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Fullerene Anions of Different Sizes and Shapes: A ^{13}C NMR and Density-Functional Study

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A combined experimental and theoretical study was conducted on numerous higher fullerene anions with different sizes and shapes, C_{76}-D_2, C_{78}-C_{2v}, C_{78}-D_3, C_{84}-D_2, and C_{84}-D_{2d}. The corresponding fullerenes were reduced by lithium metal to diamagnetic multiply charged anions. The centers of gravity of the ^{13}C NMR spectra of all the multiply charged anions were deshielded, relative to those of the neutral fullerenes. The results of density functional (DFT) computations of the ^{13}C NMR spectra and the molecular orbitals (MOs) of possible polyanion reduction products suggest that hexaanions were the species formed.

Introduction

Extensive investigations on numerous higher fullerenes (C_n, $n > 70$) began over a decade ago.[1] After these became available, ^{13}C NMR spectroscopy was used as the major structural tool for determining their symmetries.[2] Theoretical[3] and experimental[4] investigations have been carried out to link the size and shape of the higher fullerenes to their chemical and physical properties. However, a clear connection was not found in most of the studies. Moreover, fullerenes with the same number of carbon atoms and the same molecular symmetry can behave differently.[5]

An important characteristic of the π-systems of fullerenes is their ability to accept a relatively large number of electrons,[6] as shown by their electrochemistry.[6,7] This can be explained by the availability of low-lying unoccupied molecular orbitals[6,8] that result in high electron affinities.[6,9] The reduction of C_{60} and C_{70} by alkali metals has been thoroughly investigated;[10] each gave only one diamagnetic anion, characterized as a hexaanion. The magnetic properties of $C_{60}{}^{6-}$ and $C_{70}{}^{6-}$ vs. their corresponding neutral fullerenes alternate positions.[10−12]

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The dia-tropicity of C_{60} is dramatically enhanced as a result of the addition of six electrons. On the other hand, C_{70}^{6-} shows a reduced diatropicity compared with the neutral fullerene. Since the hexaanions of C_{60}^{6-} and C_{70}^{6-} show the same ^{13}C NMR spectral patterns as the corresponding neutral fullerenes,[13] the reductions do not result in connectivity changes.[10a] However, due to anisotropy effects in both systems,[14] the centers of gravity of the ^{13}C NMR spectra are shifted to lower field compared to their neutral analogues. C_{60}^{6-} is deshielded by 14 ppm compared to neutral C_{60} (156[10a] and 142[13] ppm, respectively). In C_{70}^{6-}, some of the ^{13}C NMR signals are deshielded and some shielded,[10b,15] but overall, the center of gravity of the ^{13}C NMR spectrum of C_{70}^{6-} is slightly (0.9 ppm) deshielded.

Several reduction waves, generally six, have been observed in electrochemical studies conducted on many higher fullerenes.[16] Calculations predict that the magnetic properties of the higher fullerenes should depend on their reduction state.[3a,17] However, the anions of the higher fullerenes have not been characterized by NMR.

We now report the reduction of higher fullerenes of the following symmetries, C_{76} (D_2), C_{78} (D_3, 1), C_{78} (C_{2v}, 2),[18] C_{84} (D_2, 22),[18] and C_{84} (D_{2d}, 23),[18] to their respective diamagnetic multiply charged anions and record the ^{13}C NMR spectra. Density functional calculations were performed to assist in NMR spectral assignments and in the determination of the reduction states of the multiply charged anions.

Results and Discussion

^{13}C NMR Spectra Measurements. The C_{76}, C_{84}, and C_{78} fullerenes were reduced with lithium metal in the presence of a small amount of corannulene serving as an electron shuttle.[10b−g] Their ^{13}C NMR spectra indicated that reductions to diamagnetic species had occurred. All the anionic fullerene products had the appropriate number of lines required by the symmetry of their neutral parents. These fullerene multiply charged anions exhibit anisotropic effects since the center of gravity of each multiply charged anion spectrum was shifted 5.5−8.5 ppm to lower field, compared to the neutral fullerene.

