

Internal Magnetic Fields of Dianions of Fullerene C₆₀ and Its Cage-Opened Derivatives Studied with Encapsulated H₂ as an NMR Probe**

Michihisa Murata, Yuta Ochi, Fumiyuki Tanabe, Koichi Komatsu,* and Yasujiro Murata*

The aromaticity of spherical conjugated π systems of fullerene C₆₀ and its derivatives has been investigated both theoretically and experimentally.^[1] The six-membered rings (6-MRs) of C₆₀ usually have diamagnetic ring currents, whereas the five-membered rings (5-MRs) display paramagnetic ring currents.^[1b] Saunders et al. developed a useful method to measure the magnetic field inside the fullerene cage by incorporating an NMR-active nucleus, ³He, inside the cage at an occupation level of roughly 0.1%.^[2] The ³He NMR signal of ³He@C₆₀ is observed at $\delta = -6.4$ ppm with reference to the signal of dissolved free ³He gas as a result of compensation of the opposing effects of the ring currents. The chemical shift of ³He inside the C₆₀ cage was shown to be sensitive toward functionalization on the exterior of the cage and ranges from $\delta = -6$ to -17 ppm.^[2,3] Interestingly, when He@C₆₀ acquires extra six electrons, the ³He signal shifts to dramatically higher field ($\delta = -48.7$ ppm), reflecting the strong shielding effect of C₆₀⁶⁻.^[4] This was clearly supported by both experimental^[4b] and theoretical^[1a] data, which indicate that all of the 6-MRs and 5-MRs of the fullerene cage of C₆₀⁶⁻ show diamagnetic ring currents.

Fullerene C₆₀ can accept one to six electrons in its threefold degenerate LUMOs. Among the anionic states of C₆₀, the dianion C₆₀²⁻ is of particular importance in synthetic chemistry for introduction of two functional groups on the surface of the C₆₀ cage.^[5,6] While the electronic structure of C₆₀²⁻ is still under discussion, an EPR study of C₆₀²⁻ in dimethyl sulfoxide demonstrated that it has a singlet ground state ($S=0$) with a low-lying excited triplet state ($S=1$).^[7] However, little is known about the aromaticity of C₆₀²⁻. According to the “ $2(N+1)^2$ rule”^[1f] describing the spherical aromaticity of I_h -symmetrical fullerenes which was proposed by Hirsch et al., the 62- π -electron system of C₆₀²⁻ should not

have aromatic character. Meanwhile, we have succeeded in synthesizing fullerene C₆₀ encapsulating molecular hydrogen at an occupation level of 100% (H₂@C₆₀).^[8] Here we report the result of our study on the magnetic fields inside the dianions of C₆₀ as well as its cage-opened derivatives by using encapsulated H₂ as an NMR probe.^[9]

The dianion of H₂@C₆₀ was generated by treating H₂@C₆₀ with an excess of CH₃SNa, which has been commonly used to generate C₆₀²⁻,^[6] in CD₃CN under vacuum. The reaction mixture was stirred for three hours at room temperature and a dark red solution was obtained, which shows a Vis/NIR absorption at $\lambda_{\text{max}} = 944$ nm indicating the generation of H₂@C₆₀²⁻.^[7,10] The ¹³C NMR spectrum displays a broad signal at around 183 ppm, which is consistent with a previous report for empty C₆₀²⁻.^[11] The ¹H NMR spectrum of H₂@C₆₀²⁻ exhibits no signal in the high-field region between 0 ppm and -15 ppm (vs. TMS), where the signals of encapsulated hydrogen inside neutral fullerenes have been observed.^[9,12] Instead, we found that a slightly broadened H₂ signal of H₂@C₆₀²⁻ appears at surprisingly low field, $\delta = 26.36$ ppm (Figure 1). This signal is

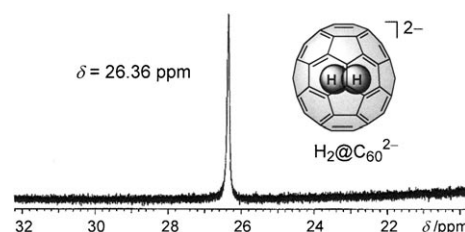


Figure 1. ¹H NMR spectrum (300 MHz, CD₃CN) of H₂@C₆₀²⁻.

shifted 27.8 ppm downfield relative to that of neutral H₂@C₆₀ ($\delta = -1.45$ ppm^[8c,9] in 1,2-Cl₂C₆D₄). This indicates that the overall aromaticity of C₆₀ decreases drastically upon two-electron reduction, while, in sharp contrast, the overall aromaticity is reported to increase significantly for C₆₀⁶⁻.^[1a,4]

