

# $^1\text{H}$ NMR of $\text{C}_{61}\text{H}_2^{6-}$ : the aromatic character of $\text{C}_{60}$ upon reduction—a view from the bridge of $\text{C}_{61}\text{H}_2$

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Received (in Cambridge, UK) 20th September 1999, Accepted 27th October 1999

The  $^1\text{H}$  NMR spectrum of the fulleroid  $\text{C}_{61}\text{H}_2^{6-}$  consists two high field doublets, providing experimental evidence for diamagnetic five-membered rings in  $\text{C}_{60}^{6-}$ .

Aromaticity, one of the most important and interesting concepts of organic chemistry, has undergone certain modifications since the original proposition by Hückel in 1931.<sup>1</sup> The theory was then devoted to single  $\pi$ -conjugated ring systems, later expanded to polycyclic molecules<sup>2</sup> and recently to non-planar molecules.<sup>3</sup>

The discovery of fullerenes<sup>4</sup> offers a new challenge in the field of aromaticity as the fullerenes are not only conjugated systems but are also spherical and therefore, no borderlines exist and numerous Kekulé structures can be assigned.<sup>5</sup> In the quest to understand the nature of the electronic structure of fullerenes their reduction is a method of choice as these molecules are capable of accepting a high number of electrons with only small changes in their rigid skeleton.

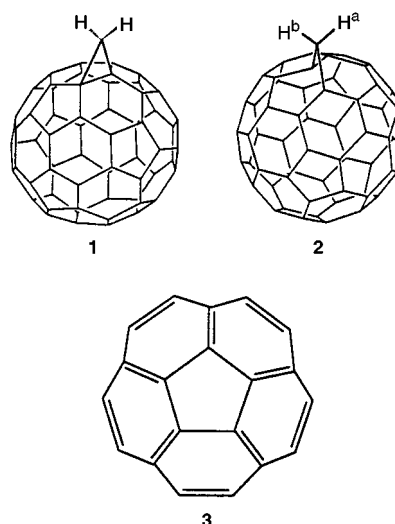
For the most abundant fullerene  $\text{C}_{60}$ , calculations,<sup>6</sup> as well as experimental data,<sup>6b,7</sup> demonstrate only a modest aromatic character. Calculations also indicate that the lowest unoccupied molecular orbital (LUMO) of  $\text{C}_{60}$  is low-lying and triply degenerate, and hence is capable of accepting six electrons,<sup>6a,8</sup> which is confirmed by the presence of six reduction waves in its cyclic voltometry.<sup>9</sup>

The magnetic ring current susceptibility of  $\text{C}_{60}^{6-}$  is expected to be very high<sup>6a</sup> in contrast to  $\text{C}_{60}$ , as was recently shown experimentally.<sup>10</sup> This is corroborated by calculations showing that the ring current of  $\text{C}_{60}$  is a result of two contributions, the diamagnetic six-membered rings (6-MRs) and the paramagnetic five-membered rings (5-MRs). These two opposite contributions cancel each other in  $\text{C}_{60}$ , leading to a low magnetic susceptibility. Moreover, calculations predict that in  $\text{C}_{60}^{6-}$  the 5-MRs will be diamagnetic, which should cause a high diamagnetic ring current in the entire system.<sup>11</sup>

An accepted method of studying local ring currents in polycyclic arrays is by attaching a methylene bridge, where the protons of the bridge are located above the centers of the ring, and their chemical shifts can probe the magnetic character of each ring.<sup>2</sup>

By the addition of  $\text{CH}_2\text{N}_2$  to  $\text{C}_{60}$  two methylene adduct isomers of  $\text{C}_{61}\text{H}_2$  were prepared.<sup>12</sup> The two protons of the methylene can be located either both above two 6-MRs (**1**) or one above a 6-MR ( $\text{H}^a$ ) and the other one above a 5-MR ( $\text{H}^b$ ) (**2**). In isomer **2**, the two different protons can serve as external and localized probes for the two rings types. The  $^1\text{H}$  NMR spectrum of **2** consists of two doublets, at  $\delta$  2.84 and 6.35, which are ascribed to  $\text{H}^a$  and  $\text{H}^b$ , respectively.<sup>12a</sup> Therefore, it can be deduced that the 6-MR is diamagnetic, and the 5-MR is paramagnetic, as predicted by calculations.<sup>11</sup>