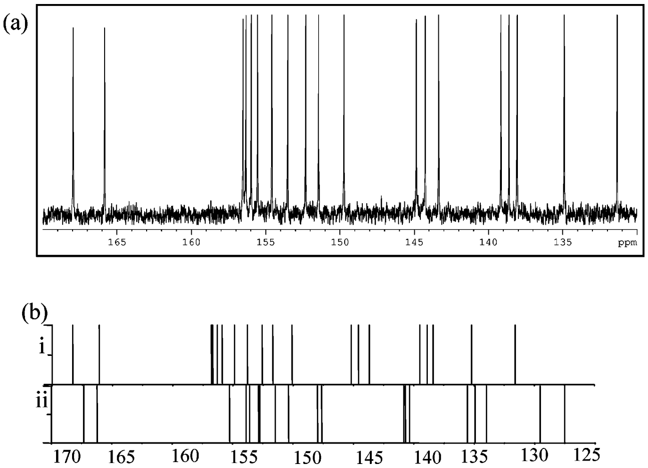

FIGURE 1. ^{13}C NMR spectra of the C_{76} multicharged anion: (a) recorded spectrum; (b) (i) experimental shifts and (ii) computed C_{76}^{6-} shifts.

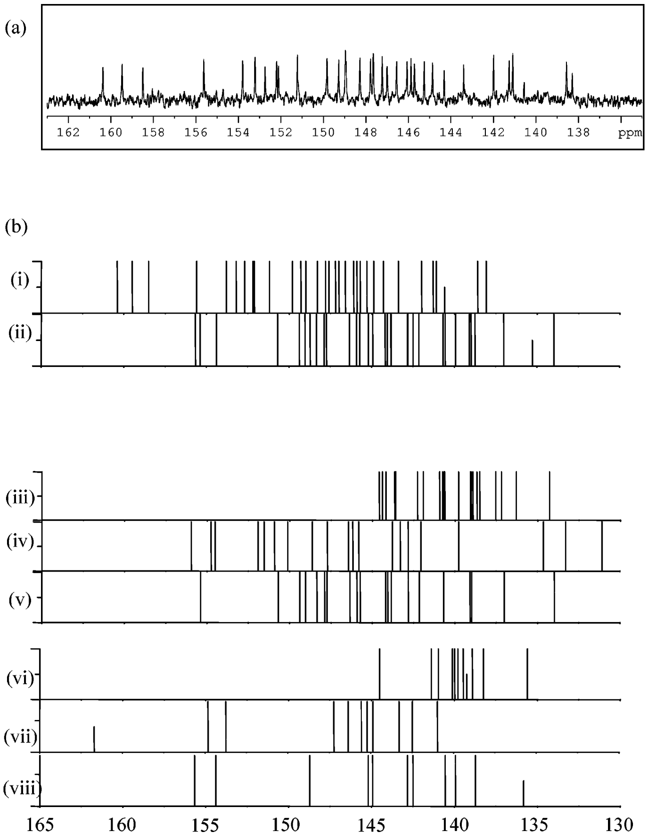

FIGURE 2. ^{13}C NMR spectra of C_{84} multicharged anions: (a) recorded spectrum; (b) (i) experimental shifts and (ii) computed C_{84}^{6-}(D_2, 22 and D_{2d}, 23) isomers. (iii−v) Computed C_{84}(D_2, 22) as neutral, tetra-, and hexaanions. (vi−viii) Computed C_{84}(D_{2d}, 23) neutral, tetra- and hexaanions.

Reduction of C_{76}. The ^{13}C NMR spectrum of the reduced C_{76} contains 19 lines of equal intensities, as expected from its D_2 symmetry[1a,2a] (Figure 1). The center of gravity of its spectrum, 149.5 ppm (Figure 1a), is deshielded by 6.8 ppm from the neutral C_{76}.

