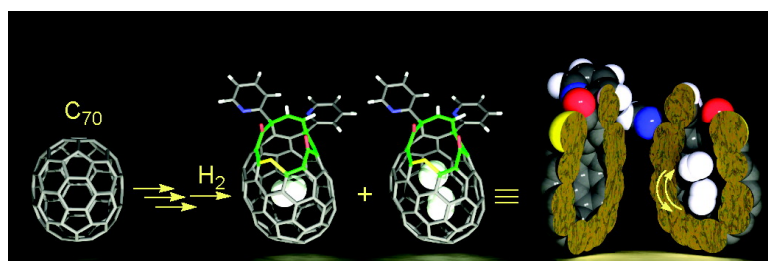


## Encapsulation and Dynamic Behavior of Two H Molecules in an Open-Cage C

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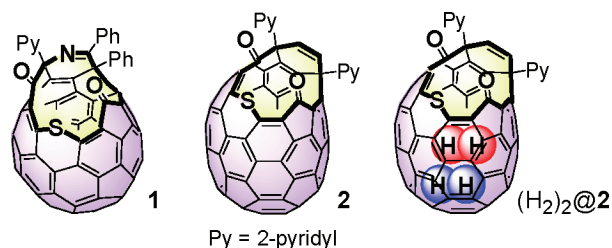
## Encapsulation and Dynamic Behavior of Two H<sub>2</sub> Molecules in an Open-Cage C<sub>70</sub>

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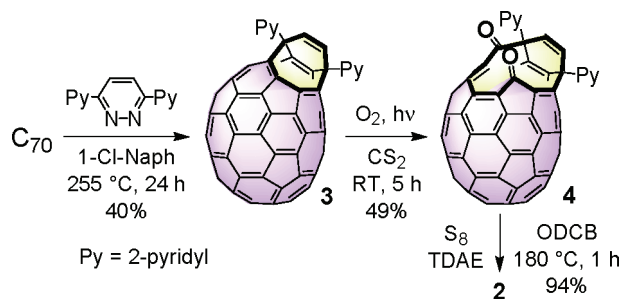
The molecular surgical approach is quite promising for the synthesis of yet-unknown endohedral fullerenes. This involves creation of an opening on the fullerene cage, insertion of a small guest through the opening, and closure of the opening with retention of the guest inside the fullerene.<sup>1,2</sup> So far, several open-cage C<sub>60</sub> derivatives, which can encapsulate He,<sup>3,4</sup> H<sub>2</sub>,<sup>3,5,6</sup> H<sub>2</sub>O,<sup>7</sup> or CO<sup>8</sup> as a guest atom or molecule, have been reported. Since the inner space of C<sub>70</sub> is larger than that of C<sub>60</sub>, a possibility of encapsulation of more than one small molecule emerges.<sup>9</sup> However, examples of open-cage C<sub>70</sub> derivatives are quite limited,<sup>10</sup> probably due to the difficulty in synthesis and in characterization for their nonsymmetrical structures. Here we report the synthesis of an open-cage C<sub>70</sub> derivative, which is able to encapsulate two molecules of H<sub>2</sub>, together with studies on the dynamic behavior of the guest molecules.



Applying the similar procedure used for the synthesis of open-cage C<sub>60</sub> **1**,<sup>11</sup> open-cage C<sub>70</sub> **2** was synthesized in 18% total yield as shown in Scheme 1. A thermal reaction of C<sub>70</sub> with 3,6-di(2-pyridyl)pyridazine in 1-chloronaphthalene (1-Cl-Naph) gave open-cage C<sub>70</sub> **3** having an eight-membered ring opening in a one-pot reaction. The photooxidation of one of the C=C double bonds in **3** by irradiation with visible light afforded open-cage C<sub>70</sub> **4** having a 12-membered ring opening. Then, the insertion of a sulfur atom on the rim of the opening in **4** was achieved in the presence of tetrakis(dimethylamino)ethylene (TDAE) in *o*-dichlorobenzene (ODCB) to give **2**.<sup>12</sup> The structure of **2** was unambiguously determined by the single crystal X-ray analysis (Figure 1).<sup>12</sup>

The energies required for insertion of the first and the second H<sub>2</sub> molecules into **2** were calculated to be 31.2 and 31.0 kcal/mol at the B3LYP/6-31G\*\*//B3LYP/3-21G level of theory,<sup>3,13</sup> which are almost the same value calculated for **1** (31.1 kcal/mol),<sup>5a</sup> indicating that the opening size of **2** is almost the same as that of **1**. In contrast, the destabilization caused by encapsulation of two molecules of H<sub>2</sub> in **2** was +4.0 kcal/mol, which is smaller than that of **1** (+9.4 kcal/mol), suggesting the possibility of encapsulation of two H<sub>2</sub> molecules.

