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

Tamar Sternfeld,† Carlo Thilgen,‡ Zhongfang Chen,§ Ilii Siefke Siefken,* Paul von Ragüé Schleyer,†† Walter Thiel,‡ François Diederich,† and Mordeai Rabinovitz*†

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich, Switzerland, Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany, Computational Chemistry Annex, The University of Georgia, Athens, Georgia 30602-2525, and Max-Planck-Institut für Kohlenforschung, 45466 Mülheim an der Ruhr, Germany

mordeai@ums.huji.ac.il

Received March 28, 2003

A combined experimental and theoretical study was conducted on numerous higher fullerene anions with different sizes and shapes, $C_{76}$-$D_{2}$, $C_{78}$-$C_{2}$, $C_{78}$-$D_{3}$, $C_{84}$-$D_{2}$, and $C_{84}$-$D_{23}$. 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 Theoretical3 and experimental4 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 $\pi$-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 orbitals6,8 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 hexa-anion. The magnetic properties of $C_{60}^-$ and $C_{70}^-$ vs. their corresponding neutral fullerenes alternate positions.10–12


The dia-tropicity of C₆₀ is dramatically enhanced as a result of the addition of six electrons. On the other hand, C₇₀⁵⁻ shows a reduced diaotropicity compared with the neutral fullerene. Since the hexaanions of C₆₀⁵⁻ and C₇₀⁵⁻ show the same ¹³C NMR spectral patterns as the corresponding neutral fullerenes,¹³ the reductions do not result in connectivity changes.¹⁰b However, due to anisotropy effects in both systems,¹⁴ the centers of gravity of the ¹³C NMR spectra are shifted to lower field compared to their neutral analogues. C₆₀⁵⁻ is deshielded by 14 ppm compared to neutral C₆₀ (156¹⁰a and 142¹⁰ ppm, respectively). In C₇₀⁵⁻, some of the ¹³C NMR signals are deshielded and some shielded,¹⁰b,¹⁵ but overall, the center of gravity of the ¹³C NMR spectrum of C₇₀⁵⁻ 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, C₇₆ (D₂), C₇₈ (D₃h), C₇₈ (C₂ᵥ), ², C₇₈ (D₂ᵥ), ¹³ and C₇₈ (D₂ᵥ), ²³ to their respective diamagnetic multiply charged anions and record the ¹³C 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

¹³C NMR Spectra Measurements. The C₇₆, C₈₄, and C₇₈ fullerenes were reduced with lithium metal in the presence of a small amount of corannulene serving as an electron shuttle.¹⁰b–⁹ Their ¹³C 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.

Reduction of C₇₆. The ¹³C NMR spectrum of the reduced C₇₆ contains 19 lines of equal intensities, as expected from its D₂ symmetry¹¹a,²a (Figure 1). The center of gravity of its spectrum, 149.5 ppm (Figure 1a), is deshielded by 6.8 ppm from the neutral C₇₆.

Reduction of C₈₄. Reduction of an isomeric C₈₄ mixture containing the main isomers of D₂ and D₂ᵥ symmetries in a nearly 2:1 ratio led to a ¹³C NMR spectrum with 31 lines of equal intensity and one line of half intensity (140.6 ppm), as expected²¹–² (Figure 2a). The D₂ isomer has 21 different carbons, and the D₂ᵥ isomer of gravity of its spectrum, 149.5 ppm (Figure 1a), is deshielded by 6.8 ppm from the neutral C₇₆.
and 13 lines for the D only 13 major absorptions (Figure 3i), which we assign two isomers. The room-temperature spectrum contains statements at different temperatures distinguish between the smaller HOMO.