Reduction of C_{84}. Reduction of an isomeric C_{84} mixture containing the main isomers of D_2 and D_{2d} symmetries in a nearly 2:1 ratio led to a ^{13}C NMR spectrum with 31 lines of equal intensity and one line of half intensity (140.6 ppm), as expected[2d−f] (Figure 2a). The D_2 isomer has 21 different carbons, and the D_{2d}isomer

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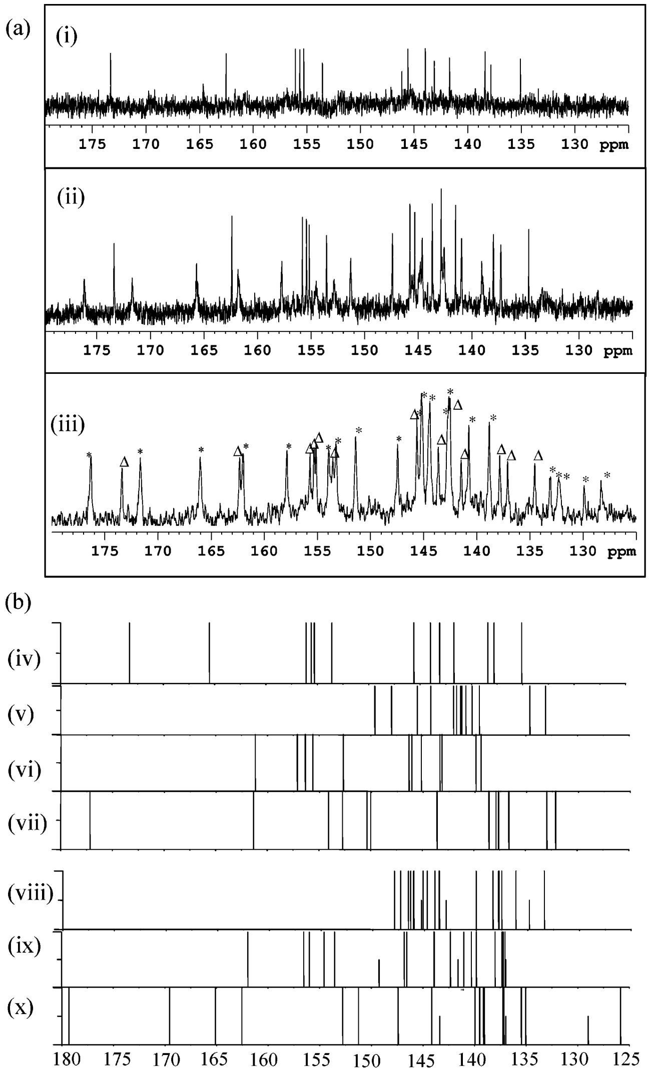

FIGURE 3. ^{13}C NMR spectra of C_{78} anions: (a) recorded spectrum at (i) 298 K, (ii) 200 K, (iii) 170 K (△ designates D_3, asterisk designates C_{2v}, 2); (b) (iv) experimental shifts and the computed NMR spectra of (v−vii) as neutral, di- and hexaanions of $C_{78}(D_3, 1)$, (viii−x) as neutral, di-and hexaanions of C_{78}-(C_{2v}, 2).

has 11 lines (10 of them represent eight carbons and one represents four carbons).[2c−f] The center of gravity of the combined spectra, at 148.2 ppm, is deshielded by 8.2 ppm from that of the original, neutral C_{84} isomer mixture.[2d−f]

Reduction of C_{78}. A mixture of two isomers of C_{78} with C_{2v} and D_3 symmetries[2b] was reduced. According to these symmetries, the ^{13}C NMR spectrum of the mixture is expected to contain 34 lines (21 lines for the C_{2v} isomer and 13 lines for the D_3 isomer).[2b−d] ^{13}C NMR measurements at different temperatures distinguish between the two isomers. The room-temperature spectrum contains only 13 major absorptions (Figure 3i), which we assign to the D_3 isomer. Lowering the temperature results in the appearance of another set of broad lines (Figure 3ii-iii). The relative intensity of the second set increases when the temperature is further decreased, and at 170 K (Figure 3iii), it is possible to detect 21 lines in addition to the 13 lines of the D_3 isomer. These new lines are assigned to the C_{2v} isomer. This behavior may be due to the smaller HOMO−LUMO gap in the multiply charged anion of the C_{2v} isomer. The B3LYP/6-31G* calculations show 1.05 and 2.02 eV gaps for the hexaanion and neutral species, respectively (see below). Hence, the C_{2v} isomer may have some triplet character, which broadens the NMR bands, especially at higher temperatures. Early observations of Olah and co-workers,[10a] who reduced a mixture of C_{60} and $C_{70,}$ were quite similar. Unlike the $C_{60}{}^{6-}$ spectrum, the $C_{70}{}^{6-}$ signals were detectable only at low temperatures.

