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NMR Studies on Monofunctionalized Fullerenyl Cation and Anion Encapsulating a H_2 Molecule

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: ^{1}H NMR chemical shifts of molecular hydrogen encapsulated in dichloromethyl–C_{60} cation and (1-octynyl)–C_{60} anion were studied to clarify the difference in magnetic shielding effects inside the fullerene cages. The signals of the H_2 molecule inside both cationic and anionic C_{60} cages appeared at lower fields than those of the neutral counterparts. These results were interpreted based on the results of NICS calculations. It was demonstrated that the H_2 molecule inside the C_{60} cages can serve as an excellent NMR probe of aromaticity for both cationic and anionic C_{60} derivatives.

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

Introduction

Fullerene C_{60} has a curved but fully conjugated polycyclic 60 π-electron system with empty space inside. Theoretical and experimental investigations into the magnetic properties of fullerenes have revealed that the six-membered rings (6-MRs) of C_{60} possess weak diamagnetic ring currents, whereas the five-membered-rings (5-MRs) have strong paramagnetic ring currents.[1] Saunders et al. established a high-temperature and high-pressure method to introduce a ^{3}He atom as an NMR-active nucleus inside the C_{60} cage at an occupation level of roughly 0.1%.[2] The magnetic shielding effect inside the C_{60} cage was then measured by ^{3}He NMR experiment. A sharp signal of ^{3}He inside the C_{60} cage appears at $\delta = -6.36$ ppm relative to the resonance of free ^{3}He dissolved in 1-methylnaphthalene, as a result of the compensation of opposite shielding effects by the ring currents in 6-MRs and 5-MRs.[3] The chemical shift of ^{3}He inside C_{60} was shown to be sensitive toward chemical functionalization of the C_{60} cage. A large number of C_{60} derivatives bearing organic addend(s) at the 1,2-position(s) encapsulating ^{3}He were synthesized, and the NMR chemical shift of the ^{3}He signal has been shown to be in the range of $\delta = -7.2$ to $\delta = -9.7$ ppm.[4] Interestingly, when ^{3}He@C_{60} acquires six extra electrons, the ^{3}He signal shifts dramatically to higher field ($\delta = -48.7$ ppm), reflecting the strong shielding effect of $C_{60}{}^{6-}$.[5] The highly aromatic character of the $C_{60}{}^{6-}$ inner surface was supported by both experimental[5b] and theoretical[1d] studies, which indicated that all of the 6-MRs and 5-MRs of $C_{60}{}^{6-}$ possess diamagnetic ring currents. In a related study, Taylor et al. reported the synthesis and ^{3}He NMR studies of cationic species of ^{3}He@C_{60} derivative **1**$^+$ and demonstrated that the aromaticity of the C_{60} π system slightly decreases upon formation of cation **1**$^+$ from its neutral precursor **2**.[6] However, research on the aromaticity of ionic C_{60} and its derivatives has been limited to these two reports

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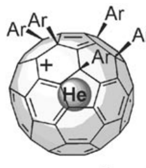
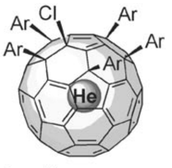
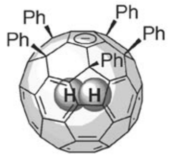


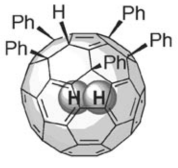


(Ar = 4-fluorophenyl)

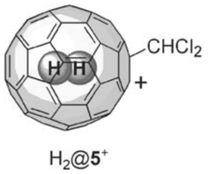
$^3He@\mathbf{1}^+$ $^3He@\mathbf{2}$



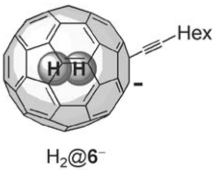
$H_2@\mathbf{3}^-$



$H_2@\mathbf{4}$



$H_2@\mathbf{5}^+$



$H_2@\mathbf{6}^-$

until we succeeded in synthesizing C_{60} encapsulating a H_2 molecule at an occupation level of 100%.[7]

The H_2 molecule encapsulated in C_{60} can also be used as a sensitive NMR probe in the same way as ^3He, with the advantage that it can be used in commonly accessible ^1H NMR spectroscopy.[8] Actually, we recently proved the drastic decrease in overall aromaticity of C_{60} upon two-electron reduction based on the remarkably large downfield shift of the H_2 signal of $H_2@C_{60}^{2-}$ ($\delta = +26.36$ ppm in CD_3CN vs. TMS) relative to that of neutral $H_2@C_{60}$ ($\delta = -1.45$ ppm in 1,2-$Cl_2C_6D_4$).[9] The ^1H NMR measurement of anionic $H_2@C_{60}$ derivative $\mathbf{3}^-$ revealed that aromaticity of the fullerenyl cage of $\mathbf{3}^-$ is almost comparable to that of the neutral counterpart **4**, despite the existence of an aromatic cyclopentadienyl anion moiety on the C_{60} cage.[10] On the other hand, we previously reported dichloromethyl–C_{60} cation $\mathbf{5}^{+}$[11] as well as 1-octynyl–C_{60} anion $\mathbf{6}^{-}$[12] as stable ionic species in solution. Both $\mathbf{5}^+$ and $\mathbf{6}^-$ have only one organic addend on the C_{60} cage, and these compounds appear to be well suited for the study of the difference in aromaticity between monofunctionalized C_{60} cations and anions based on the ^1H NMR chemical shifts of the encapsulated H_2 molecule. Herein, we report the generation and NMR measurements of $H_2@\mathbf{5}^+$ and $H_2@\mathbf{6}^-$, as well as an attempted generation of dichloromethyl–C_{60} anion $\mathbf{5}^-$.

