Reduction of Fulleroids C$_{70}$H$_2$: Probing the Magnetic Properties of C$_{70}^{-}$

Tamar Sternfeld,$^1$ Roy E. Hoffman,$^1$ Carlo Thilgen,$^2$ François Diederich,$^3$ and Mordecai Rabinovitz$^{*,1}$

Department of Organic Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904, Israel

Received April 24, 2000
Revised Manuscript Received June 28, 2000

Great interest in fullerene research has developed since their discovery in 1985.$^1$ The aromatic character of fullerenes, as defined by their magnetic and electronic properties, is very unique. These traits result from the closed spherical shape of fullerenes, as well as from the presence of two different types of rings, namely, five-membered rings (5-MRs) and six-membered rings (6-MRs). The magnetic susceptibility of fullerenes is lower than that of C$_{60}$, but in the charged systems, that is, C$_{70}^{-}$, leading to a low magnetic susceptibility. However, in C$_{70}^{-}$ the 5-MRs become diamagnetic, leading to a high diamagnetic ring current that prevails over the entire system.$^2$

In the case of C$_{60}$, the magnetic susceptibility of the hexaion is much greater than that of the neutral molecule.$^3$ The two opposing magnetic contributions cancel each other out in C$_{60}$, leading to a low magnetic susceptibility. However, in C$_{70}^{-}$ the 5-MRs become diamagnetic, leading to a high diamagnetic ring current that prevails over the entire system.$^2$

To observe the changes in the $^1$H NMR chemical shifts of the bridged protons in the anion compared with those of the neutral molecule, two different fulleroid isomers were synthesized by the addition of CH$_3$N$_2$ to C$_{70}$. HPLC of the mixture of the two isomers showed a ratio of 6:1. This mixture was reduced to give the bridged anions.

The $^1$H NMR spectrum of the mixture of isomers consists of two sets of doublets: at 2.95 and at 6.52 ppm for Ha and Hb of 1, respectively, and at 2.78 and at 5.23 ppm for Ha and Hb of 2, respectively.$^11$ The reduction process was carried out in a 5 mm NMR tube equipped with a top reduction chamber containing excess lithium metal with THF-d$_4$ as a solvent and in the presence

$^*$ Corresponding author. Telephone: 972-2-6585281. Fax: 972-2-6527547. E-mail: mordecai@vms.huji.ac.il.

† The Hebrew University of Jerusalem.

‡ E.Zentrum.


(12) There is a total of four theoretically possible anulenr isomers for C$_{70}$H, one involving the polar 5-MR and three involving the other 5-MR which has three different edges. The one that was not described by Smith$^{11}$ was indeed reported last year in the form of C$_{71}$Cl$_2$, see: Kiely, A. F.; Haddon, R. C.; Meier, M. S.; Selegue, J. P.; Pratt Brock, C.; Patrick, B. O.; Wang, G. –W.; Chen, Y. J. Am. Chem. Soc. 1999, 121, 7971–7972.


(14) In addition, there is negligible change in the $^1$H NMR chemical shift between He@C$_{60}$ and the fulleroids of He@C$_{70}$, which confirms that both have the same bulk magnetic properties; Smith, A. B.; III; Strongin, R. M.; Brard, L.; Romanow, W. J.; Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J. J. Am. Chem. Soc. 1994, 116, 10831–10832.

1 2
of corannulene, acting as an “electron shuttle” which transfers electrons from the metal to the fullerenes. The solution was brought into contact with the lithium metal by repeated inversion of the tube.

The $^1$H NMR spectrum of the anions contains three doublets at $-0.255$ ppm ($J = 9.6$ Hz, strong absorption), $2.27$ ppm ($J = 9.6$ Hz, strong absorption) and $2.34$ ppm ($J = 9.1$ Hz, weak absorption). COSY experiments show a correlation between the first and the second doublet and another correlation between the third doublet and a fourth doublet at $3.6$ ppm, which appears under the solvent signal (Table 1). Unfortunately, temperature variations do not cause a significant change in its chemical shift, ruling out the use of simple 1D techniques. We succeeded in observing this doublet by performing double quantum filter (DQF) and inversion recovery experiments simultaneously, which suppressed the solvent peak and enabled the identification of the “missing” doublet (Figure 1).

The $^{13}$C NMR spectrum consists of one band at $44.87$ ppm, which was assigned to the methylene carbon of $1^e$ (by $C$–$H$ correlation), and broad bands in the region of $120–160$ ppm, assigned as the fullerene skeletons carbon atoms. The methylene carbon of $2^e$ was observed at $39.9$ ppm, by HSQC. The $J_{C,H}$ coupling constants (Table 2) are typical for an “open bond”, which indicates a strong homoaromaticity for the hexaannion.

**Table 1. $^1$H NMR Chemical Shifts (THF-d$_6$) of the Fulleroids and Their Anions.**

| C$_{60}$H$_2$ | 2.84, 6.35 ($J = 9.7$) | 2.74, 1.34 ($J = 8.9$) |
| C$_{60}$H$_2$ (1) | 2.95, 6.52 ($J = 9.8$) | 2.27, -0.255 ($J = 9.6$) |
| C$_{60}$H$_2$ (2) | 2.78, 5.23 ($J = 10$) | 2.34, 3.6 ($J = 9.1$) |

*a* Taken from ref 10. *b* Taken from ref 9. *c* Taken from ref 11.