When the ^{13}C NMR spectra of C_{78} were examined as a function of the reduction time, the 13 lines assigned to the D_3 isomer appeared first. This agrees with expectations: the C_{2v} isomer was computed[19] to be more stable than the D_3 isomer and its HOMO−LUMO gap was larger.[20]

The ^{13}C NMR centers of gravity of both reduced isomers are shifted to lower fields compared to the neutral C_{78} precursors, by 8.5 and 5.5 ppm for the D_3 and C_{2v} multiply charged anions, respectively.

Density Functional Study. The diamagnetic reduction products of C_{60} and C_{70}, as characterized by their NMR spectra, are hexaanions. A central concern of the present study is to determine the reduction state reached by the multiply charged anions of the higher fullerenes. Density functional computations provide essential information. The energies and the multiplicity of the unoccupied molecular orbitals (UMOs) indicate the ability of the system to accept electrons upon reduction. Comparisons between the experimental data and the computed ^{13}C NMR chemical shifts of possible diamagnetic di-, tetra-, and hexaanions can help establish the reduction state.

Figure 4 summarizes the B3LYP/6-31G* frontier molecular orbitals (HOMO, LUMO, and lowest UMOs) of the higher fullerenes studied here. The di-, tetra-, and hexaanions of C_{76}, C_{78} (C_{2v}), and C_{84} (D_2) can have closed shell configurations. In addition, the di- and hexaanions of C_{78} (D_3) and the tetra- and hexaanions of C_{84} (D_{2d}) also have closed shells because of the degenerate LUMO + 1 or LUMO orbitals. As such, closed-shell anions may be possible for the reduced higher fullerenes; B3LYP/6-31G* computations were performed on these structures. The energy gaps between the HOMO and the first three unoccupied MOs (LUMO, LUMO + 1, and LUMO + 2) are summarized in Table 1.

Species with very small HOMO−LUMO gaps are unstable toward electron additions and are not likely to exist, especially under the present experimental conditions using lithium as the reducing agent. This consideration precludes $C_{76}{}^{2-}$, $C_{76}{}^{4-}$, $C_{78}{}^{4-}$ (C_{2v}), and $C_{84}{}^{2-}$(D_2) as possibilities for the experimentally observed anions. NMR computations were performed for the remaining candidates to assist the spectral assignments. The com-

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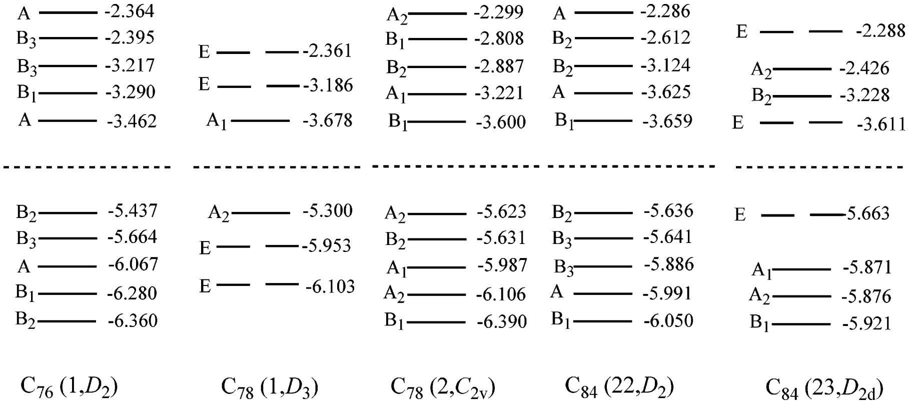

FIGURE 4. B3LYP/6-31G* frontier molecular orbitals (MO) of higher fullerenes.

