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Reduction of Fulleroids $C_{71}H_2$: Probing the Magnetic Properties of C_{70}^{6-}

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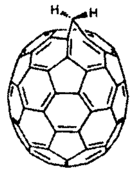
Great interest in fullerene research has developed since their discovery in 1986.[1] The aromatic character of fullerenes, as defined by their magnetic and electronic properties, is very unique. These traits result from the closed spherical shape of fullerenes, as well as from the presence of two different types of rings, namely, five-membered rings (5-MRs) and six-membered rings (6-MRs). The magnetic susceptibility of fullerenes is the outcome of two opposing contributions: a diamagnetic contribution from 6-MRs and a paramagnetic contribution arising from 5-MRs.[2] The addition of electrons to this new π-conjugated carbon allotrope led to question of the aromaticity of anionic fullerenes, especially the hexaanions, since reduction of fullerenes brings about considerable changes in the magnetic susceptibility.[3]

In the case of C_{60}, the magnetic susceptibility of the hexaanion is much greater than that of the neutral molecule.[4] The two opposing magnetic contributions cancel each other out in C_{60}, leading to a low magnetic susceptibility. However, in C_{60}^{6-} the 5-MRs become diamagnetic, leading to a high diamagnetic ring current that prevails over the entire system.[2]

The magnetic behavior of C_{70} shows an opposite trend to that of C_{60}. Neutral C_{70} shows a higher magnetic susceptibility than C_{60}, but in the charged systems, that is, C_{70}^{6-}, the magnetic susceptibility is lower than that of C_{60}^{6-}.[3] This trend is even more pronounced in ^{3}He NMR measurements[5] of the endohedral compounds[6] He@C_{70} and He@C_{70}^{6-}, thus demonstrating that the C_{70}^{6-} is less aromatic than C_{70}. Measuring the local aromaticity of the rings is the only way to rationalize the aromatic behavior of C_{70} and its hexaanion. The magnetic character of the anion is determined by the location of the extra electrons in C_{70}^{6-} and from their influence on the local ring currents. Therefore, understanding the local changes should provide insight into the nature of fullerenes. Until now, only quantum mechanical studies of the local ring current were performed.[7] These calculations indicate that the paramagnetic ring currents disappear in C_{70}^{6-}; however, there is a decrease in the diamagnetic ring currents as well, which results in an overall decrease of the C_{70}-fullerene diamagnetism.[7a,b]

In this study we aim to detect local ring currents in C_{70}^{6-} experimentally and compare them to those of neutral C_{70}. For this purpose we studied bridged C_{70}-fullerenes, where the protons of the bridges are located above the centers of rings. This positioning enables the protons to sense the magnetic character of each ring: an accepted method for the study of local ring currents in polycyclic π-arrays,[8] including C_{60}.[9,10]

C_{70} has two different types of 5-MRs and three different types of 6-MRs, allowing four possible annulene isomers (fulleroids) for $C_{71}H_2$; however, only two of them have been detected.[11,12] The fulleroids retain the basic fullerene electronic structure due to strong homoaromatic interaction, so that perturbation of the π-system is minimal.[13,14] Therefore, it is reasonable to deduce information of the precursor fullerene from the behavior of the fulleroid. In both these isomers one of the bridge protons is located above the 6-MR (**Ha**) and the other above the 5-MR (**Hb**). In the major isomer (**1**), the bridge is located at the molecular pole, unlike the minor isomer (**2**).[11] It can be said that the four protons in the two isomers can serve as external localized probes for aromaticity, allowing distinction between rings that differ by size (5-MR and 6-MR) as well as their location on the fullerene.



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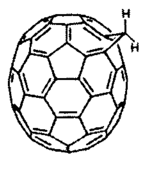

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To observe the changes in the ^{1}H NMR chemical shifts of the bridged protons in the anion compared with those of the neutral molecule, two different fulleroid isomers were synthesized by the addition of CH_2N_2 to C_{70}. HPLC of the mixture of the 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 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_8 as a solvent and in the presence

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(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163. (b) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213−1235. (c) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1−67. (d) Thilgen, C.; Diederich, F. *Top. Curr. Chem.* **1999**, *199*, 135−171.

(2) Haddon, R. C. *Science* **1993**, *261*, 1545−1550.

(3) Haddon, R. C.; Pasquarello, A. *Phys. Rev. B.* **1994**, *50*, 16 459−16 463.

(4) Elser, V.; Haddon, R. C. *Nature* **1987**, *325*, 792−794.

(5) Shabtai, E.; Weitz, A.; Haddon, R. C.; Hoffman, R. E.; Rabinovitz, M.; Khong, A.; Cross, R. J.; Saunders: M.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1998**, *120*, 6389−6393.

(6) Saunders: M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693−1697. (b) Saunders: M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256−258;

(7) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Phys. Rev. A.* **1993**, *47*, 1783−1789. (b) Bühl, M. *Chem. Eur. J.* **1998**, *4*, 734−739. (c) Krygowski, T. M.; Ciesièlski, A. *J. Chem. Inf. Comput. Sci.* **1995**, *35*, 1001−1003.

(8) Minkin, V. I.; Glukhovtsev, N. M.; Simkin, B. Ya. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley: New York, 1994.

(9) Sternfeld, T.; Wudl, F.; Hummelen, K.; Weitz, A. Haddon, R. C.; Rabinovitz, M. *Chem. Commun.* **1999**, 2411−2412.

(10) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301−7302.

(11) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492−5502. (b) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2187−2188.

(12) There is a total of four theoretically possible annulene isomers for $C_{71}H_2$; 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.

