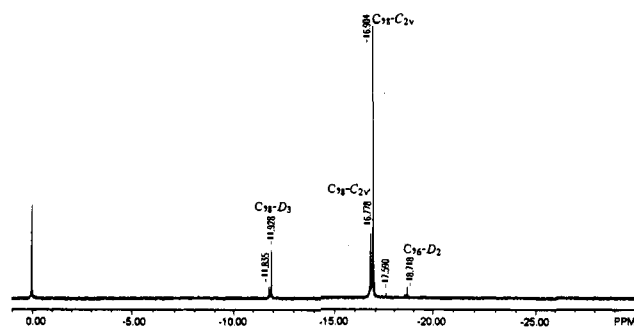
Results

A mixture of higher fullerenes from Rice University (about 25 mg) containing C_{60}, C_{70}, and small amounts of C_{76}, C_{78}, and C_{84} was labeled under our usual conditions[4] with ^{3}He and analyzed by helium NMR.[5,10] In addition to the signals corresponding to C_{60}, C_{70}, and the reference (dissolved ^{3}He), peaks were observed at -8.42, -8.97, -11.92, -16.91, and -18.72 ppm. A partial separation of this mixture was carried out using HPLC (at Rice) and helium spectra of the fractions were obtained. The first two peaks were preliminarily assigned to isomers of C_{84}, the next two to C_{78}, and the last one to C_{76}.

Two fractions of higher fullerenes prepared at the ETH were

Figure 1. ^{3}He NMR spectrum of a highly purified fullerene fraction containing mostly C_{78}.

Figure 2. ^{3}He NMR spectrum of a highly purified fullerene fraction containing mostly C_{84}.

treated in a similar fashion.[11,12] The first one (Figure 1), enriched in C_{78}, gave helium peaks at -18.72 (C_{76}), -18.58,[13] -17.59, -16.90, -16.78, -11.93, and -11.84 (C_{78}). The second fraction (Figure 2), enriched in C_{84}, showed peaks at -8.96, $-7.51/-7.55$, $-8.41/-8.37$, and $-9.61/-9.65$ (in each of these pairs, the second peak is the minor one). The peaks corresponding to the three major components of the C_{78} fraction are also observed. Two more peaks are seen at -10.50 and -11.12 ppm. One additional signal appears far from the previous ones, at -24.35 ppm.[14] Spectra of both C_{78} and C_{84} samples, taken in o-dichlorobenzene, produced the same pattern of signals, except that all of them showed a downfield shift of about 0.3 ppm with respect to dissolved helium. It is likely that a solvent effect on the dissolved helium is responsible for this shift.[15] An additional sample of C_{84} prepared under the same conditions as the one we labeled was found to contain
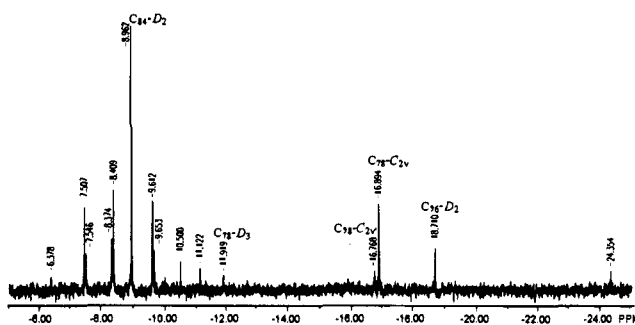
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(10) The ^{3}He NMR spectra were obtained in a Bruker AM-500 NMR spectrometer using a 9 μs pulse and a 1 s delay between pulses. The samples were dissolved in a mixture of 1-methylnaphthalene and CD_2Cl_2 (about 4:1). A small amount of $Cr(acac)_3$ was added to speed up relaxation, and about 0.25 mL of ^{3}He gas was bubbled through the solution to act as a reference. In both spectra, a line broadening factor of 2 Hz was used.

(11) The high-pressure labeling with ^{3}He was carried out at about 51 000 psi, at 620 °C, for 5 h. The C_{78} sample originally contained 11 mg of which 4.9 mg were recovered. For the C_{84} sample, 14 mg were treated, and 7.9 mg were recovered. In both instances, water was used to generate the high pressure.