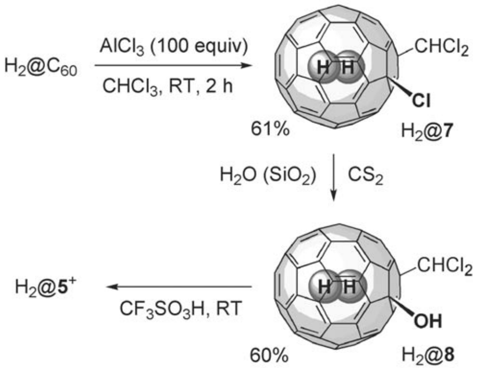
Abstract in Japanese:

水素分子を内包したジクロロメチルC_{60}カチオンおよび1-オクチニルC_{60}アニオンを発生させたところ、内包水素のNMRシグナルは対応する中性の前駆体より低磁場に観測された。NICS計算結果より、これはカチオンではカチオン中心炭素を含む五員環とその両側の六員環の常磁性環電流の寄与によるものと考えられ、一方、アニオンでは骨格全体の六員環の芳香族性が低下したことが要因であると示された。内包水素は、それを覆うカチオン性あるいはアニオン性C_{60}骨格とほとんど電子的相互作用をもたないことが示され、今後様々なフラーレンイオン種の芳香族性の解明に役立つものと期待される。

Results and Discussion

Generation of Dichloromethylfullerenyl Cation Encapsulating H_2

Dichloromethyl–C_{60} cation encapsulating a H_2 molecule, $H_2@\mathbf{5}^+$, was generated following the procedure for formation of empty $\mathbf{5}^+$.[11] As shown in Scheme 1, a solution of $H_2@C_{60}$ (occupation level of 9%) in $CHCl_3$ was stirred in the presence of a large excess of aluminum(III) chloride at room temperature for two hours to give the 1,4-adduct $H_2@\mathbf{7}$ in 61% yield. Upon silica-gel column chromatography, $H_2@\mathbf{7}$ was readily converted into fullerenol $H_2@\mathbf{8}$ in 60% yield. The NMR signals of the H_2 molecule inside $H_2@\mathbf{7}$ and $H_2@\mathbf{8}$ were observed at $\delta = -6.00$ and -6.03 ppm in CS_2–$CDCl_3$ (1:1), respectively, indicating that the magnetic shielding effect is nearly the same as far as the addition pattern (1,4-) is the same. Then, a brown powder of fullerenol $H_2@\mathbf{8}$ was added to triflic acid to give a reddish purple solution of cation $H_2@\mathbf{5}^+$. The ^1H NMR spectrum of this solution exhibited a singlet from the dichloromethyl proton at $\delta = 6.44$ ppm, which was exactly the same value as that reported for empty $\mathbf{5}^+$.[11] A small signal assignable to the encapsulated H_2 molecule appeared at $\delta = -2.89$ ppm, as shown in Figure 1, which was not observed for empty $\mathbf{5}^+$.



Scheme 1. Generation of dichloromethyl–C_{60} cation $H_2@\mathbf{5}^+$.

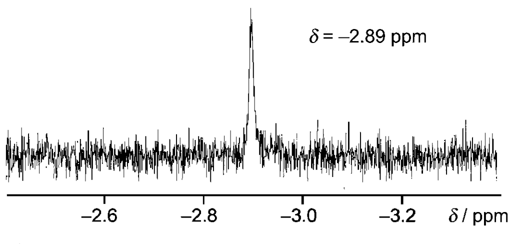
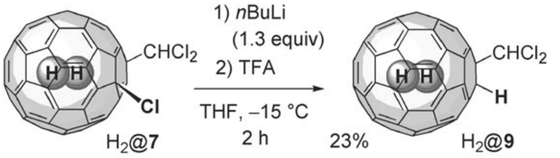


Figure 1. ^1H NMR (400 MHz, C_6D_{12} as an external standard) signal of the encapsulated H_2 molecule of $H_2@\mathbf{5}^+$ in CF_3SO_3H.

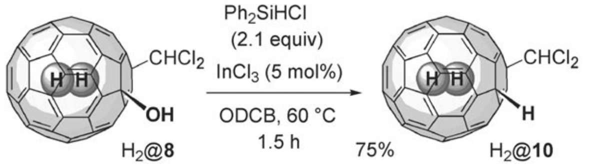
The NMR signal of the H_2 molecule shifted to lower field by 3.14 ppm relative to that of H_2@**8**, indicating that the overall aromaticity of the C_{60} π system of H_2@**5**$^+$ decreased as compared to that of **8**.

