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Internal Magnetic Fields of Dianions of Fullerene C_{60} and Its Cage-Opened Derivatives Studied with Encapsulated H_2 as an NMR Probe**

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The aromaticity of spherical conjugated π systems of fullerene C_{60} and its derivatives has been investigated both theoretically and experimentally.[1] The six-membered rings (6-MRs) of C_{60} 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, ^{3}He, inside the cage at an occupation level of roughly 0.1%.[2] The ^{3}He NMR signal of ^{3}He@C_{60} is observed at $\delta = -6.4$ ppm with reference to the signal of dissolved free ^{3}He gas as a result of compensation of the opposing effects of the ring currents. The chemical shift of ^{3}He inside the C_{60} 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@C_{60} acquires extra six electrons, the ^{3}He signal shifts to dramatically higher field ($\delta = -48.7$ ppm), reflecting the strong shielding effect of C_{60}^{6-}.[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 C_{60}^{6-} show diamagnetic ring currents.

Fullerene C_{60} can accept one to six electrons in its threefold degenerate LUMOs. Among the anionic states of C_{60}, the dianion C_{60}^{2-} is of particular importance in synthetic chemistry for introduction of two functional groups on the surface of the C_{60} cage.[5,6] While the electronic structure of C_{60}^{2-} is still under discussion, an EPR study of C_{60}^{2-} 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 C_{60}^{2-}. 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 C_{60}^{2-} should not have aromatic character. Meanwhile, we have succeeded in synthesizing fullerene C_{60} encapsulating molecular hydrogen at an occupation level of 100% (H_2@C_{60}).[8] Here we report the result of our study on the magnetic fields inside the dianions of C_{60} as well as its cage-opened derivatives by using encapsulated H_2 as an NMR probe.[9]

The dianion of H_2@C_{60} was generated by treating H_2@C_{60} with an excess of CH_3SNa, which has been commonly used to generate C_{60}^{2-},[6] in CD_3CN 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 $\lambda_{max} = 944$ nm indicating the generation of H_2@C_{60}^{2-}.[7,10] The ^{13}C NMR spectrum displays a broad signal at around 183 ppm, which is consistent with a previous report for empty C_{60}^{2-}.[11] The ^{1}H NMR spectrum of H_2@C_{60}^{2-} 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 H_2 signal of H_2@C_{60}^{2-} appears at surprisingly low field, $\delta = 26.36$ ppm (Figure 1). This signal is shifted 27.8 ppm downfield relative to that of neutral H_2@C_{60} ($\delta = -1.45$ ppm[8c,9] in 1,2-$Cl_2C_6D_4$). This indicates that the overall aromaticity of C_{60} decreases drastically upon two-electron reduction, while, in sharp contrast, the overall aromaticity is reported to increase significantly for C_{60}^{6-}.[1a,4]

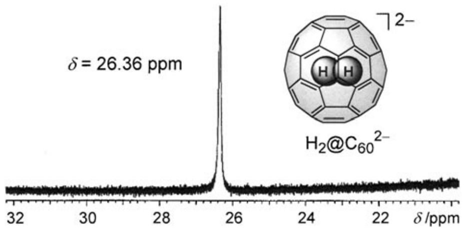

Figure 1. ^{1}H NMR spectrum (300 MHz, CD_3CN) of H_2@C_{60}^{2-}.

GIAO[13] (gauge-independent atomic orbital) calculations[14] at the B3LYP/6-31G(d) level of theory for H_2@C_{60}^{2-} in the singlet state were found to reproduce the chemical shift of H_2 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 C_{60}^{2-} 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 C_{60}^{2-}. 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

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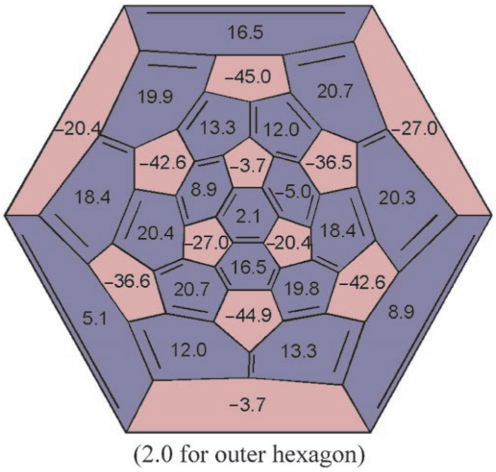
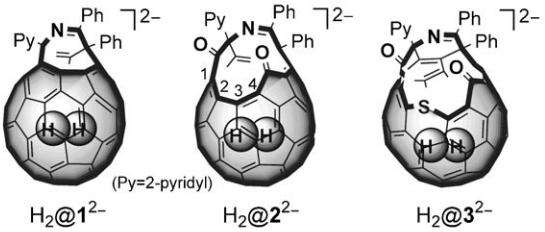


Figure 2. Schlegel diagram of the dianion C_{60}^{2-} showing the NICS patterns calculated at the B3LYP/6-31G(d) level of theory: pink regions signify diamagnetic ring currents and blue paramagnetic ring currents. (NICS values of neutral C_{60}: −2.4 for 6-MRs and 11.8 for 5-MRs.)

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 ^{1}H 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 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

Table 1: Experimental and calculated ^{1}H 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**$^{2-}$
δ(expt)[a]	26.36	14.40	−0.72	8.10
δ(calcd)[b]	28.52	18.26	1.21	9.42
(δ(expt))[c]	(−1.45)	(−2.95)	(−5.80)	(−7.25)
Δδ[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-$Cl_2C_6D_4$. [d] Degree of downfield shifts of H_2 signals compared to those of neutral counterparts.

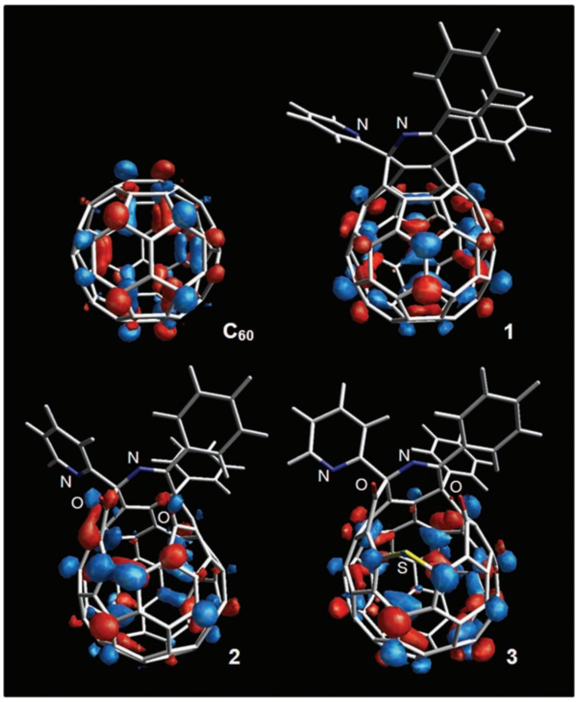


Figure 3. LUMOs of neutral C_{60} and **1**–**3** calculated at the B3LYP/6-31G(d) level of theory.

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.

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[16] We could not observe any ^{13}C NMR signals for $H_2@\mathbf{1}^{2-}$-$H_2@\mathbf{3}^{2-}$ 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.