(12) The HPLC purification for the last C_{78} and C_{84} samples was carried out (at the ETH) in two runs on a Buckyclutcher column using as eluent a mixture of n-hexane/toluene (3:2). The C_{78} fraction was further purified by means of HPLC on a polystyrene gel with dichloromethane as eluent.

(13) The smallest peak in the spectrum of the C_{78} fraction, appearing at -18.58 ppm, was reproducible in the spectra taken in 1-methylnaphthalene and o-dichlorobenzene. It remains unassigned.

(14) Two of the referees have mentioned the possibility that one or more of the peaks present in the spectrum of C_{84} correspond to oxides of the higher fullerenes, or that the peak seen at -24.35 is that of one of the isomers of $C_{70}O$. Although we cannot rule this out completely, we consider it unlikely. In none of the helium spectra we have obtained of C_{60}, C_{70}, and their derivatives have we seen any traces of the oxides of C_{60} or C_{70}, unless they were expressly synthesized. It is also relevant to mention that, prompted by our experimental results, M. Bühl has carried out *ab initio* calculations of the shieldings of helium in most of the possible IPR isomers of C_{76}, C_{78}, C_{82}, and C_{84} (Bühl, M. Unpublished). It is striking that for one particular isomer of C_{84}, the predicted helium chemical shift is far upfield, close to the position of the -24.35 peak.

(15) The small variation in chemical shifts observed by comparing Figure 1 with Figure 2 is also due to the slightly different composition of the solvent mixture used in each NMR experiment (1-methylnaphthalene/CD_2Cl_2). The dissolved ^{3}He, used as a reference, is more sensitive to changes in the solvent than the ^{3}He atoms inside the fullerenes.

about 2.3% of C_{82} by MALDI-TOF mass spectrometry,[16] making it likely that one or more of the peaks observed in this spectrum correspond to isomer(s) of C_{82}.

Conclusive assignment of all the ^{3}He NMR signals observed in our samples is not currently possible. Nevertheless, the main peaks may be tentatively assigned with the help of available theoretical and experimental data. C_{76} has two possible isomers that comply with the IPR. Only the one with D_2 symmetry has been predicted to have a closed-shell structure.[17,18] It is also the only one that has been observed experimentally.[19-21] We assign the peak observed around -18.72 ppm to ^{3}He@C_{76}-D_2 (**3**).

There are five possible C_{78} isomers that comply with the IPR.[18] Several theoretical calculations have reported somewhat different stability orders for them.[18,22-26] Experimental results support the presence of three major isomers,[21,26,27] C_{2v} (**4**), D_3 (**5**), and C_{2v}, (**6**). Because the isomer ratio is different in each

3 (C_{76}-D_2)

4 (C_{78}-C_{2v})   **5** (C_{78}-D_3)   **6** (C_{78}-$C_{2v'}$)
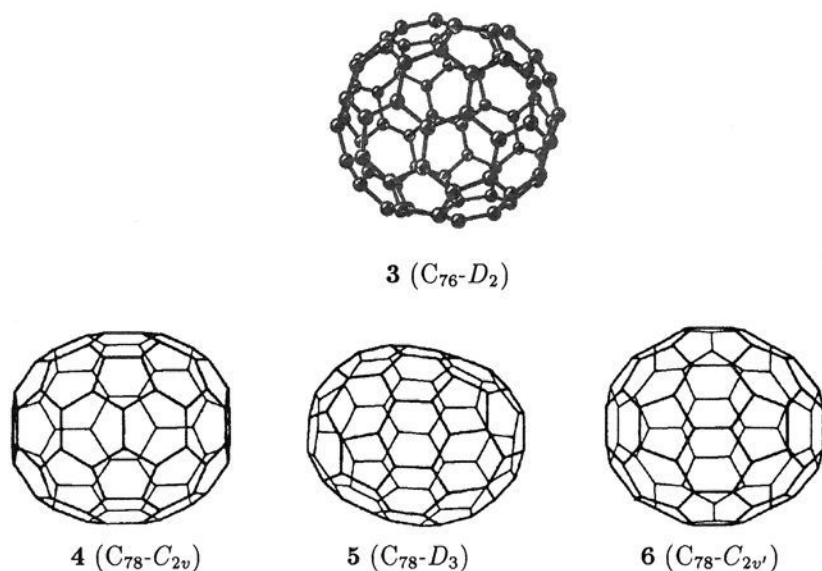
of the reports, it is likely that the distribution of C_{78} isomers depends on the experimental conditions under which it is formed. The ^{13}C NMR spectrum of C_{78} obtained by Taylor and co-workers[21] supports the presence of three major isomers of which **4** is the most abundant (about 50%), then **5** (about 30%), and last **6** (about 20%). We have assigned the major peak (-16.90 ppm) of our C_{78} mixture to **4**. The peak at -16.78 ppm was assigned to **6** on the basis of the intensity, and the fact that the calculated ^{3}He chemical shift is expected to be very similar to that of **6** (see below). The peak at -11.93 ppm is then assigned to **5**. We can further speculate about whether