K (Figure 3iii), it is possible to detect 21 lines in addition with the appearance of another set of broad lines (Figure 3ii–d). With these symmetries, the 13C NMR spectrum of the mixture 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 C84 isomer mixture.e–f

Reduction of C78. A mixture of two isomers of C78 with C2 and D3 symmetries2d was reduced. According to these symmetries, the 13C NMR spectrum of the mixture is expected to contain 34 lines (21 lines for the C2v isomer and 13 lines for the D3 isomer).2b–d 13C 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 D3 isomer. Lowering the temperature results in the appearance of another set of broad lines (Figure 3iii). 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 D3 isomer. These new lines are assigned to the C2v isomer. This behavior may be due to the smaller HOMO–LUMO gap in the multiply charged anion of the C2v 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 C2v isomer may have some triplet character, which broadens the NMR bands, especially at higher temperatures. Early observations of Olah and co-workers,10d who reduced a mixture of C60 and C70 were quite similar. Unlike the C60+ spectrum, the C70+ signals were detectable only at low temperatures.

When the 13C NMR spectra of C78 were examined as a function of the reduction time, the 13 lines assigned to the D3 isomer appeared first. This agrees with expectations: the C2v isomer was computed19 to be more stable than the D3 isomer and its HOMO–LUMO gap was larger.20

The 13C NMR centers of gravity of both reduced isomers are shifted to lower fields compared to the neutral C78 precursors, by 8.5 and 5.5 ppm for the D3 and C2v, multiply charged anions, respectively.

Density Functional Study. The diamagnetic reduction products of C60 and C70, 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 13C 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 C76, C78 (C2v), and C84 (D2v) can have closed shell configurations. In addition, the di- and hexaanions of C78 (D3) and the tetra- and hexaanions of C84 (D2d) also have closed shell 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 C2v2−, C762−, C782− (C2v), and C842− (D2v) as possibilities for the experimentally observed anions. NMR computations were performed for the remaining candidates to assist the spectral assignments. The com-

---


The correlation between the experimental and computed 13C NMR spectra cannot be determined because of the incompleteness of 13C NMR spectra are summarized in Table 2. Moreover, the center of gravity of both computed and experimental 13C NMR peaks (171.6, 176.3 ppm) are only found in the experimental spectra support the assignment of C78 (1, 139.98) to C78 (1, 145.9); C78 (2, 145.9) to C78 (2, 145.9); and C78 (3, 145.9) to C78 (3, 145.9). The C78 (2, 145.9) hexaanion spans a much larger NMR range than the computed hexaanion 13C NMR spectrum. For C84 (2, 145.9), the half-height intensity peak in the computed spectra appears at low field (161.7 ppm) for the tetraanion and high field (171.6 ppm) for the hexaanion. 

The good correlation between the calculated and experimental 13C NMR shifts for both C84 hexaanion isomers (D2 and D2o) together is 0.984. Moreover, details of the computed and experimental spectra support the assignment of C78 (C2v) and C84 (D2) hexaanions (Figure 3b). The C78 (C2v) hexaanion spans a much larger NMR range than the dianions. Furthermore, the low-field experimental 13C NMR peaks (171.6, 176.3 ppm) are only found in the computed hexaanion 13C NMR spectrum. For C84 (D2o), 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 hexaanion (Figure 2b). Comparing the high field half-height intensity peak (140.6 pm) in the experiment, we can safely claim that C84 (D2o), rather than C84 (D2o), was formed experimentally.

Separate calculations of the C84 (D2o) isomers, D2 (Figure 2ii–v) and D2o (Figure 2iv–vii), 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 13C NMR shifts of the C78 (2v) isomers (Figure 3b) supports the signal assignment based on the temperature-dependent experiments.

**Conclusions**

Higher fullerences C76, C78, and C84 are reduced to diamagnetic multiply charged anions without changing magnetic properties.