Here we report the reduction of **2** to a hexaanion and the characterization of the anion by NMR.<sup>13</sup> The reduction was carried out, in a 5 mm NMR tube equipped with a reduction



chamber on top, in  $\text{THF}-d_8$ , with excess lithium metal and in the presence of corannulene (**3**). Lithium metal reduction of fullerenes requires extreme conditions, including the use of an ultrasonic bath. However, it has previously been reported that polycyclic molecules and especially **3** could serve as 'electron shuttles' which transport electrons in etheral solution to fullerenes, and thus enable the reduction of the insoluble  $\text{C}_{60}$  under mild conditions.<sup>10</sup> The solution was brought into contact with the lithium metal by repeatedly inverting the tube, and formation of the anion was detected by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^7\text{Li}$  NMR spectroscopy.

The  $^1\text{H}$  NMR spectrum of the anion (Table 1) shows two doublets at  $\delta$  1.34 and 2.74 ( $J = 8.93$  Hz). The  $\Delta\delta$  between these two peaks is significantly smaller than the difference between the peaks of the neutral molecule [ $\Delta\delta(\mathbf{2}) = 3.51$  ppm compared with  $\Delta\delta(\mathbf{2}^{6-}) = 1.4$  ppm].<sup>12a</sup> The small  $\Delta\delta$  of  $\mathbf{2}^{6-}$  suggests a similar magnetic environment for the two protons, in contrast to the neutral molecule, and moreover, the two protons of  $\mathbf{2}^{6-}$  are shielded. Since they are located above the centers of the rings, it confirms that these two rings are both diamagnetic, and thus the 5-MR is forced to become diamagnetic.

The  $^{13}\text{C}$  NMR spectrum of  $\mathbf{2}^{6-}$  shows an NMR band at  $\delta$  37.08 assigned to the methylene carbon, and the fullerene

**Table 1** Proton and carbon chemical shifts

	$\delta_{\text{C}}$	$\delta_{\text{H}}$	Ref.
$\text{C}_{60}$	142.68		16
$\text{C}_{60}^{6-}$	156.7		14
$\text{C}_{61}\text{H}_2$ ( <b>2</b> )	38.4 ( $\text{CH}_2$ ), 135.15–149.25	2.84, 6.35	12(a)
$\text{C}_6\text{H}_2^{6-}$ ( $\mathbf{2}^{6-}$ )	37.08 ( $\text{CH}_2$ ), 138.07–164.68	1.34, 2.74	

skeleton NMR bands appear in the region  $\delta$  138.07–164.68. The  $^7\text{Li}$  NMR spectrum shows an absorption at  $\delta$  1.93 (200 K, relative to 1 M LiCl in  $\text{D}_2\text{O}$  at 298 K). Comparison of these chemical shifts to those of  $\text{C}_{60}^{6-}$  ( $\delta_{\text{C}}$  156.7 and  $\delta_{\text{Li}}$  1.6)<sup>14</sup> shows two phenomena: (i) the reduction of **2** leads to a hexaanion, as does  $\text{C}_{60}^{6a,8,9}$  (ii) the character of  $2^{6-}$  is ‘fullerene like’ and has a similar charge distribution and aromaticity to  $\text{C}_{60}^{6-}$ .

Charging of  $\text{C}_{61}\text{H}_2$  not only sheds light on the magnetic properties of its hexaanion, but it also contributes to the understanding of the nature of the building blocks of  $\text{C}_{60}$  itself. These results are in a good agreement with calculation,<sup>11</sup> and with  $^3\text{He}$  chemical shift measurement<sup>15</sup> of  $\text{He}@C_{60}$  and  $\text{He}@C_{60}^{6-}$  that have been previously reported.<sup>10</sup> While the  $^3\text{He}$  served as an endohedral probe of the bulk magnetic properties, the protons in **2** serve as external and localized probes. Therefore, it can be concluded that the extra electrons of  $\text{C}_{60}^{6-}$  convert 5-MRs from paramagnetic building blocks (‘anti-aromatic’) to components having diamagnetic nature (‘aromatic’). The change of the ring current in the 5-MRs on the one hand, and the similarity of the aromatic 6-MRs in the neutral and the charged species on the other, demonstrates and rationalizes the highly aromatic character of  $\text{C}_{60}^{6-}$ .