TABLE 1. Orbital Energies and Gaps for the HOMO and Three UMOs (eV)

	HOMO	LUMO	LUMO + 1	LUMO + 2	gap	gap + 1	gap + 2
C_{76} (1,D_2)	−5.44	−3.46	−3.29	−3.22	1.98	2.15	2.22
C_{76}^{2-} (1,D_2)	1.73	2.26	2.62	3.14	0.53	0.89	1.41
C_{76}^{4-} (1,D_2)	7.55	7.88	8.99	9.01	0.33	1.44	1.46
C_{76}^{6-} (1,D_2)	13.09	14.66	14.71	14.78	1.57	1.62	1.69
C_{78} (1,D_3)	−5.30	−3.68	−3.19	−3.19	1.62	2.11	2.11
C_{78}^{2-} (1,D_3)	1.31	2.47	2.47	3.27	1.16	1.16	1.96
C_{78}^{6-} (1,D_3)	13.08	14.41	14.41	14.69	1.33	1.33	1.61
C_{78} (2,C_{2v})	−5.62	−3.60	−3.22	−2.89	2.02	2.40	2.73
C_{78}^{2-} (2,C_{2v})	1.39	2.51	2.72	2.74	1.12	1.33	1.35
C_{78}^{4-} (2,C_{2v})	7.61	8.07	8.61	8.84	0.46	1.00	1.23
C_{78}^{6-} (2,C_{2v})	13.15	14.20	14.58	14.72	1.05	1.43	1.57
C_{84} (22,D_2)	−5.64	−3.66	−3.63	−3.12	1.98	2.01	2.52
C_{84}^{2-} (22,D_2)	1.21	1.83	2.24	2.91	0.62	1.03	1.70
C_{84}^{4-} (22,D_2)	6.66	7.78	8.35	8.81	1.12	1.69	2.15
C_{84}^{6-} (22,D_2)	12.52	13.91	14.22	14.27	1.39	1.70	1.75
C_{84} (23,D_{2d})	−5.66	−3.61	−3.61	−3.23	2.05	2.05	2.43
C_{84}^{4-} (23,D_{2d})	6.60	7.76	8.37	8.85	1.16	1.77	2.25
C_{84}^{6-} (23,D_{2d})	12.52	13.97	14.23	14.23	1.45	1.71	1.71

TABLE 2. Computed and Measured (in Parentheses) ^{13}C NMR Centers of Gravity of Fullerenes and Their Anions (ppm)

	neutral	dianion	tetraanion	hexaanion
C_{60}	138.7[a] (143.2)[b]			158.7 (156.7)[f]
C_{70}	145.6[a] (145.0)[b]			142.2 (145.9)[f]
C_{76} (1,D_2)	142.9[a] (142.7)[c]			146.5 (149.5)
C_{78} (1,D_3)	139.6[a] (141.1)[d]	143.0		146.5 (149.6)
C_{78} (2,C_{2v})	142.2[a] (141.9)[d]	145.3		146.2 (147.4)
C_{84} (22,D_2)	140.3[a] (140.43)[e]		145.9	144.6[g]
C_{84} (23,D_{2d})	139.9[a] (139.98)[e]		147.2	144.9[g]

[a] Reference 25. [b] Reference 13. [c] Reference 2a. [d] Reference 2b. [e] Reference 2e. [f] Reference 10a. [g] The center of gravity in the spectrum for the isomeric mixture is 148.2 ppm.

puted ^{13}C NMR spectra are compared with the experimental results in Figures 1−3. The computed ^{13}C NMR spectra for the neutral analogues also are shown. Moreover, the center of gravity of both computed and experimental ^{13}C NMR spectra are summarized in Table 2.

The very good general agreement between the computed hexanions and the experimental ^{13}C NMR spectra strongly support the conclusion that the higher fullerenes form hexaanions upon reduction. The correlation coefficients (R^2) between the computed and measured C_{76}^{6-} and C_{78}^{6-} (D_3) spectra are 0.996 and 0.974, respectively.