Attempted Generation of the Dichloromethylfullerenyl Anion

It is well recognized that the acidity of a proton directly attached to the C_{60} cage is quite high.[12,13] For example, a pK_a value of 5.7 has been reported for *t*Bu–C_{60}–H.[13] Thus, we first examined a halogen–lithium exchange reaction of H_2@**7** to prepare the precursor of anion H_2@**5**$^-$. The reaction of H_2@**7** with *n*BuLi in THF at −15 °C and subsequent protonation with trifluoroacetic acid gave the desired 1,2-adduct H_2@**9** in 23 % yield (Scheme 2). Since the yield of isolated H_2@**9** was not sufficient for further investigation of the anion, we pursued an alternative method to prepare H_2@**9**. Baba et al. developed an efficient method to reduce tertiary alcohols by the use of chlorodiphenylsilane and a catalytic amount of indium(III) chloride.[14] By applying this reaction to fullerenol H_2@**8** in 1,2-dichlorobenzene (ODCB), 1,4-adduct H_2@**10** was obtained in 75 % yield as a major product (including 6 % of 1,2-adduct H_2@**9** as a minor product), as shown in Scheme 3. The NMR signals of the H_2 molecule inside H_2@**9** and H_2@**10** were observed at $\delta = -4.62$ and −5.78 ppm in CS_2–$CDCl_3$ (1:1), respectively, reflecting the different addition patterns of the organic substituents on the C_{60} cage. It should be noted that the NMR chemical shifts of exohedral protons in the dichloromethyl groups of H_2@**9** and H_2@**10** were less sensitive toward the positions of the substituents and were in a similar region, such as $\delta =$ 6.96 ppm for H_2@**9** and $\delta = 7.03$ ppm for H_2@**10** in CS_2–$CDCl_3$ (1:1).

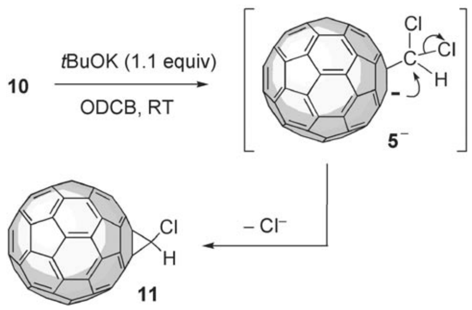


Scheme 2. Synthesis of 1,2-adduct H_2@**9** by halogen–lithium exchange.



Scheme 3. Synthesis of 1,4-adduct H_2@**10** by direct reduction of fullerenol H_2@**8**.

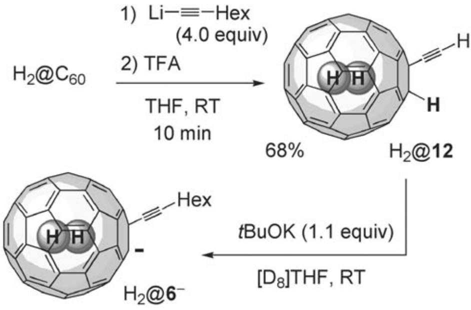
It was reported that a monofunctionalized C_{60} anion generated in THF exhibits a deep green color.[12] However, when the brown solution of empty **10** was treated with 1.1 equiv of *t*BuOK in ODCB, the color of the solution remained unchanged. This turned out to be due to the intramolecular nucleophilic substitution of anionic intermediate **5**$^-$ proceeding immediately to give new methanofullerene derivative **11** (Scheme 4). Although a dark green solution was obtained when the above reaction was conducted in benzonitrile, it gradually turned to brown even under vacuum at 0 °C because of the formation of **11**.



Scheme 4. Attempted generation of dichloromethyl–C_{60} anion **5**$^-$.

Generation of 1-Octynylfullerenyl Anion Encapsulating H_2

In contrast to the instability of anion **5**$^-$, 1-octynyl–C_{60} anion **6**$^-$ has been reported to be stable in solution under vacuum even for half a year. Hence, we tried to generate H_2@**6**$^-$ encapsulating H_2 following the previously reported method for empty **6**$^-$.[12] The reaction of H_2@C_{60} (occupation level of 9 %) with 1-octynyllithium proceeded smoothly at room temperature in THF to give a dark green solution. This solution was protonated with trifluoroacetic acid to afford 1,2-adduct H_2@**12** in 47 % yield (Scheme 5). When a THF solution of H_2@**12** was treated with 1.2 equiv of *t*BuOK, the brown solution immediately turned into a dark green solution again, indicating the formation of desired anion H_2@**6**$^-$. The ^{1}H NMR spectrum of this solution exhibited no signal for the proton directly attached to the C_{60} cage.[12] Furthermore, as shown in Figure 2, a new signal corresponding to



Scheme 5. Generation of 1-octynyl–C_{60} anion H_2@**6**$^-$.