GIAO^[13] (gauge-independent atomic orbital) calculations^[14] at the B3LYP/6-31G(d) level of theory for H₂@C₆₀²⁻ in the singlet state were found to reproduce the chemical shift of H₂ as $\delta = 28.52$ ppm. Thus, we carried out NICS^[15] (nucleus-independent chemical shifts) calculations for all the 6-MRs and 5-MRs of empty C₆₀²⁻ at the same level of theory, in order to interpret the changes in diamagnetic and paramagnetic ring currents of all the conjugated cyclic π systems of C₆₀²⁻. The resulting NICS values are shown in Figure 2 in a Schlegel diagram. They indicate that upon two-electron reduction the ring currents of all 6-MRs become paramagnetic while those of all 5-MRs become diamagnetic. To the best of our knowledge, this is the first case in which the

[*] Prof. Dr. K. Komatsu
Department of Environmental and Biotechnological
Frontier Engineering
Fukui University of Technology
Gakuen, Fukui 910-8505 (Japan)
Fax: (+81) 776-29-7891
E-mail: komatsu@fukui-ut.ac.jp

Dr. M. Murata, Y. Ochi, F. Tanabe, Prof. Dr. Y. Murata
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611-0011 (Japan)
Fax: (+81) 774-38-3178
E-mail: yasujiro@scl.kyoto-u.ac.jp

[**] This research was supported by KAKENHI from MEXT/JSPS and the PRESTO program sponsored by JST.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

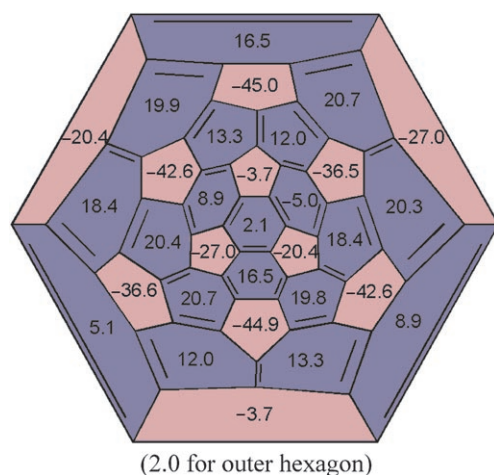
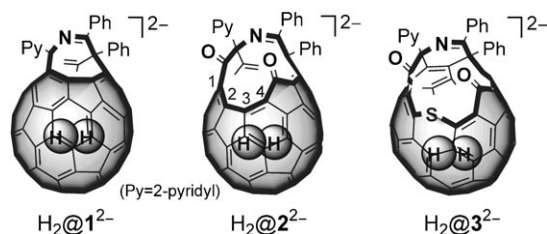


Figure 2. Schlegel diagram of the dianion C_{60}^{2-} showing the NICS patterns calculated at the B3LYP/6-31G(d) level of theory: pink regions signify diamagnetic ring currents and blue paramagnetic ring currents. (NICS values of neutral C_{60} : -2.4 for 6-MRs and 11.8 for 5-MRs.)

aromatic and antiaromatic character of 6-MRs and 5-MRs is entirely opposite to those of neutral fullerene and its derivatives. Because there are more 6-MRs than 5-MRs, the antiaromatic character caused by 6-MRs overwhelms the aromatic character caused by 5-MRs, resulting in the strong deshielding effect inside the cage.

We extended this study to the dianions of the cage-opened C_{60} derivatives $H_2@1$, $H_2@2$, and $H_2@3$, with 8-, 12-, and 13-membered-ring orifices,^[9] respectively, in order to see if the reversal of aromaticity/antiaromaticity for 6-MRs and 5-MRs takes place even for heavily functionalized fullerenes. $H_2@$



1^{2-} – $H_2@3^{2-}$ ^[16] were generated in the same way as $H_2@C_{60}^{2-}$. The observed 1H NMR chemical shifts for the encapsulated H_2 in $H_2@1^{2-}$ – $H_2@3^{2-}$ and calculated values at the GIAO-B3LYP/6-31G(d) level are summarized in Table 1, together with the extent of the downfield shift upon two-electron reduction. Although the H_2 signal of $H_2@C_{60}^{2-}$ appears furthest downfield, the large downfield shift still occurs for dianionic cage-opened fullerenes $H_2@1^{2-}$ – $H_2@3^{2-}$ in spite of their partially ruptured π systems. The GIAO calculations reproduce this trend, although there is a tendency to overestimate the magnetic deshielding effects of the fullerene cages (Table 1).