While the C_{78}^{6-} (C_{2v}), C_{84}^{6-} (D_2), and C_{84}^{6-} (D_{2d}) correlations cannot be determined because of the incomplete assignments of their individual spectra, the overall correlation between the experimental and computed ^{13}C NMR shifts for both C_{84} hexaanion isomers (D_2 and D_{2d}) together is 0.984. Moreover, details of the computed and experimental spectra support the assignment of C_{78} (C_{2v}) and C_{84} (D_2) hexaanions (Figure 3b). The C_{78} (C_{2v}) hexaanion spans a much larger NMR range than the dianions. Furthermore, the low-field experimental ^{13}C NMR peaks (171.6, 176.3 ppm) are only found in the computed hexaanion ^{13}C NMR spectrum. For C_{84} (D_{2d}), the half-height intensity peak in the computed spectra appears at low field (161.7 ppm) for the tetraanion and at high field (135.8 ppm) for the hexanion (Figure 2b). Comparing the high field half-height intensity peak (140.6 pm) in the experiment, we can safely claim that C_{84}^{6-}(D_{2d}), rather than C_{84}^{4-}(D_{2d}), was formed experimentally.

Separate calculations of the C_{84}^{6-} isomers, D_2 (Figure 2iii−v) and D_{2d} (Figure 2vi−viii), showed nearly the same centers of gravity (144.6 and 144.9 ppm, respectively); therefore, we assume that these two isomers have similar magnetic properties.

The good correlation between the calculated and experimental ^{13}C NMR shifts of the C_{78}^{6-} isomers (Figure 3b) supports the signal assignment based on the temperature-dependent experiments.

Conclusions

Higher fullerenes C_{76}, C_{78}, and C_{84} are reduced to diamagnetic multiply charged anions without changing their symmetries. Even though many electrons are added, the overall ^{13}C NMR chemical shifts (i.e., the centers of gravity) of all of the multiply charged anions are deshielded, compared to the neutral fullerenes. Comparisons of the experimental with the DFT-computed ^{13}C NMR spectra, as well as MO energy considerations, agree that hexaanions were produced. Therefore, like C_{60} and C_{70}, the higher fullerenes can also accept six electrons in their π-systems and form stable diamagnetic hexaanions.

Changing the temperature of the mixture of C_{78} multiply charged anions enabled the experimental identification of the two D_3 and C_{2v} isomers. However, the two anionic D_2 and D_{2d} isomers of C_{84} could not be distinguished

Experimental Section

Purification of the Higher Fullerenes. A fullerene soot extract (1,2-dichlorobenzene) enriched in C_n ($n > 70$) was filtered through a plug of SiO_2 prior to HPLC (high-performance liquid chromatography) purification. Preparative HPLC: Buckyclutcher I (Regis) stationary phase,[21] 10 μm; 500 mm × 21.1 mm i.d. column; hexane/toluene 6:4 eluent, 6 mL min^{-1} flow rate; detection at $\lambda = 310$ nm. Fractions (approximate retention times): C_{60} (60 min), C_{70} (70 min), C_{76} (80 min), C_{78} [isomeric mixture containing C_{78}-C_{2v} and C_{78}-D_3] (85 min), C_{84} [isomeric mixture containing C_{84}-D_2 and C_{84}-D_{2d}] (95 min). Due to considerable overlap, the C_{76} and C_{78} fractions needed to be reprocessed several times with tail and head fractions being discarded, respectively, in each run. The final purity was determined by analytical HPLC to be ≥97% for C_{76}, C_{78}, and C_{84}: Buckyclutcher I (Regis) stationary phase, 5 μm; 250 mm × 4.6 mm i.d. column; hexane/toluene 6:4 eluent, 1 mL min$-^{1}$ eluent; detection at $\lambda = 310$ nm. Retention times: C_{60} (5.85 min), C_{70} (8.49 min), C_{76} (12.25 min), C_{78} [isomeric mixture containing C_{78}-C_{2v} and C_{78}-D_3] (12.96 min), C_{84} [isomeric mixture containing C_{84}-D_2 and C_{84}-D_{2d}] (15.58 min).