(16) The percentages reflect only the total area of the peaks corresponding to C_{82} and C_{84}. The mass spectrum was taken in the positive-ion mode with 2,5-dihydroxybenzoic acid (0.1 M in MeCN/EtOH/H$_2$O) as a matrix. The acceleration voltage was 15 kV in the linear and 16.5 kV in the reflectron mode.

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the additional peaks at -11.84 and -17.59 ppm correspond to the other two C_{78} isomers which comply with the IPR, and which are expected to be higher in energy.

There is substantial theoretical[28-31] and experimental[20,21,27,32] evidence supporting the existence of two major C_{84} isomers as the most stable forms for this fullerene. They are the D_2 (**7**) and D_{2d} (**8**) forms, assumed to be present in a 2:1 ratio after

7 (C_{84}-D_2)   **8** (C_{84}-D_{2d})
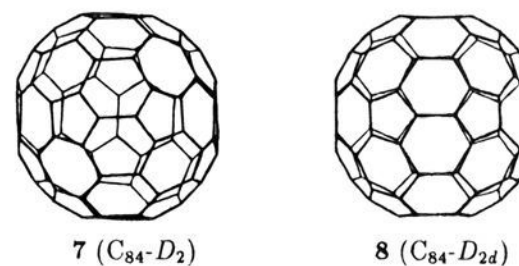
isolation from the crude fullerene mixtures. For C_{84}, twenty-four isomeric structures that follow the IPR have been described.[18] Taylor and co-workers have acknowledged that the fraction containing C_{84} they obtained during fullerene synthesis contained additional unidentified isomers.[21] We tentatively assign the peak aqt -8.96 ppm in our C_{84} ^{3}He spectrum to **7**. Even though **7** and **8** were found by ^{13}C NMR to exist in a 2:1 ratio, we see more than one peak with a similar ratio to the main signal. If the high-pressure labeling did not appreciably change the isomer ratio found in the original mixture, we can speculate that other isomers found in relatively large amounts are not seen by ^{13}C NMR because they have lower symmetry and give rise to a large number of weak signals in the ^{13}C NMR spectrum. It is also possible that, as is the case with C_{78}, the isomer composition of all higher fullerenes varies according to the conditions of preparation.

The amount of C_{82} determined by mass spectroscopy may be used as a guide in looking for a peak corresponding to this fullerene in the spectrum of the C_{84} mixture. Table 1 includes the percentage of each peak observed in the spectra shown in Figures 1 and 2. For the C_{84} fraction, we also include the percentage of each peak considering only those that are not seen in the spectrum of the C_{78} fraction, and which should correspond mostly to C_{82} and C_{84} (the peak at -24.35 ppm may be due to something very different but it is also included there[14]). The chemical shift of ^{3}He@C_{82} is calculated to be in between those of C_{78} and C_{84} (see below). Only the peaks at -10.50 and -11.12 ppm seem to be present in an amount small enough to be considered as possibly corresponding to C_{82}, although no definite assignment can be made.

