

A Bowl-Shaped Fullerene Encapsulates a Water into the Cage

Sho-ichi Iwamatsu,^{*,†} Takashi Uozaki,[†] Kaoru Kobayashi,[‡] Suyong Re,[‡] Shigeru Nagase,[‡] and Shizuaki Murata^{†,§}

Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan, Institute for Molecular Science, Okazaki 444-8585, Japan, and CREST, Japan Science and Technology Agency (JST)

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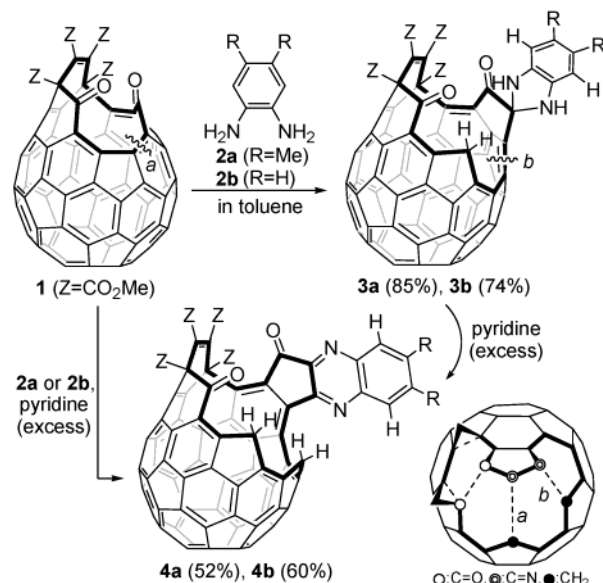
Endohedral complexes of fullerenes have been expected to constitute new fields of material science and technology,¹ but the impracticality of their preparations has remained a fundamental problem. Based on this standpoint, the controlled carbon–carbon bond cleavage of the fullerene cage has received much attention, because the resulting open-cage derivatives allow small molecules access into their internal cavities.² Recently, such encapsulations of helium and molecular hydrogen were achieved independently by the research groups of Rubín and Komatsu.^{3,4} However, due to their narrow orifice, these methods required drastic conditions even in the case of smallest molecules. It is necessary for the encapsulation under mild and practical conditions that the efficient methods for the ring expansion of the initially generated orifice be developed.

Recently, we reported the ring expansion of the 12-membered ring in the diketone derivative of C₆₀ (**1**) using the regioselective hydroamination reactions with aromatic hydrazines.^{5,6} Although the orifice in the product was still not wide enough for mild molecular encapsulation, this result prompted us to apply multifunctionalized reagents for further intramolecular cage scission. Herein, we report the syntheses of novel bowl-shaped fullerene derivatives by the sequential carbon–carbon bond scissions of **1**, and evidence of the first spontaneous encapsulation of molecular water in the product.

The reaction of **1** with 4,5-dimethyl-1,2-phenylenediamine (**2a**) proceeded at room temperature in toluene to give a dark green solid (**3a**) in 85% yield.⁷ When the same reaction was carried out at 60 °C, the color of the solution gradually changed from green to dark red, and a reddish-orange solid (**4a**) was obtained in 45% yield as an exclusive product. The transformation from **3a** to **4a** was promoted by excess diamine or base, and **4a** was obtained in 52% yield in the presence of an excess amount of pyridine. In the same manner, **3b** and **4b** were prepared in 74% and 60% yields, respectively.

The structures of the products **3** and **4** given in Scheme 1 were assigned by spectral analyses selectively depicted below.⁷ The ES-mass spectrum of **3a** showed a molecular ion peak at *m/z* 1172 indicating that the product was exactly the 1:1 adduct of **1** and **2a**. In the ¹H NMR spectrum, a pair of methylene protons was observed at δ 4.16 and 3.87 ppm (*J* = 19 Hz) together with two labile NH protons at δ 8.09 and 4.63 ppm. The ¹³C NMR and DEPT135 spectra showed one methylene carbon (δ 39.33 ppm) and one quarternary carbon (δ 73.67 ppm) with two ketone carbonyl carbons (δ 190.55 and 181.70 ppm).⁷ The chemical shift of the former showed good agreement with that of the product obtained by the reaction of **1** with phenylhydrazine,^{6a} and the latter was consistent with a carbon substituted by two amino groups. Therefore, we concluded that the C–C bond scission specifically occurred at

Scheme 1. Reactions of **1** with Phenylenediamines^a



^a A schematic model of compound **4** is shown at the bottom-right.

position “a” in the structure of **1** and that **3a** has the 16-membered orifice shown as bold lines in Scheme 1.