(13) Haddon, R. C. *Nature* **1995**, *378*, 249−255.

(14) In addition, there is negligible change in the ^{3}He NMR chemical shift between ^{3}He@C_{70} and the fulleroids of ^{3}He@$C_{71}H_2$, 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-Vazquez, H. A.; Cross, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 10831−10832.

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Table 1. ^{1}H NMR Chemical Shifts (THF-d_8) of the Fulleroids and Their Anions.

	neutral	hexaanion
$C_{61}H_2$	2.84, 6.35 ($J = 9.7$)[a]	2.74, 1.34 ($J = 8.9$ Hz)[b]
$C_{71}H_2$ (**1**)	2.95, 6.52 ($J = 9.8$ Hz)[c]	2.27, −0.255 ($J = 9.6$ Hz)
$C_{71}H_2$ (**2**)	2.78, 5.23 ($J = 10$ Hz)[c]	2.34, 3.6 ($J = 9.1$ Hz)

[a] Taken from ref 10. [b] Taken from ref 9. [c] Taken from ref 11.

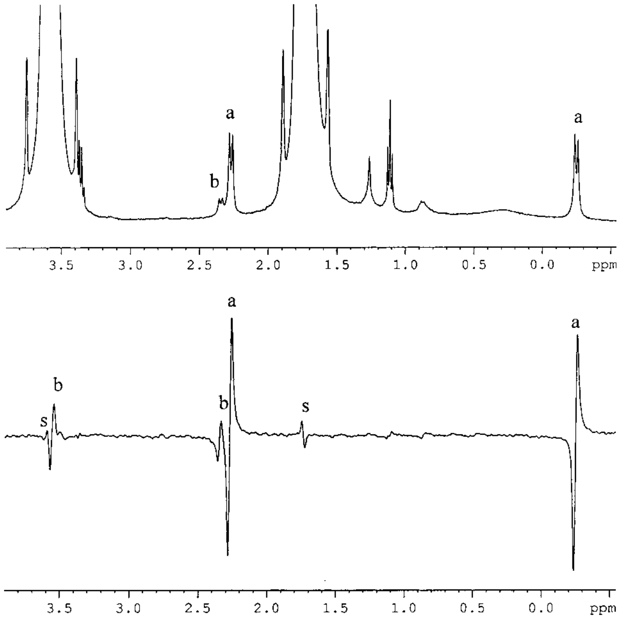

Figure 1. ^{1}H NMR spectrum of **1**$^{6-}$ and **2**$^{6-}$ (top), and the same spectrum after inversion recovery and DQF experiments (bottom). (a: refers to **1**$^{6-}$; b: refers to **2**$^{6-}$; s: the solvent bands, THF-d_8).

of corannulene, acting as an "electron shuttle" which transfers electrons from the metal to the fullerenes.[5] The solution was brought into contact with the lithium metal by repeated inversion 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,[15] which suppressed the solvent peak and enabled the identification of the "missing" doublet (Figure 1).

Table 2. ^{13}C NMR Chemical Shifts (THF-d_8) and Coupling Constants of the Methylene Bridge in the Neutral and Charged Fulleroids

	1[a]	**1**$^{6-}$	**2**[a]	**2**$^{6-}$
δ ($^{13}CH_2$)	34.0	44.87		39.9
$^1J_{C,H}$[b]	150.2	129	149.8	139
	145.7	132	146.4	

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

The ^{13}C NMR spectrum consists of one band at 44.87 ppm, which was assigned to the methylene carbon of **1**$^{6-}$ (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**$^{6-}$ was observed at 39.9 ppm, by HSQC. The $^1J_{C,H}$ coupling constants (Table 2) are typical for an "open bond",[16] which indicates a strong homoaromaticity for the hexaanion, similar to that of the neutral molecule. This strengthens the assumption that these methylene bridges cause only a small perturbation of the π-conjugation of the hexaanion. The carbon and the lithium NMR chemical shifts are in the same range as those of $C_{70}Li_6$,[17] thus supporting this assumption. These shifts also indicate that $C_{71}H_2$ and C_{70} are both reduced to a hexaanion.[18]

Consequently, the results of the reduction of $C_{71}H_2^{6-}$ provide insight into the aromatic character of C_{70}^{6-}. 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 a 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_{70}^{6-}, as in C_{60}^{6-}, 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 on 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_{70}'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}^{6-}, the charge distribution is mostly concentrated on the C_{70}^{6-}'s poles, and is not equally shared by all of the 5-MRs of the fullerene.[9] 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}, C_{70} and their hexaanions stems from their different geometry and symmetry. While C_{60} is an icosahedral molecule, C_{70} has a lower symmetry (D_{5h}) and is close to an ellipsoid. Therefore, in C_{60}^{6-} 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}^{6-} 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[5] and the bridged anion of $C_{61}H_2$,[9] this study clarifies the puzzling behavior of charged fullerenes. The lower magnetic susceptibility of C_{70}^{6-} as opposed to that of C_{60}^{6-} and the neutral C_{70} can be rationalized in terms of nonhomogeneous charge distribution of the extra electrons on the C_{70} skeleton.

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(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 $C_{71}H_2^{6-}$ clearly visible.

(16) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243−255.

(17) Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Young, K. B.; Malhorta, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205−3206. (b) we find the chemical shifts of ^{7}Li NMR in fullerene anions in the range of −2.0 to +2.0 ppm, depending on temperature.

(18) A characterization as hexaanion is based on (a) cyclic voltometry: Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980. (b) HMO calculations: Fowler, P. W.; Woolrich, J. *Chem. Phys. Lett.* **1986**, *127*, 78−83.