Discussion

We conclude from these results that the high-temperature, high-pressure method of labeling introduces ^{3}He into many (perhaps all) of the higher fullerenes. It is likely that bonds in the fullerenes are broken reversibly at high temperatures, allowing atoms of the surrounding gas to go in and out of the cage (the window mechanism). We do not know whether labeling through this mechanism occurs in all the higher fullerenes with the same efficiency. It is also possible that some of the isomers decompose under the experimental conditions at a faster rate than others, or even that isomerization occurs,

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Table 1. Calculated and Experimental ^{3}He Chemical Shifts (ppm) of Some Isomers of the Higher Fullerenes[a]

δ_{exp}	assign[b]	$\delta_{H\&P}$	$\delta_{B\&T}$	percent[c] total	percent[c] partial
			C$_{78}$ Spectrum		
−11.835	?	−	−	2.83	−
−11.928	C$_{78}$−D$_3$	−5.6	−14.1	11.42	−
−16.778	C$_{78}$−C$_{2v'}$	−6.4	−16.5	15.28	−
−16.904	C$_{78}$−C$_{2v}$	−7.6	−16.7	66.18	−
−17.590	?	−	−	1.18	−
−18.576	?	−	−	0.64	−
−18.718	C$_{76}$−D$_2$	−8.0	−17.8	2.47	−
			C$_{84}$ Spectrum		
−6.377	C$_{60}$−I$_h$	−4.9	−11.7	1.52	−
−7.507	?	−	−	9.10	11.28
−7.546	?	−	−	4.08	5.07
−8.374	?	−	−	5.54	6.87
−8.409	?	−	−	11.08	13.74
−8.962	C$_{84}$−D$_2$	−4.7	−12.8	28.87	35.81
−9.612	?	−	−	9.76	12.11
−9.653	?	−	−	4.50	5.58
−10.500	?	−	−	3.12	3.86
−11.122	?	−	−	2.42	3.01
−11.919	C$_{78}$−D$_3$	−5.6	−14.1	1.66	−
−16.768	C$_{78}$−C$_{2v'}$	−6.4	−16.5	2.08	−
−16.894	C$_{78}$−C$_{2v}$	−7.6	−16.7	9.48	−
−18.710	C$_{76}$−D$_2$	−8.0	−17.8	4.64	−
−24.354	?	−	−	2.15	2.66
−28.80	C$_{70}$−D$_{5h}$	−11.4	−23.0	−	−
−	C$_{82}$−C$_2$	−5.3	−12.9	−	−
−	C$_{84}$−D$_{2d}$	−4.0	−12.8	−	−

[a] Haddon and Pasquarello[35] (H&P) and Bühl and Thiel[38] (B&T) used MNDO geometries to calculate the ^{3}He chemical shifts, except for C$_{84}$ where B&T used SCF/SV/DZ data. The shifts were calculated by H&P using the London approach, while B&T employed GIAO/SCF calculations at the TZP(He)/DZ(C) level of theory. In order to make a direct comparison between the results of both sets of calculations and the experimental values, the shielding due to the σ framework must be kept in mind for the London calculations.[7b,34] [b] These are tentative assignments. [c] The percentage of the total considers all significant peaks. The partial percentage includes only those peaks observed in the spectrum of the C$_{84}$ fraction that are not observed in the other spectrum (see text).

but this is less likely.[33] Any of these factors would result in a fullerene mixture with a ^{3}He content not exactly reflecting the original composition.

It is striking that the helium chemical shifts of the higher fullerenes, C$_{76}$, C$_{78}$, and C$_{84}$, fall in the region between those of C$_{60}$ and C$_{70}$. One of Haddon's original conclusions was that the shielding felt by the atoms inside fullerenes seemed to be a function of the ratio of six- to five-membered rings. Hence, one might have expected a further upfield shift for the larger fullerenes, because they have more six-membered rings while the number of five-membered rings remains the same. However, the bonding character of both the five- and six-membered rings changes from one structure to another. The observed trend of the chemical shifts is a large jump upfield on going from C$_{60}$ to C$_{70}$, and then downfield shifts as the size of the fullerene increases further.