### Scheme 1



Treatment of **2** as a powder with high-pressure hydrogen gas (890 atm) at 230 °C resulted in a total of almost 100% encapsulation of H<sub>2</sub> molecule(s) as judged from the <sup>1</sup>H NMR shown in Figure 2. A sharp singlet signal appeared at exceptionally high field (−16.51 ppm), in addition to a small signal at −15.22 ppm. The former is attributed to the signal of a single H<sub>2</sub> molecule inside **2** being subjected to a strong shielding effect of the fullerene cage. Then the latter can be assigned to the signal of two molecules of H<sub>2</sub> inside **2**, from the analogy of the <sup>3</sup>He NMR signal of two atoms of <sup>3</sup>He encapsulated in a C<sub>70</sub> cage of a Bingel addition product, which is slightly downfield shifted as compared with that of only one <sup>3</sup>He atom in the C<sub>70</sub> cage.<sup>9</sup> From the integrated peak areas, the yield of H<sub>2</sub>@**2** and (H<sub>2</sub>)<sub>2</sub>@**2** was determined as 97% and 3%, respectively.

The H<sub>2</sub>@**2** complex was quite stable at room temperature. However, the H<sub>2</sub> molecule escaped upon heating above 160 °C. The escaping rates at 160, 170, 180, and 190 °C followed first order kinetics. From the Arrhenius plot, the activation parameters were determined as E<sub>a</sub> = 33.8 ± 0.1 kcal/mol, ΔG<sup>‡</sup> (25 °C) = 35.3 ± 0.1 kcal/mol, ΔH<sup>‡</sup> = 32.9 ± 0.1 kcal/mol, and ΔS<sup>‡</sup> = −8.2 ± 0.2 cal/mol·K. Upon MALDI-TOF MS spectroscopy, the molecular ion peak corresponding to H<sub>2</sub>@**2** was clearly observed at *m/z* 1113

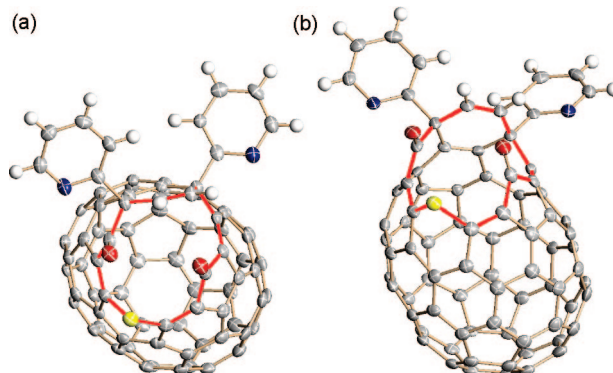
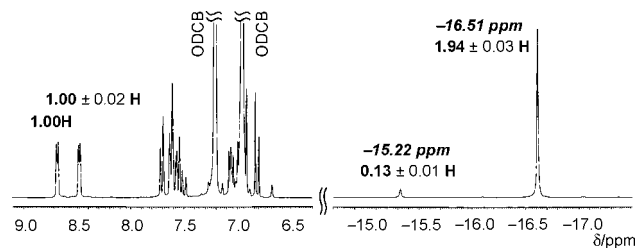


Figure 1. X-ray structure of open-cage C<sub>70</sub> **2**: (a) top view and (b) side view.

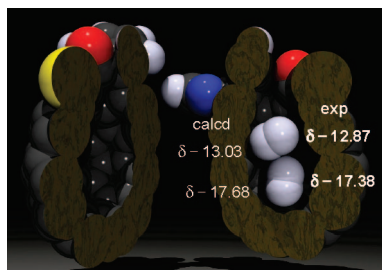
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**Figure 2.**  $^1\text{H}$  NMR (300 MHz, ODCB- $d_4$ ) spectrum of the mixture of  $(\text{H}_2)_2@2$  and  $\text{H}_2@2$  (3:97). The integrated peak areas are shown with reference to the peak area of the signal for 6-pyridyl proton at  $\delta$  8.68.



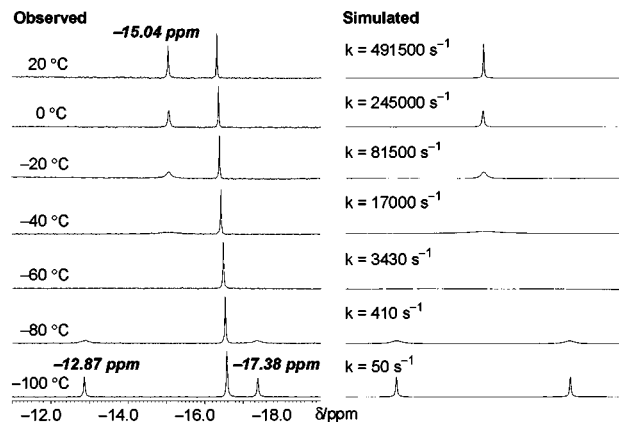
**Figure 3.** Cut-out view of the space-filling model of  $(\text{H}_2)_2@2$  calculated at the B3LYP/6-31G\* level of theory.