The NICS calculations at the B3LYP/6-31G(d) level of theory indicated that the aromatic and antiaromatic characters of 6-MRs and 5-MRs are mostly reversed for $H_2@1^{2-}$ and

Table 1: Experimental and calculated 1H NMR chemical shifts for molecular hydrogen encapsulated in dianions of C_{60} and a series of cage-opened fullerene derivatives.

	$H_2@C_{60}^{2-}$	$H_2@1^{2-}$	$H_2@2^{2-}$	$H_2@3^{2-}$
$\delta(\text{expt})^{[a]}$	26.36	14.40	-0.72	8.10
$\delta(\text{calcd})^{[b]}$	28.52	18.26	1.21	9.42
$(\delta(\text{expt}))^{[c]}$	(-1.45)	(-2.95)	(-5.80)	(-7.25)
$\Delta\delta^{[d]}$	27.81	17.36	5.08	15.35

[a] At 300 MHz in CD_3CN . [b] GIAO-B3LYP/6-31G(d). [c] Values^[9] of the neutral counterparts, at 300 MHz in $1,2\text{-Cl}_2C_6D_4$. [d] Degree of downfield shifts of H_2 signals compared to those of neutral counterparts.

$H_2@3^{2-}$ in the same way as those for $H_2@C_{60}^{2-}$. On the other hand, the reversal of aromaticity occurs only to a small extent for $H_2@2^{2-}$ based on the NICS calculations (see the Supporting Information), reflecting the smallest downfield shift of the H_2 signal ($\Delta\delta = 5.08$ ppm, Table 1). As we reported previously, the LUMO of neutral $2^{[8a]}$ is relatively localized at the butadiene moiety (C1–C4) on the rim of the orifice. Therefore, the distribution of the two added electrons would be rather restricted for $H_2@2^{2-}$ as compared to the other three systems, $H_2@C_{60}^{2-}$, $H_2@1^{2-}$, and $H_2@3^{2-}$, whose LUMOs in the neutral state were shown to delocalize almost completely throughout the fullerene carbon skeleton (Figure 3). Thus, the spherical delocalization of the LUMO is considered to be responsible for the drastic change in magnetic fields inside the fullerene cages upon two-electron reduction.

In summary, dianions of C_{60} and its cage-opened derivatives showed dramatic decrease in the overall aromaticity of fullerene π systems. It was indicated that the aromatic and

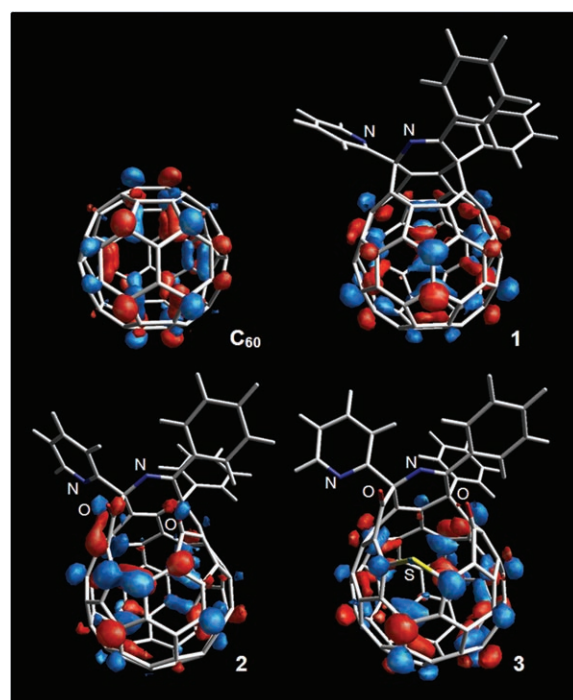


Figure 3. LUMOs of neutral C_{60} and 1–3 calculated at the B3LYP/6-31G(d) level of theory.

antiaromatic character of the 6-MRs and 5-MRs of dianionic fullerene cages is reversed as compared to their neutral counterparts when added electrons can be delocalized over the fullerene cages.

Received: November 17, 2007

Published online: February 1, 2008

Keywords: aromaticity · density functional calculations · fullerenes · NMR spectroscopy · ring currents