---

**Figure 1.** $^1$H NMR spectrum of $1^e$ and $2^e$ (top), and the same spectrum after inversion recovery and DQF experiments (bottom). (a) refers to $1^e$; (b) refers to $2^e$; (c) the solvent bands, THF-d$_6$.

---

**Table 2. $^{13}$C NMR Chemical Shifts (THF-d$_6$) and Coupling Constants of the Methylenic Bridge in the Neutral and Charged Fulleroids.**

<table>
<thead>
<tr>
<th>1$^e$</th>
<th>1$^e$ $^*$</th>
<th>2$^e$</th>
<th>2$^e$ $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ ($^1$CH$_2$)</td>
<td>34.0</td>
<td>44.87</td>
<td>39.9</td>
</tr>
<tr>
<td>$^{1}$J$_{C,H}$</td>
<td>150.2</td>
<td>129</td>
<td>149.8</td>
</tr>
<tr>
<td>145.7</td>
<td>132</td>
<td>146.4</td>
<td></td>
</tr>
</tbody>
</table>

*a* Taken from ref 11. *b* Top row: high-field absorption; bottom row: low-field absorption.

---

similar to that of the neutral molecule. This strengthens the assumption that these methylene bridges cause only a small perturbation of the $\pi$-conjugation of the hexaannion. The carbon and the lithium NMR chemical shifts are in the same range as those of C$_{70}$Li. Thus supporting this assumption. These shifts also indicate that C$_{71}$H$_2$ and C$_{70}$ are both reduced to a hexaannion.

Consequently, the results of the reduction of C$_{71}$H$_2$ provide insight into the aromatic character of C$_{70}$, which supports the assumption that these methylene bridges cause only a small perturbation of the $\pi$-conjugation of the hexaannion. The carbon and the lithium NMR chemical shifts are in the same range as those of C$_{70}$Li, thus supporting this assumption. These shifts also indicate that C$_{71}$H$_2$ and C$_{70}$ are both reduced to a hexaannion.

The $^1$H NMR chemical shifts exhibit three facets: (i) Both isomers show a center of gravity of the $^1$H NMR spectrum that appear at higher field than that of the neutral molecule, and the chemical shift differences ($\Delta\delta$), between the two doublets is lessened. This leads to the conclusion that the extra electrons in C$_{60}^e$, as in C$_{60}^e$, are mainly located in the 5-MRs, rendering them diatropic (Table 1). (ii) A full assignment of the $^1$H NMR chemical shifts can be obtained, as proton Ha of both isomers is located above a 6-MR of the same type. It follows that the absorptions of Ha in 1 and 2 appear at 2.27 and 2.34 ppm, respectively, and the absorptions of Hb appear at $-0.255$ and 3.6 ppm for 1 and 2, respectively. This assignment strengthens the conclusion that the extra electrons are located mainly in the 5-MRs, but that the distribution is not equal between the different types of 5-MRs. (iii) In isomer 1, where the bridge is at the C$_{60}$’s poles, the change in the $^1$H NMR chemical shifts is much more significant, and the shifts appear at a higher field, than in 2. Therefore, it can be deduced that unlike C$_{60}^e$, the charge distribution is mostly concentrated on the C$_{70}^e$’s poles, and is not equally shared by all of the 5-MRs of the fullerene. The diamagnetism of the polar 5-MRs is much stronger than that of the nonpolar 5-MRs and also than that of 6-MRs. Apparently, the significant difference in the properties of C$_{60}^e$ and their hexaannions stems from their different geometry and symmetry. While C$_{60}$ is an icosahedral molecule, C$_{70}$ has a lower symmetry ($D_{5d}$) and is close to an ellipsoid. Therefore, in C$_{60}^e$ the charge is distributed symmetrically over all 5-MRs, and the global ring current magnetic susceptibility of the fullerene is very high. In contrast, the charge distribution in C$_{70}^e$ is unsymmetrical; and, the extra charge is concentrated at the 5-MR located at the poles. Together with the study of fullerene anions with endohedral helium and the bridged anion of C$_{60}$, this study clarifies the puzzling behavior of charged fullerenes. The lower magnetic susceptibility of C$_{70}^e$ as opposed to that of C$_{60}^e$ and the neutral C$_{70}$ can be rationalized in terms of nonhomogeneous charge distribution of the extra electrons on the C$_{70}$ skeleton.

Acknowledgment. We thank the Research and Development Authority of the Hebrew University of Jerusalem, and the US-Israel Binational Science Foundation (BSF). F. D. and C. T. are grateful to the Swiss National Science Foundation for financial support.

JA0014077

(15) The signal at 3.6 ppm was expected to have an intensity of 1% of the solvent signal. A gradient enhanced DQF experiment reduced the solvent signal. To observe the desired signal we also took advantage of the difference in relaxation times by preceding the DQF sequence by an inversion pulse. This suppressed the solvent signal by 3 orders of magnitude, leaving the desired signal of C$_{60}$H$_2$ clearly visible.