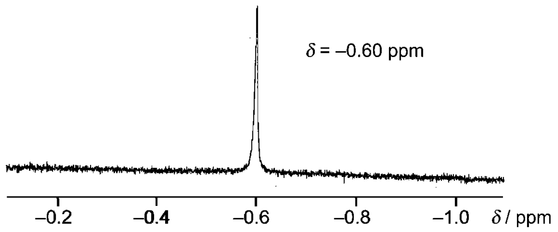


Figure 2. ^{1}H NMR (400 MHz) signal of the encapsulated H_2 molecule of $H_2@\mathbf{6}^-$ in [D$_8$]THF.

the encapsulated H_2 molecule appeared at $\delta = -0.60$ ppm, which was shifted downfield by 4.15 ppm as compared to that of neutral precursor $H_2@\mathbf{12}$ ($\delta = -4.75$ ppm in CS_2–$CDCl_3$ (1:1)). The weaker magnetic shielding effect inside the C_{60} cage of $\mathbf{6}^-$ is attributed to a decrease in aromatic character of the C_{60} π system of $\mathbf{6}^-$.

NICS Calculations for Dichloromethyl–C_{60} Cation and 1-Octynyl–C_{60} Anion

The NMR signal of the encapsulated H_2 molecule of cation $H_2@\mathbf{5}^+$ ($\delta = -2.89$ ppm in CF_3SO_3H) was shifted downfield by 1.73 ppm relative to that of the neutral precursor, 1,2-adduct $H_2@\mathbf{9}$ ($\delta = -4.62$ ppm in CS_2–$CDCl_3$ (1:1)). This apparently indicates that the magnetic shielding effect inside the C_{60} cage of $\mathbf{5}^+$ is weaker than that of **9**. To interpret the changes in diamagnetic and paramagnetic ring currents of all the π-conjugated cyclic units of the C_{60} cage, the nucleus-independent chemical shift (NICS)[15] calculations[16] were performed for all the 6-MRs and 5-MRs of cation $\mathbf{5}^+$ as well as **9** at the GIAO-B3LYP/6-311G(d,p) level of theory for the structures optimized at the B3LYP/6-31G(d) level. As shown in Figure 3, it turned out that the 5-MR (denoted as A) of $\mathbf{5}^+$ including the cationic center possesses high antiaromaticity (NICS = +12.8). In addition, it is noted that the two 6-MRs (B) also have antiaromaticity with a positive NICS value (NICS = +3.7) whereas the corresponding 6-MRs (C) of **9** exhibit aromatic character (NICS = −6.5). Owing to this difference, the contribution of the paramagnetic ring currents dominates in the fullerene π system of $\mathbf{5}^+$, which results in a downfield shift of the H_2 signal of $H_2@\mathbf{5}^+$ relative to that of $H_2@\mathbf{9}$. It should be noted that this interpretation for the monofunctionalized C_{60} cation $\mathbf{5}^+$ is consistent with that for pentafunctionalized C_{60} cation $^3He@\mathbf{1}^+$ reported by Taylor et al.[6]

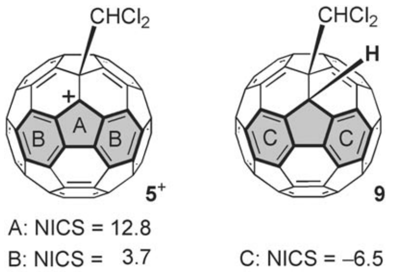


Figure 3. Selected NICS values of $\mathbf{5}^+$ and **9** calculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory.

The NMR signal of the H_2 molecule inside anion $H_2@\mathbf{6}^-$ ($\delta = -0.60$ ppm in [D$_8$]THF) is also downfield shifted by 4.15 ppm relative to that of neutral precursor $H_2@\mathbf{12}$ ($\delta = -4.75$ ppm in CS_2–$CDCl_3$ (1:1)), and by 2.29 ppm relative to that of cation $H_2@\mathbf{5}^+$. Thus, the magnetic shielding effect inside the C_{60} cage of anion $\mathbf{6}^-$ is relatively weak, the overall aromaticity of $\mathbf{6}^-$ being relatively decreased as compared with the case of cation $H_2@\mathbf{5}^+$. The results of NICS calculations for empty $\mathbf{6}^-$ and **12** are shown in Figure 4 in Schlegel diagrams. They suggest that the aromatic character of $\mathbf{6}^-$ decreases not only in the specific 6-MRs around the anionic center but in most of the 6-MRs of the entire C_{60} cage; that is, the aromatic characters of the sixteen 6-MRs out of eighteen 6-MRs decrease (decrease in absolute NICS value by 0.3–7.3) with the exception of two rings (increase in absolute NICS value by 0.2 and 0.5). On the other hand, the antiaro-