$(M + 1)$  with the laser power slightly above the threshold for ionization. When the stronger laser power was used, the molecular ion peak decreased and instead, the peaks at  $m/z$  840 and 842 corresponding to  $\text{C}_{70}$  and  $\text{H}_2@C_{70}$  appeared in a 2:1 ratio. This result indicates that the opening of  $\text{H}_2@2$  can be closed with retention of the encapsulated  $\text{H}_2$  molecule by laser irradiation in gas-phase, as was also observed for  $\text{H}_2@1$ .<sup>5a</sup>

In the  $^1\text{H}$  NMR spectrum shown in Figure 2, only one signal was observed for the two encapsulated  $\text{H}_2$  molecules of  $(\text{H}_2)_2@2$ , indicating a rapid exchange of their relative positions at the NMR time scale. If such an exchange is slowed down, the two  $\text{H}_2$  molecules should exhibit different NMR chemical shifts; the  $\text{H}_2$  molecule near the bottom would suffer stronger shielding effect by the fullerene cage than the other one. Calculated chemical shifts (GIAO-B3LYP/6-311G\*\*//B3LYP/6-31G\*) were  $-17.68$  ppm and  $-13.03$  ppm for the  $\text{H}_2$  molecule near the bottom and for the other one, respectively (Figure 3). The averaged value of them ( $-15.36$  ppm) as well as the calculated value for  $\text{H}_2@2$  ( $-16.43$  ppm) are in good agreement with the observed values ( $-15.22$  and  $-16.51$  ppm, respectively).

The content of double-hydrogen complex  $(\text{H}_2)_2@2$  was only 3% and could not be increased by changing experimental conditions.<sup>12</sup> However,  $(\text{H}_2)_2@2$  was found to be enriched by the use of recycling HPLC (Buckyprep/toluene).<sup>12</sup> After enrichment, the molar ratio of  $(\text{H}_2)_2@2$  to  $\text{H}_2@2$  became 1:2 based on the integration of two NMR signals at  $-15.22$  and  $-16.51$  ppm at  $20^\circ\text{C}$ .

As shown in Figure 4, when the temperature was lowered to  $-40^\circ\text{C}$ , the signal at  $-15.22$  ppm became broadened while another signal corresponding to  $\text{H}_2@2$  remained unchanged. The signal for  $(\text{H}_2)_2@2$  disappeared at  $-60^\circ\text{C}$  and then reappeared as two new peaks at  $-80^\circ\text{C}$ , which became sharp at  $-100^\circ\text{C}$  with the chemical shift of  $-12.87$  and  $-17.38$  ppm. These values are supported by DFT calculations (Figure 3). This dynamic behavior apparently corresponds to the positional exchange of two  $\text{H}_2$  molecules encapsulated inside **2**. From the line-shape analysis and resulting Arrhenius plot, the activation parameters were determined as  $E_a = 8.0 \pm 0.2$  kcal/mol,  $\Delta G^\ddagger$  ( $25^\circ\text{C}$ ) =  $9.5 \pm 0.2$  kcal/mol,  $\Delta H^\ddagger = 7.6 \pm 0.2$  kcal/mol, and  $\Delta S^\ddagger = -6.4 \pm 0.7$  cal/mol·K. The results



**Figure 4.** Low-temperature  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2\text{-CD}_2\text{Cl}_2$  (4:1)) spectra of the mixture of  $(\text{H}_2)_2@2$  and  $\text{H}_2@2$  (1:2): (a) observed spectra and (b) simulated spectra with estimated rate constants.

shown above clearly demonstrate that two molecules of  $\text{H}_2$  were encapsulated inside **2** although the molecular ion peak for  $(\text{H}_2)_2@2$  was not observed in the MALDI-TOD MS analysis.

In summary, new open-cage  $\text{C}_{70}$  **2** was synthesized and was shown to encapsulate a  $\text{H}_2$  molecule in high yield. Moreover, two molecules of  $\text{H}_2$  were introduced into **2**, and the dynamic behavior, that is, the positional exchange, of two  $\text{H}_2$  molecules was observed. Closure of the opening in **2** would afford novel endohedral fullerenes,  $\text{H}_2@C_{70}$  and  $(\text{H}_2)_2@C_{70}$ , which is now in progress.

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**Supporting Information Available:** Complete ref 13, experimental procedures, spectroscopic data, the results of calculations, and X-ray crystallographic data for **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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