---

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

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
<th>LUMO + 1</th>
<th>LUMO + 2</th>
<th>gap</th>
<th>gap + 1</th>
<th>gap + 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C76</td>
<td>-11.7</td>
<td>-5.0</td>
<td>-5.0</td>
<td>-5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>C78</td>
<td>-11.7</td>
<td>-5.0</td>
<td>-5.0</td>
<td>-5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>C80</td>
<td>-11.7</td>
<td>-5.0</td>
<td>-5.0</td>
<td>-5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

---

**TABLE 2. Computed and Measured (in Parentheses) 13C NMR Centers of Gravity for Fullerences and Their Anions (ppm)**

<table>
<thead>
<tr>
<th></th>
<th>neutral</th>
<th>dianion</th>
<th>tetraanion</th>
<th>hexaanion</th>
</tr>
</thead>
<tbody>
<tr>
<td>C76</td>
<td>138.3</td>
<td>(143.2)</td>
<td>145.6</td>
<td>(156.7)</td>
</tr>
<tr>
<td>C78</td>
<td>145.6</td>
<td>(145.0)</td>
<td>145.6</td>
<td>(148.5)</td>
</tr>
<tr>
<td>C80</td>
<td>145.6</td>
<td>(148.5)</td>
<td>145.6</td>
<td>(151.0)</td>
</tr>
</tbody>
</table>

---

**Figure 4.** B3LYP/6-31G* frontier molecular orbitals (MO) of higher fullerenes.
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 hexaannions were produced. Therefore, like C$_{60}$ and C$_{70}$, the higher fullerenes can also accept six electrons in their $\pi$-systems and form stable diamagnetic hexaannions.

Changing the temperature of the mixture of C$_{78}$ multiply charged anions enabled the experimental identification of the two D$_3$ and D$_{2d}$ isomers. However, the two anionic D$_3$ and D$_{2d}$ isomers of C$_{60}$ 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: Buckyclustcher I (Regis) stationary phase, 210 $\mu$m, 500 mm x 21.1 mm i.d. column; hexanetoluene 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$_{84}$ [isomeric mixture containing C$_{76}$-C$_2$ and C$_{78}$-D$_3$] (85 min), C$_{86}$ [isomeric mixture containing C$_{84}$-D$_3$ and C$_{86}$-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 $\approx 97\%$ for C$_{76}$, C$_{78}$, and C$_{84}$. Buckyclustcher I (Regis) stationary phase, 5 $\mu$m; 250 mm x 4.6 mm i.d. column; hexanetoluene 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$_{84}$ [isomeric mixture containing C$_{76}$-C$_2$ and C$_{78}$-D$_3$] (19.96 min), C$_{86}$ [isomeric mixture containing C$_{84}$-D$_3$ and C$_{86}$-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 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$_{n}$-$^{13}$C NMR (100.613 MHz, THF-d$_8$, 220 K): 131.6, 135.2, 134.6, 139.9, 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$_{60}$-$^{13}$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, 156.5, 157.9, 160.4 ppm.

C$_{76}$-$^{13}$C NMR (100.613 MHz, THF-d$_8$, 298 K): 135.1, 137.8, 138.4, 141.7, 143.1, 144.0, 144.6, 153.6, 155.3, 155.6, 161.5, 161.6, 173.3 ppm.

C$_{84}$-$^{13}$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.

**Calculations.** Full geometry optimization and NMR chemical shielding calculations were performed for each fullerene isomer in the given symmetry at the B3LYP/$6$-31G* density functional level of theory. NMR chemical shielding values were evaluated employing the gauge-independent atomic orbital (GIAO) method. 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 hexaannions were referenced to C$_{60}$ and then converted to TMS scale using the experimental value for C$_{60}$ ($\delta = 156.7$ ppm). The computed $^{13}$C NMR spectra of the neutral fullerenes were taken from Kertesz. Further studies 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.

**Supporting Information Available:** B3LYP/6-31G*-optimized structures and total energies of C$_{76}$-D$_2$ (n = 0, 2, 4, 6), C$_{78}$-D$_2$ (n = 0, 2, 6), C$_{80}$-D$_2$ (n = 0, 2, 4, 6), and C$_{86}$-D$_2$ (n = 0, 4, 6). This material is available free of charge via the Internet at http://pubs.acs.org.

J O0030106N

(22) The integration of the peaks is difficult because of the broad spectrum.