We thank the Research and Development Authority of the Hebrew University of Jerusalem for financial support.

## Notes and references

- 1 E. Hückel, *Z. Phys.*, 1931, **70**, 204; E. Hückel, *Z. Phys.*, 1931, **72**, 310.
- 2 V. I. Minkin, N. M. Glukhovteev and B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, 1994.
- 3 R. C. Haddon, *J. Am. Chem. Soc.*, 1987, **109**, 1676.
- 4 H. W. Kroto, J. R. Heath, C. S. O’Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162; H. W. Kroto, A. W. Allaf and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
- 5 D. J. Klein, T. G. Schmalz, G. E. Hite and W. A. Seitz, *J. Am. Chem. Soc.*, 1986, **108**, 1301.
- 6 (a) V. Elser and R. C. Haddon, *Nature*, 1987, **325**, 792; (b) R. C. Haddon, L. F. Schneemeyer, J. V. Waszczak, S. H. Glarum, R. Tycko, G. Dabbagh, A. R. Kortan, A. J. Muller, A. M. Muijsce, M. J. Rosseinsky, S. M. Zahurak, A. V. Makhija, F. A. Thiel, K. Raghavachari, E. Cockayne and V. Elser, *Nature*, 1991, **350**, 46; (c) R. S. Ruoff, D. Beach, J. Cuomo, T. McGuire, R. L. Whetten and F. Diederich, *J. Phys. Chem.*, 1991, **95**, 3457; (d) A. P. Ramirez, R. C. Haddon, O. Zhou, R. M. Fleming, J. Zhang, S. M. McClure and R. E. Smalley, *Science*, 1994, **265**, 84.
- 7 For example: R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren and F. J. Hollander, *Science*, 1991, **252**, 313.
- 8 P. W. Fowler and J. Woolrich, *Chem. Phys. Lett.*, 1986, **127**, 78; A. J. Stone and D. I. Wales, *Chem. Phys. Lett.*, 1986, **128**, 501.
- 9 F. Zhou, C. Jehoulet and A. J. Bard, *J. Am. Chem. Soc.*, 1992, **114**, 11 004; Q. Xie, E. Pérez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978; Y. Ohsawa and T. Saji, *J. Chem. Soc., Chem. Commun.*, 1992, 781.
- 10 E. Shabtai, A. Weitz, R. C. Haddon, R. E. Hoffman, M. Rabinovitz, A. Khong, R. J. Cross, M. Saunders, P. C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 6389.
- 11 A. Pasquarello, M. Schlüter and R. C. Haddon, *Science*, 1992, **257**, 1660; M. Pasquarello, M. Schlüter and R. C. Haddon, *Phys. Rev. A*, 1993, **47**, 1783; R. C. Haddon, *Science*, 1993, **261**, 1545.
- 12 (a) T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7301; (b) A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens and R. C. King, *J. Am. Chem. Soc.*, 1993, **115**, 5829.
- 13 A justification for using the fulleroid **2** as an analogous system to  $\text{C}_{60}$  is based on the small change of the  $^3\text{He}$  chemical shift between  $^3\text{He}@C_{60}$  and  $^3\text{He}@C_{61}\text{H}_2$ , which is evidence that both have the same bulk magnetic properties and there is no perturbation of the  $\text{C}_{60}$   $\pi$ -system in  $\text{C}_{61}\text{H}_2$  (see ref. 15).
- 14 J. W. Bausch, G. K. S. Parakash and G. A. Olah, *J. Am. Chem. Soc.*, 1991, **113**, 3205.
- 15 M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi and A. Khong, *Science*, 1996, **271**, 1693; M. Saunders, H. A. Jiménez-Vázquez, B. W. Bangerter and R. J. Cross, *J. Am. Chem. Soc.*, 1994, **116**, 3621; M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg and F. A. L. Anet, *Nature*, 1994, **367**, 256.
- 16 R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423.

Communication 9/07604B