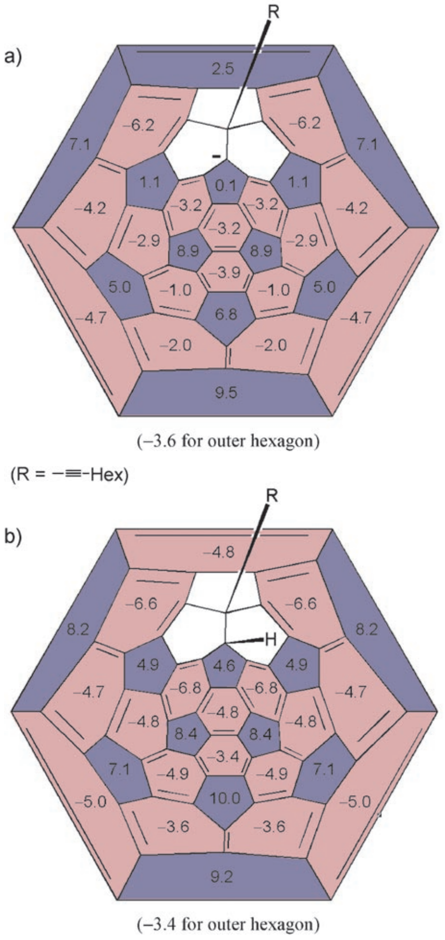


Figure 4. Schlegel diagrams of a) anion $\mathbf{6}^-$ and b) **12** showing the NICS values calculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory: pink regions represent negative NICS values and blue regions represent positive values.

matic character of the 5-MRs slightly increases for three rings out of ten rings (increase in absolute NICS value by 0.3–0.5) while others decrease (decrease in absolute NICS value by 1.1–3.8). Since there are more 6-MRs than 5-MRs in the C_{60} cage, the large decrease in aromatic character caused by the 6-MRs overwhelms the decrease in antiaromatic character caused by the 5-MRs. This can be taken as the main reason for the observed downfield shift for the H_2 signal of H_2@**6**$^-$.

The downfield shifts of the H_2 signals of cation H_2@**5**$^+$ and anion H_2@**6**$^-$ relative to the neutral counterparts were thus limited to a small extent (absolute $\Delta\delta$ values, 1.73 and 4.15 ppm) as compared to the large shifts reported for hexaanion ^{3}He@C_{60}^{6-} ($\Delta\delta = -42.3$ ppm) and dianion H_2@C_{60}^{2-} ($\Delta\delta = +27.8$ ppm).

Endohedral Chemical Shifts of Encapsulated H_2 Molecule and NICS Values at the Center of the Fullerene Cages

In this work, we prepared several neutral or ionic C_{60} derivatives encapsulating molecular hydrogen, and examined the magnetic shielding effects inside the C_{60} cages by means of ^{1}H NMR spectroscopy. To examine if the density functional calculations can reproduce the chemical shifts of the H_2 molecule, GIAO calculations at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory were conducted to give the results shown in Table 1, together with the NICS values. All chemical shifts are the averaged values of those for two hydrogen atoms, which are expressed with reference to that for TMS calculated at the same level of theory. The GIAO calculations were found to reproduce the experimental chemical shifts qualitatively, with a tendency to underestimate the magnetic shielding effects inside the C_{60} cages by a range of 2.1–3.2 ppm.

Table 1. Experimental and calculated NMR chemical shifts for encapsulated hydrogen of a series of neutral and ionic H_2@C_{60} derivatives together with the NICS values at the center of the corresponding empty C_{60} cages.

	δ (exptl) [ppm]	δ (calcd)[a] [ppm]	NICS[b]
H_2@C_{60}	−1.44[c]	+1.79	−3.25
H_2@**5**$^+$	−2.89[d]	−0.78	−5.72
H_2@**6**$^-$	−0.60[e]	+1.66	−3.35
H_2@**7**	−6.00[f]	−3.79	−8.96
H_2@**8**	−6.03[f]	−3.84	−8.84
H_2@**9**	−4.62[f]	−2.27	−7.20
H_2@**10**	−5.78[f]	−3.27	−8.48
H_2@**12**	−4.75[f]	−2.53	−7.37

[a] Caculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory. [b] Values at the center of the empty C_{60} cages calculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory. [c] Value taken from reference [7a]. [d] At 400 MHz in CF_3SO_3H. [e] At 300 MHz in [D$_8$]THF. [f] At 300 MHz in CS_2–$CDCl_3$ (1:1).

Our previous study on the synchrotron X-ray diffraction experiment for a single crystal of an open-cage fullerene derivative[17] encapsulating H_2 clearly revealed that the electron density of the H_2 molecule is highest at the center of the fullerene cage.[18] The NMR resonance of the encapsulated H_2 molecule also gives direct information about the intensity of the magnetic field at the center of the C_{60} cage. Thus, the NMR chemical shift of the encapsulated H_2 molecule inside the C_{60} cage should have correlation with the NICS value calculated at the center of the corresponding empty C_{60} cage. The NICS values at the center of the C_{60} cages were calculated at the B3LYP/6-311G(d,p) level of theory for structures of a series of neutral and ionic C_{60} derivatives without a H_2 molecule, optimized at the B3LYP/6-31G(d) level, as shown in Table 1. As expected, when the experimentally observed chemical shifts of encapsulated H_2 are plotted against the corresponding NICS values at the center of empty C_{60} cages, a linear relationship is clearly recognized (Figure 5). In addition, a similar relation is also found between the NICS values and calculated chemical shifts of encapsulated H_2 molecules at the same level of theory. These data indicate that the ^{1}H NMR chemical shift of the encapsulated H_2 molecule serves as an excellent probe for the magnetic field at the center of the C_{60} cages, as has been observed for ^{3}He,[3b] and, thus, for the aromaticity of the conjugated π systems of the fullerenes. As judged from the linear relationship, the encapsulated H_2 molecule does not have specific electronic interactions with the C_{60} cage even when it is positively or negatively charged. Hence, the chemical shift of the H_2 molecule inside the C_{60} cages is a good criterion for the validity of NICS calculations, exactly as ^{3}He has been used for that reason.[1g]