Based on the experimental data available for C$_{60}$ and C$_{70}$, the London calculations carried out by Haddon and co-workers seem to provide a good account of the magnetic suscepti-bilities.[7,8a,9] The ring current contribution to the chemical shift is underestimated by a factor of 2 in ^{3}He@C$_{70}$ perhaps because the usual line current approximation fails to capture the distribution of the current flow on the inside and outside of the curved fullerene surface. Furthermore, Bühl and co-workers

have shown that the fullerene π-electron ring currents are not solely responsible for the shieldings inside the fullerene molecules.[34]

Recently, Haddon and Pasquarello have carried out London calculations to obtain the π-electron ring current contribution to the diamagnetic susceptibility in larger fullerenes.[35] The calculations were first applied to the isomers of C$_{70}$, C$_{76}$, C$_{78}$, C$_{82}$, and C$_{84}$ that have been characterized to date (see Table 1). The molecular geometries used were those obtained from the MNDO calculations of Raghavachari.[28,36] None of these fullerenes was found to have a π-electron magnetic susceptibility larger than C$_{70}$. The values of the NMR shielding were found to vary in more or less the same manner as the magnetic susceptibilities. In particular, both C$_{84}$ isomers had the values farther downfield of the group. These results are consistent with our experimental findings. All the chemical shifts we see for C$_{76}$, C$_{78}$, and C$_{84}$ fall between those of C$_{60}$ and C$_{70}$. Furthermore, the signals that we have attributed to the isomers of C$_{84}$ are the ones at the lowest field.

There are two reports of *ab initio* calculations of the ^{3}He chemical shifts of He@C$_{60}$ and He@C$_{70}$.[34,37] Bühl and Thiel have recently reported *ab initio* calculations of the expected chemical shifts of ^{3}He inside the known isomers of C$_{76}$, C$_{78}$, C$_{82}$, and C$_{84}$.[38] These calculations reproduce the general trends we have observed and seem to be accurate to within a few ppm. They are also in qualitative agreement with Haddon's calculations but the results seem to be more accurate. It has not yet been possible to see any qualitative relation between the experimental or any theoretical results and the structures assigned. In Haddon's calculations, Bühl calculations, and our experimental results, C$_{76}$ has the chemical shift at the highest field, while C$_{84}$ has the lowest-field shift. These data, as well as preliminary assignments, are summarized in Table 1. A more accurate assessment of the average error for either type of calculation must await a rigorous means of assigning the helium peaks of the new isomers to specific structures. If it became possible to make more accurate predictions from calculations at higher levels, it might be possible to use them to aid in making these assignments.

Haddon and Pasquarello also calculated π-electron magnetic susceptibilities for the fullerenes C$_{120}$, C$_{180}$, C$_{240}$, and C$_{540}$ using the structures determined by Bakowies and Thiel.[39] They predicted that for this series the magnetic susceptibilities should increase monotonically with fullerene size, tending to approach the magnetic susceptibility of graphite. The chemical shift of ^{3}He@C$_n$, however, should remain approximately constant at least within the approximation used to calculate them. The apparently random fluctuation of chemical shifts in the smaller fullerenes (C$_{60}$–C$_{84}$) was attributed to quantum size effects that tend to disappear as the size increases. The helium chemical shifts might exhibit less variation in the regime where the magnetic susceptibilities trend toward the graphite value.[35]

(33) It is known that some chiral isomers do not racemize on heating to 700 °C. See: Hawkins, J. M.; Nambu, M.; Meyer, A. *J. Am. Chem. Soc.* **1994**, *116*, 7642−7645.

(34) Bühl, and co-workers found that, in addition to the π-electrons, the σ-framework is partially responsible for the helium shielding, and that the magnitude is very similar in C$_{60}$ and C$_{70}$, about 5.3 ppm. See: Bühl, M.; Thiel, W.; Jiao, H.; Schleyer, P. v. R.; Saunders, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6005−6006.

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