- [1] a) V. Elser, R. C. Haddon, *Nature* **1987**, 325, 792–794; b) A. Pasquarello, M. Schlüter, R. C. Haddon, *Science* **1992**, 257, 1660–1661; c) R. C. Haddon, *Science* **1993**, 261, 1545–1550; d) A. Pasquarello, M. Schlüter, R. C. Haddon, *Phys. Rev. A* **1993**, 47, 1783–1789; e) M. Bühl, *Chem. Eur. J.* **1998**, 4, 734–739; f) A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2000**, 112, 4079–4081; *Angew. Chem. Int. Ed.* **2000**, 39, 3915–3917; g) M. Bühl, A. Hirsch, *Chem. Rev.* **2001**, 101, 1153–1183.
- [2] M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, A. Khong, *Science* **1996**, 271, 1693–1697.
- [3] a) M. Saunders, H. A. Jiménez-Vázquez, B. W. Bangerter, R. J. Cross, *J. Am. Chem. Soc.* **1994**, 116, 3621–3622; b) A. B. Smith III, R. M. Strongin, L. Brard, W. J. Romanow, M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, *J. Am. Chem. Soc.* **1994**, 116, 10831–10832; c) M. Rüttimann, R. F. Haldimann, L. Isaacs, F. Diederich, A. Khong, H. A. Jiménez-Vázquez, R. J. Cross, M. Saunders, *Chem. Eur. J.* **1997**, 3, 1071–1076; d) O. V. Boltalina, M. Bühl, A. Khong, M. Saunders, J. M. Street, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1475–1479.
- [4] a) E. Shabtai, A. Weitz, R. C. Haddon, R. E. Hoffman, M. Rabinovitz, A. Khong, R. J. Cross, M. Saunders, P.-C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1998**, 120, 6389–6393; b) T. Sternfeld, F. Wudl, K. Hummelen, A. Weitz, R. C. Haddon, M. Rabinovitz, *Chem. Commun.* **1999**, 2037–2039; c) T. Sternfeld, R. E. Hoffman, M. Saunders, R. J. Cross, S. Syamala, M. Rabinovitz, *J. Am. Chem. Soc.* **2002**, 124, 8786–8787.
- [5] a) R. Subramanian, K. M. Kadish, M. N. Vijayashree, X. Gao, M. T. Jones, *J. Phys. Chem.* **1996**, 100, 16327–16335; b) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa, K. M. Kadish, *J. Am. Chem. Soc.* **1998**, 120, 9220–9227; c) Y.-H. Zhu, L.-C. Song, Q.-M. Hu, C.-M. Li, *Org. Lett.* **1999**, 1, 1693–1695.
- [6] a) E. Allard, L. Riviere, J. Delaunay, D. Dubois, J. Cousseau, *Tetrahedron Lett.* **1999**, 40, 7223–7226; b) E. Allard, J. Delaunay, F. Cheng, J. Cousseau, J. Orduna, G. Javier, *Org. Lett.* **2001**, 3, 3503–3506; c) F. Cheng, Y. Murata, K. Komatsu, *Org. Lett.* **2002**, 4, 2541–2544.
- [7] P. C. Trulove, R. T. Carlin, G. R. Eaton, S. S. Eaton, *J. Am. Chem. Soc.* **1995**, 117, 6265–6272.
- [8] a) Y. Murata, M. Murata, K. Komatsu, *Chem. Eur. J.* **2003**, 9, 1600–1609; b) Y. Murata, M. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2003**, 125, 7152–7153; c) K. Komatsu, M. Murata, Y. Murata, *Science* **2005**, 307, 238–240; d) K. Komatsu, Y. Murata, *Chem. Lett.* **2005**, 34, 886–891.
- [9] M. Murata, Y. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2006**, 128, 8024–8033.
- [10] R. Subramanian, P. Bolas, M. N. Vijayashree, F. D'Souza, M. T. Jones, K. M. Kadish, *J. Chem. Soc. Chem. Commun.* **1994**, 1847–1848.
- [11] P. D. W. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R. D. Bolskar, Y. Sun, C. A. Reed, *J. Am. Chem. Soc.* **1995**, 117, 2907–2914.
- [12] a) Y. Matsuo, H. Isobe, T. Tanaka, Y. Murata, M. Murata, K. Komatsu, E. Nakamura, *J. Am. Chem. Soc.* **2005**, 127, 17148–17149; b) Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, R. J. Cross, *Angew. Chem.* **2001**, 113, 1591–1594; *Angew. Chem. Int. Ed.* **2001**, 40, 1543–1546; c) S.-i. Iwamatsu, S. Murata, Y. Andoh, M. Minoura, K. Kobayashi, N. Mizorogi, S. Nagase, *J. Org. Chem.* **2005**, 70, 4820–4825.
- [13] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, 112, 8251–8260.
- [14] Gaussian03 (Revision D.02): M. J. Frisch et al., see the Supporting Information.
- [15] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, 118, 6317–6318.
- [16] We could not observe any ^{13}C NMR signals for $\text{H}_2@1^{2-}\text{-H}_2@3^{2-}$ most likely because of thermal population of the triplet excited states,^[11] although the possibility of formation of radical trianions cannot be rigorously ruled out.