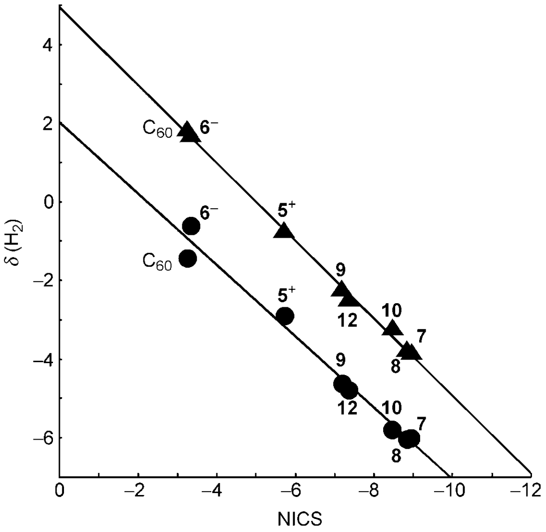


Figure 5. The experimental chemical shifts (●) and calculated chemical shifts of the encapsulated H_2 (▲), plotted against the NICS values at the center of the cages of a series of empty C_{60} derivatives.

Conclusions

In this work, we demonstrated that the dichloromethyl–C_{60} cation and the 1-octynyl–C_{60} anion encapsulating a H_2 molecule exhibit ^1H NMR signals at low magnetic fields as compared to the corresponding neutral derivatives. The magnetic fields inside the C_{60} cages bearing the positive or negative charges were interpreted based on the results of density functional calculations. According to the linear relationship between experimental chemical shifts of the encapsulated H_2 molecule and the NICS values at the center of the corresponding empty C_{60} cages, $H_2@C_{60}$ is shown to be useful as an NMR probe for the spherical aromaticity not only for the neutral C_{60} derivatives but also for the ionic C_{60} derivatives as well.

Experimental Section

General

The ^1H and ^{13}C NMR measurements were carried out on Varian Mercury 300 and JEOL AL-400 instruments, and the chemical shifts are reported in ppm from tetramethylsilane. UV/Vis spectra were recorded on a Shimadzu UV-3150 spectrometer. IR spectra were taken with a Shimadzu FT-IR-8600 spectrometer. FAB mass spectra were recorded on a JEOL Mstation JMS-700. APCI mass spectra were measured on a Finnigan-MAT TSQ 7000 spectrometer. The high-pressure liquid chromatography (HPLC) was performed by use of a Cosmosil Buckyprep column (4.6 mm × 250 mm) for analytical purpose. Fullerene C_{60} was purchased from Matsubo Co. Fullerene C_{60} encapsulating a H_2 molecule, $H_2@C_{60}$, was synthesized as reported previously.[7,8] All other reagents were of the reagent grade obtained commercially.

Synthesis

H_2@**7**: To a solution of $H_2@C_{60}$ (occupation level of 9%; 51 mg, 0.071 mmol) in dry $CHCl_3$ (50 mL) was added aluminum(III) chloride (940 mg, 7.1 mmol) at room temperature. The mixture was stirred for 70 min and quenched by the addition of cold water (50 mL). The product was extracted with CS_2 and the organic layer was washed with a 10% aqueous solution of $NaHCO_3$ (50 mL) and with water (50 mL) and dried over $MgSO_4$. Evaporation of the solvent gave a dark brown solid, which was dissolved in ODCB (4.5 mL). This solution was subjected to preparative HPLC using Cosmosil 5PBB columns (two directly connected columns, 20 mm × 250 mm, with ODCB as a mobile phase; flow rate: 3.0 mL min^{-1}) to give H_2@**7** (36.2 mg, 0.043 mmol, 61%) as a dark brown solid. ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta = 6.97$ (s, 1 H), −6.00 ppm (s, 0.18 H). Reported data for **7**: ^1H NMR (270 MHz, CS_2–$CDCl_3$ (2:1)): $\delta = 6.98$ ppm (s).[11]

