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Methane in an Open-Cage [60]Fullerene

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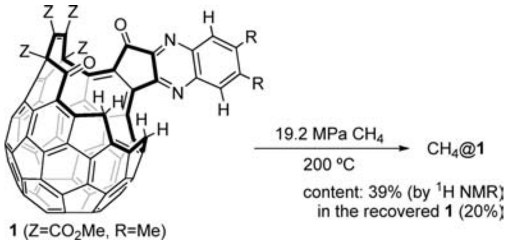
Among the many chemical modifications of fullerenes, carbon−carbon bond cleavage reactions are important because they result in the formation of "open-cage fullerenes," which can allow atoms and small molecules into the inner sphere of fullerenes.[1,2] The closing of the opening, after putting a chemical species inside, gives an endohedral fullerene compound.[3] Pure $H_2@C_{60}$ was recently synthesized using this strategy[4,5] in sufficient amounts to be used for a variety of fundamental studies.[6−8]

When a chemical species is moved through the hole in an open-cage fullerene, applicable substrates are mainly restricted by the size of the opening. We have expanded the size of an opening on C_{60} by successive cage scissions and synthesized the compound **1** (Scheme 1).[9,10] This has the largest opening of all the open-cage fullerenes made to date,[4,9−11] and we have achieved the encapsulations of H_2O, CO, N_2, NH_3, and noble gas atoms.[9,12−14] Here, we report the encapsulation of methane in **1** and the spectroscopic properties of a methane molecule in a chemically modified C_{60} cage. The kinetic diameter of methane is 0.38 nm. However, taking electrons of fullerene carbons into account, the effective inner space of C_{60} is estimated to be ~0.35 nm in diameter.[3] Therefore, methane might be one of the largest guests for C_{60}. Although some computational studies have been done for $CH_4@C_{60}$,[15−17] there have been no experimental reports to date.

In preliminary theoretical studies,[18] the required energy for the methane insertion through the opening of **1** was estimated to be +37.3 kcal/mol at the B3LYP/6-31G(d,p)//B3LYP/3-21G level (Figure 1a). It suggests that both high pressure and high temperature are essential, but insertion is possible. For the product $CH_4@$**1** (Figure 1b), the B3LYP calculation suggested repulsive destabilization, whereas the MPWB1K calculation predicted associative stabilization.[18,19] These trends are consistent with the calculations for $CH_4@C_{60}$.[15−17] Since the van der Waals attraction is an important part of the interaction, electron correlation must be included.

The encapsulation experiment was performed at 200 °C under 19.2 MPa of a methane gas using 1-methylnaphthalene as a solvent. Due to the high temperature, significant decomposition of **1** took place during the reaction. After purification by using silica gel chromatography, 20% of **1** was recovered. The fraction of $CH_4@$**1** in the recovered **1** was estimated to be 39% by ^{1}H NMR (see below). As in the case of $H_2@C_{60}$,[4] the fraction of $CH_4@$**1** could be enriched by further HPLC purification using a buckyprep column. The methane content was improved up to 66% after several repeated purifications.[18] At present, however, qualitative isolation of pure $CH_4@$**1** has not been achieved because of significant loss of the product in addition to the low recovery yield of **1**.

Scheme 1. Encapsulation of a Methane Molecule in **1**



The ^{1}H NMR spectrum of the purified **1** after the methane pressurization is shown in Figure 2. One sharp singlet assignable to CH_4 in **1** was observed at $\delta = -12.32$ ppm along with the known signal of $H_2O@$**1** ($\delta = -11.45$ ppm).[9] For a reference, the reported chemical shift of methane dissolved in $CDCl_3$ is $\delta = 0.23$ ppm.[20] This large upfield shift ($\Delta\delta = -12.5$ ppm) is caused by the magnetic shielding of the fullerene cage and is typical for the trapped atoms and molecules in fullerene derivatives. Also, it was well reproduced by the calculation ($\Delta\delta = -10.8$ ppm) at the B3LYP/6-31G(d) level.[18]

In an ordinary ^{13}C NMR spectrum, the CH_4 carbon in **1** could not be detected due to the low fraction of $CH_4@$**1**. However, the DEPT135 spectrum showed one downward signal at $\delta = -20.62$ ppm as shown in Figure 3. The reported chemical shift of methane dissolved in $CDCl_3$ is $\delta = -2.3$ ppm,[20] and the observed upfield shift ($\Delta\delta = -18.3$ ppm) was again reproduced by calculation ($\Delta\delta = -9.3$ ppm) as in the case of the CH_4 protons in ^{1}H NMR. Finally, the field-gradient HMQC spectrum showed a clear cross peak for these ^{1}H and DEPT135 NMR signals.[18] Thus, we identified these signals as the trapped CH_4 in **1**. The fraction of $CH_4@$**1** in recovered **1** was estimated from the integral value of the methane signal in

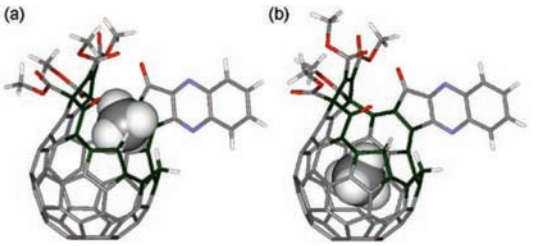


Figure 1. B3LYP/3-21G structures of (a) the transition state for the methane insertion into **1** (R = H) and (b) one rotational isomer of $CH_4@$**1**. Only methane molecules are shown by the space-filling representation (green, carbon atoms constituting the orifice of **1**; gray, carbon; white, hydrogen; blue, nitrogen; red, oxygen).