General Method of Reduction. All fullerenes were reduced in a 5 mm NMR tube equipped with an upper reduction chamber. Under inert argon atmosphere, 2–5 mg of the fullerene and a catalytic amount of corannulene were introduced into the lower chamber of the tube. Lithium wire was added under argon to the reduction chamber, and the tube was attached to a vacuum line. THF-d_8 (dried over sodium–potassium alloy, under high vacuum) was transferred to the tube under vacuum and degassed several times, and the extended tube was flame sealed under high vacuum. Reduction occurred on contact of the solution with the lithium metal in dry ice bath (−70 °C) by repeated inversions of the tube. The formation of the anions was detected by the change of the corannulene color to green, due to the formation of the corannulene monoanion, and was monitored by ^{13}C NMR spectroscopy.

NMR Data. $C_{76}{}^{6-}$. ^{13}C NMR (100.613 MHz, THF-d_8, 220 K): 131.6, 135.2, 138.4, 138.9, 139.5, 143.7, 144.6, 145.2, 150.1, 151.7, 152.6, 153.8, 154.9, 155.9, 156.3, 156.7, 156.8, 166.1, 168.3 ppm.

$C_{84}{}^{6-}$-D_2 + D_{2d}. ^{13}C NMR (100.613 MHz, THF-d_8, 220 K): 138.1, 138.6, 140.6 (half-height), 141.1, 141.3, 142.0, 143.4, 144.3, 144.9, 145.3, 145.7, 145.9, 146.1, 146.6, 147.0, 147.2, 147.6, 147.8, 148.3, 149.0, 149.3, 149.8, 151.2, 152.1, 152.2, 152.7, 153.2, 153.8, 155.6, 158.5, 159.5, 160.4 ppm.

$C_{78}{}^{6-}$-D_3. ^{13}C NMR (100.613 MHz, THF-d_8, 298 K): 135.1, 137.8, 138.4, 141.7, 143.1, 144.0, 145.6, 153.6, 155.3, 155.6, 156.1, 165.5, 173.3 ppm.

$C_{78}{}^{6-}$-C_{2v}. ^{13}C NMR (100.613 MHz, THF-d_8,170 K): 128.3, 129.9, 132.2, 132.3, 133.1, 138.8, 140.7, 142.5, 143.6, 144.4, 145.2, 145.6, 147.5, 151.4, 153.3, 153.9, 157.8, 162.0, 166.0, 171.6, 176.3 ppm.[22]

Calculations. Full geometry optimization and NMR chemical shielding calculations were performed for each fullerene isomer in the given symmetry at the B3LYP[23]/6-31G* density functional level of theory. NMR chemical shielding values were evaluated employing the gauge-independent atomic orbital (GIAO) method.[24] For di- and tetraanions, ^{13}C chemical shifts were calculated relative to C_{60} and converted to TMS scale. The ^{13}C chemical shifts or the hexaanions were referenced to $C_{60}{}^{6-}$ and then converted to TMS scale using the experimental value for $C_{60}{}^{6-}$ ($\delta = 156.7$ ppm).[10a] The computed ^{13}C NMR spectra of the neutral fullerenes were taken from Kertesz.[25] Former studies[25,26] have shown that highly accurate computations of fullerene ^{13}C NMR chemical shifts can be expected at density functional levels. All calculations were carried out with the Gaussian 98 program.[27]

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Supporting Information Available: B3LYP/6-31G*-optimized structures and total energies of $C_{76}{}^{n-}$-D_2 ($n = 0, 2, 4, 6$), $C_{78}{}^{n-}$-D_3 ($n = 0, 2, 6$), $C_{78}{}^{n-}$-C_{2v} ($n = 0, 4, 6$), $C_{84}{}^{n-}$-D_2 ($n = 0, 2, 4, 6$), and $C_{84}{}^{n-}$-D_{2d} ($n = 0, 4, 6$). This material is available free of charge via the Internet at http://pubs.acs.org.

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