H_2@**8**: To a CS_2 solution (45 mL) of H_2@**7** (occupation level of 9%; 30.9 mg, 0.038 mmol) was added silica gel (230–400 mesh, 17 g), and the solvent was removed under reduced pressure. The residual silica gel powder, on which H_2@**7** was adsorbed, was added to the top of a chromatography column (25 mm × 400 mm) filled with silica gel (230–400 mesh). The column was eluted with toluene (flow rate: 30 mL min^{-1}). The fraction containing the major component was collected and evaporated under reduced pressure to give fullerenol H_2@**8** (18.1 mg, 0.022 mmol, 60%) as a dark brown solid. ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta =$ 6.96 (s, 1 H), 4.10 (s, 1 H), −6.03 ppm (s, 0.18 H). Reported data for **8**: ^1H NMR (400 MHz, CS_2–$CDCl_3$ (4:1)): $\delta = 6.94$ (s, 1 H), 4.01 ppm (s, 1 H).[11]

Generation of H_2@**5**$^+$: To a brown solid of H_2@**8** (occupation level of 5%; 3.0 mg, 0.0036 mmol) was added triflic acid (0.8 mL) dropwise at room temperature. The mixture was sonicated to give a reddish purple solution. This was subjected to an NMR measurement using [D$_{12}$]cyclohexane as an external standard. ^1H NMR (400 MHz, CF_3SO_3H): $\delta = 6.44$ (s, 1 H), −2.89 ppm (s, 0.10 H). Reported data for **5**$^+$: ^1H NMR (400 MHz, CF_3SO_3H): $\delta = 6.44$ ppm (s).[11]

H_2@**9**: To a brown suspension of H_2@**7** (occupation level of 5%; 19.7 mg, 0.023 mmol) in THF (25 mL) was added 1.6 N *n*BuLi in hexane (15 µL, 0.024 mmol) at −15 °C under argon. After being stirred for 2 h, the mixture was treated with excess trifluoroacetic acid to give a brown suspension. To the suspension was added toluene (30 mL), and the resulting brown solution was washed with a saturated aqueous solution of $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to give a residual brown solid, which was dissolved in ODCB (5 mL). This solution was subjected to preparative HPLC using Cosmosil 5PBB columns (two directly connected columns, 20 mm × 250 mm, with ODCB as a mobile phase; flow rate: 3 mL min^{-1}) to give H_2@**9** (4.4 mg, 23%) as a brown solid. UV/Vis (cyclohexane): λ_{max} ($\log \varepsilon$) = 211 (4.74), 255 (4.58), 310 (4.11), 430 nm (3.20); ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta = 7.34$ (s, 1 H), 6.98 (s, 1 H), −4.62 ppm (s, 0.10 H); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$ (3:1)): $\delta = 152.70$, 149.36, 146.49, 146.33, 146.18, 145.99 (2), 145.76, 145.39, 145.32, 145.21, 145.18, 145.10, 144.56, 144.06, 142.96, 142.53, 142.39, 142.22, 141.96, 141.84, 141.52, 141.46, 140.99, 140.30, 139.74, 138.09, 136.06, 130.27, 127.34, 80.48, 72.80, 55.85 ppm; IR (KBr): $\tilde{\nu} = 1515$, 1429, 1215, 1186, 1064, 840, 801, 793, 779, 739, 732, 703, 583, 527 cm^{-1}; HRMS (+FAB): calcd for $C_{61}H_2Cl_2$ ($[M]^+$ of **9**): 805.9504; found: 805.9518.

H_2@**10**: To a mixture of indium(III) chloride (0.3 mg, 0.002 mmol) and H_2@**8** (occupation level of 9%; 7.0 mg, 0.0085 mmol) in dry ODCB (4 mL) was added chlorodiphenylsilane (5 µL, 0.026 mmol) under argon. The brown solution was stirred at 60 °C for 1.5 h. After cooling to room temperature, the reaction mixture was transferred to pentane (50 mL) with vigorous stirring to give brown precipitates. The precipitates, collected by centrifuge, were further washed with pentane (50 mL) twice. The solid was dissolved in CS_2 (20 mL) and the resulting solution was filtered through a filter paper. The filtrate was evaporated under reduced pressure to give H_2@**10** contaminated with 6% of H_2@**9** (5.3 mg, 0.0066 mmol, 75% (calculated H_2@**10**, 5.0 mg, 69%)) as a brown solid. H_2@**10**: UV/Vis (cyclohexane): λ_{max} ($\log \varepsilon$) = 210 (5.34), 257 (4.88), 324 (4.37), 448 nm (3.63); ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta = 7.03$ (s, 1 H), 6.45 (s, 1 H), −5.78 ppm (s, 0.18 H); ^{13}C NMR (75 MHz, [D$_4$]ODCB): $\delta = 153.30$ (2), 151.68, 149.24, 148.75, 148.71, 148.66, 148.28, 148.21, 147.25, 147.18, 147.16, 146.86, 146.79, 146.72 (2), 146.48, 146.15, 145.59, 145.44, 145.36, 145.28, 144.96, 144.84, 144.64, 144.51, 144.32, 144.30, 144.21, 144.12, 143.95, 143.91, 143.78, 143.61, 143.55, 143.52, 143.15, 143.13, 143.05, 143.03, 143.00, 142.64, 142.57, 142.52, 142.49, 142.36, 142.27, 142.06, 141.91, 141.84, 141.21, 141.11, 139.87, 139.71, 139.12, 138.71, 137.97, 137.60, 77.74, 65.38, 48.95 ppm; IR (KBr): $\tilde{\nu} =$ 1458, 1429, 1187, 833, 809, 788, 764, 751, 742, 729, 716, 704 cm^{-1}; HRMS (+FAB): calcd for $C_{61}H_2Cl_2$ ($[M]^+$ of **10**): 805.9504; found: 805.9483.