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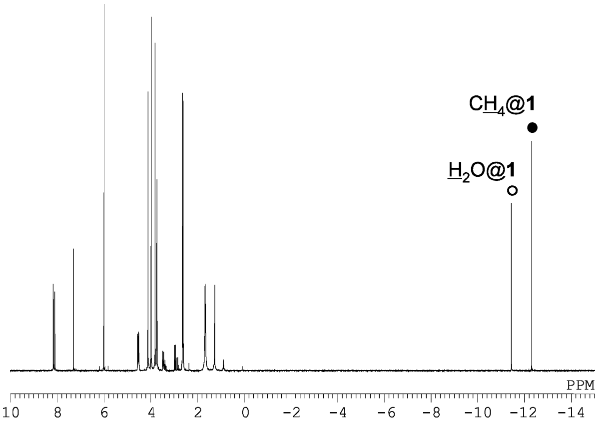

Figure 2. ^1H NMR spectrum of $CH_4@\mathbf{1}$ in 1,1,2,2-tetrachloroethane-d_2.

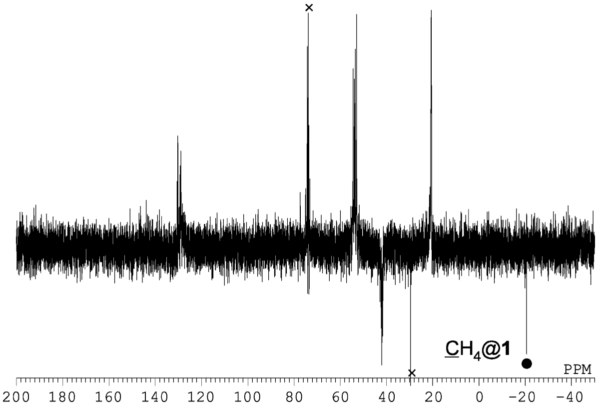

Figure 3. DEPT135 spectrum of $CH_4@\mathbf{1}$ in 1,1,2,2-tetrachloroethane-d_2. " × " indicates impurities derived from used solvents.

the ^1H NMR spectrum relative to the signal at $\delta = 8.15$ ppm assignable to one proton of the quinoxaline moiety in **1**. The sharp singlet signals of the guest CH_4 in both ^1H NMR and DEPT135 spectra suggest its free rotation in the NMR time scale, despite the narrow cavity of C_{60}.[18] Meanwhile, both methylene protons and carbons on the orifice of the host **1** showed detectable but small shifts in the ^1H and ^{13}C NMR spectra (≤ 0.2 ppm for each signal). These data suggest a small interaction between the trapped methane and **1**.

In other measurements,[18] the electrospray mass spectrum of $CH_4@\mathbf{1}$ showed the corresponding $[M + 16]$ ion peaks in the range $m/z = 1188-1190$ (Figure 4). Since the same peaks were also observed for oxidized **1** which formed during the measurement, total intensities of these ion peaks did not match with the fraction of $CH_4@\mathbf{1}$ estimated by ^1H NMR. In the IR spectrum, although a significant blue shift has been predicted for the methane C−H stretching vibrations of $CH_4@C_{60}$ in theory,[16] the trapped methane in **1** could not been identified because of its weak absorption in addition to low content of $CH_4@\mathbf{1}$. Also, no detectable change was observed in the UV/vis spectrum.

In summary, we succeeded in the encapsulation of a methane molecule in an open-cage C_{60} derivative for the first time and demonstrated that even methane can rotate freely in the C_{60} cavity. Future work, especially isolation of the pure product, will provide additional and valuable information.

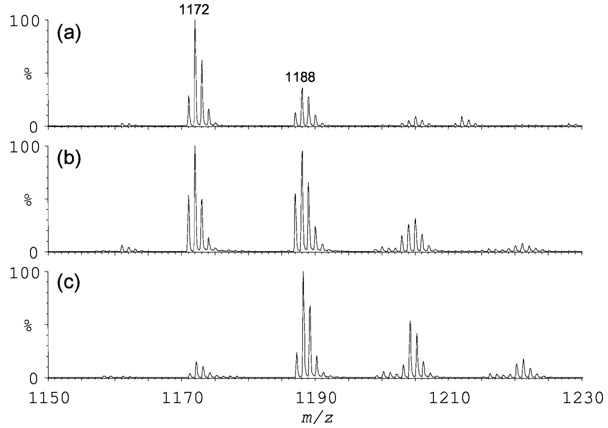

Figure 4. ES-MS spectra (negative ion mode) of (a) **1**, (b) $CH_4@\mathbf{1}$ (CH_4 content: 28%), and (c) $CH_4@\mathbf{1}$ enriched by HPLC (CH_4 content: 66%).

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Supporting Information Available: Experimental procedures, copies of spectra, and molecular modeling coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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