11: To a brown solution of **10** (38.2 mg, 0.047 mmol) in ODCB (20 mL) was added *t*BuOK (5.4 mg, 0.048 mmol) at room temperature under argon. After being stirred for 24 h, the mixture was treated with excess trifluoroacetic acid. The solution was then diluted with toluene (10 mL), and the resulting brown solution was washed with a saturated aqueous solution of $NaHCO_3$ (30 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to give a residual brown solid. This solid was dissolved in ODCB (6 mL), and the resulting solution was subjected to preparative HPLC using Cosmosil 5PBB columns (two directly connected columns, 20 mm × 250 mm, with ODCB as a mobile phase; flow rate: 3 mL min^{-1}) to give **11** (10.6 mg, 0.014 mmol, 29%) as a brown solid. UV/Vis ($CHCl_3$): λ_{max} ($\log \varepsilon$) = 260 (5.08), 326 (4.54), 428 (3.37), 486 (3.15), 686 nm (2.28); ^1H NMR (300 MHz, CS_2–C_6D_6 (5:1)): $\delta = 5.50$ ppm (s); ^{13}C NMR (100 MHz, CS_2–C_6D_6 (5:1)): $\delta = 146.60$, 145.56, 145.52, 145.50, 145.42, 145.36, 145.08, 145.05 (2), 144.94, 144.81, 144.78 (2), 144.60, 143.93, 143.89, 143.56, 143.49, 143.32 (2), 143.15, 142.81, 142.49, 142.48, 142.38, 141.57, 141.40, 139.70, 136.91, 128.54 (2), 75.24, 44.01 ppm; IR (KBr): $\tilde{\nu} = 1428$, 1186, 859, 819, 740, 711, 577, 561, 526, 500, 474, 448, 403 cm^{-1}; HRMS (+FAB): calcd for $C_{61}HCl$ ($[M]^+$): 767.9766; found: 767.9756.

H_2@**12**: A solution of 1-octynyllithium was prepared by adding 1.6 N *n*BuLi in hexane (0.83 mL, 1.33 mmol) to a stirred solution of 1-octyne (0.22 mL, 1.43 mmol) in THF (1.95 mL) at 0 °C and stirring for 30 min. To a vigorously stirred suspension of $H_2@C_{60}$ (occupation level of 9%; 16.3 mg, 0.023 mmol) in THF (16 mL) was added the solution of 1-octynyllithium dropwise at room temperature. A total of 0.20 mL

(0.090 mmol) of the solution was added over 1 min to give a dark green solution. The mixture was treated with excess trifluoroacetic acid to give a dark brown suspension, which was evaporated under vacuum. The residual solid was extracted with CS_2 (3 mL). The resulting brown solution was evaporated, and the residual brown solid was dissolved in toluene (2.5 mL). This solution was subjected to preparative HPLC using Cosmosil Buckyprep columns (two directly connected columns, 10 mm × 250 mm, with toluene as a mobile phase; flow rate: 4 $mL\,min^{-1}$) to give H_2@**12** (12.7 mg, 0.015 mmol, 68 %) as a brown solid. ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta = 6.96$ (s, 1H), 2.62 (t, 2H), 1.83 (m, 2H), 1.63 (m, 2H), 1.44 (m, 4H), 0.97 (t, 3H), −4.75 ppm (s, 0.18H). Reported data for **12**: ^1H NMR (300 MHz, CS_2–$CDCl_3$ (1:1)): $\delta = 6.96$ (s, 1H), 2.62 (t, 2H), 1.84 (m, 2H), 1.64 (m, 2H), 1.44 (m, 4H), 0.97 ppm (t, 3H).[12]

Generation of H_2@**6**$^-$: Compound H_2@**12** (occupation level of 9 %; 3.7 mg, 0.0045 mmol) was weighed into a glass tube (outer diameter: 5 mm) having an NMR tube and another branched glass tube as side arms. In the branched glass tube was placed a 0.023 M THF solution of *t*BuOK (0.22 mL, 0.0058 mmol) by the use of a long-needle syringe under argon. The whole system was connected to a vacuum line, and the solvent was evaporated. $[D_8]$THF (0.75 mL) was dried over Na and was then vacuum transferred onto *t*BuOK. The whole system was sealed under vacuum. The solution of *t*BuOK was mixed well with H_2@**12** to give a dark green suspension. The suspension was filtered through a cotton plug placed in the glass tube, and the dark green filtrate was poured into the NMR tube. The NMR tube was sealed off and subjected to NMR measurement. ^1H NMR (400 MHz, $[D_8]$THF): $\delta = 2.75$ (t, 2H), 1.93 (m, 2H), −0.60 ppm (s, 0.18H) (other signals of the 1-octynyl moiety overlapped with the signals of *t*BuOK, *t*BuOH, and THF).

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