For **4a**, the ES-mass spectrum showed the same molecular ion peak at *m/z* 1172 as did **3a**. In ¹H and ¹³C NMR spectra, there were two sets of broadened signals of methylene groups [δ 4.56, 4.53, 3.48, and 2.98 ppm (each 1H) in ¹H NMR, δ 41.98 and 41.56 ppm in ¹³C NMR] confirmed by DEPT135 and HMQC spectra. These data suggest that the additional cage scission took place in an intramolecular fashion. In the ¹H NMR spectrum, two aromatic protons derived from **2a** showed significant downfield shifts relative to **3a** (ca. 1 ppm) in accordance with the formation of the quinoxaline structure. The sp³ character of the nitrogen atoms in **3** should change to sp² in **4**, and the ¹⁵N NMR spectrum supported this transformation (**3b**, δ 107.02, 105.11 ppm; **4b**, δ 328.02, 313.67 ppm).⁷ Thus, we concluded that the second C–C bond cleavage occurred at the neighboring position “b” in **3** to give **4** having two methylene carbons and the quinoxaline moiety around the orifice (Scheme 1).

Compound **4** has a 20-membered ring orifice of 6.5 Å along the long axis and 4.2 Å along the short axis at the B3LYP/6-31G(d) level (Figure 1a).⁸ One of the five-membered rings in C₆₀ completely deviates from the spherical surface by the triple bond-scission shown as the schematic model in Scheme 1. The size of the orifice seemed large enough to pass a molecular hydrogen, and it is known that the encapsulated hydrogen molecule in the open-cage C₆₀ derivatives appeared in the range of –5 to –8 ppm due to the shielding effect of the fullerene cage.^{3,4} Thereupon, we measured ¹H NMR again in a wide range for the encapsulation

[†] Nagoya University.

[‡] Institute for Molecular Science.

[§] CREST, Japan Science and Technology Agency (JST).

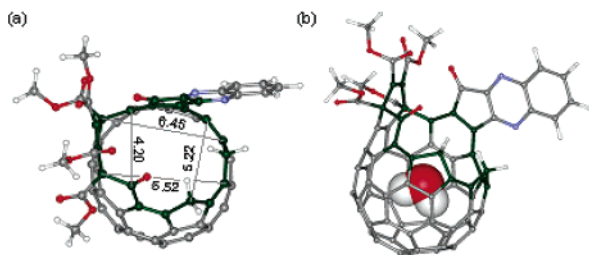


Figure 1. (a) Top view of compound **4b** (without water) at the B3LYP/6-31G(d) level. Selected atom distances are shown in angstroms. Bottom atoms are omitted for clarity. (b) The optimized structure of $\text{H}_2\text{O}@4\text{b}$ at the B3LYP/6-31G(d) level. The encapsulated water molecule is shown as the CPK model.

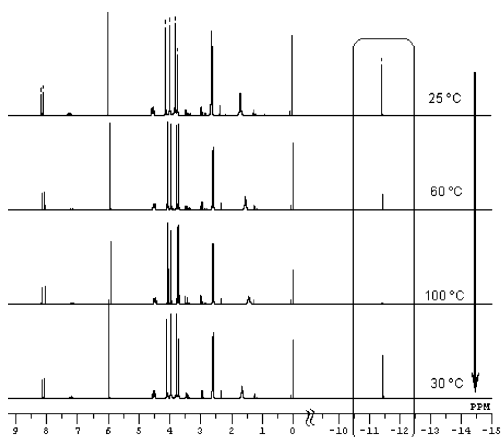


Figure 2. Variable-temperature NMR spectrum of **4a** in 1,1,2,2-tetrachloroethane- d_2 (25, 60, 100, then 30 °C).

experiments and found a missed signal in **4a**. As shown in Figure 2, there already existed a sharp singlet signal at $\delta -11.4$ ppm without any pressurization.

We could identify the identity of this unexpected signal as one molecule of water on the basis of the following. This signal disappeared by treatment with D_2O , and we first omitted the possibility that the magnetically shielded NH proton exists in **4**. The N–H coupling was not observed in the ^1H NMR spectrum, and the signal appeared as a singlet again for the ^{15}N enriched **4b**. Second, elemental analyses after drying under reduced pressure did not fit the structures **4**, but matched the monohydrate formulas of **4**.⁷ The latter indicates that the trapped water molecule is tightly bound with **4** and cannot easily escape in the solid state.

In the ^1H NMR spectrum, the integral value of this signal was approximately 1.5 relative to the signals assigned to **4** at ambient temperature. It was dissimilar to the monohydrate structure, and the signal showed temperature-dependent behavior. As shown in Figure 1, the signal intensity decreased with elevating measurement temperature, but recovered its initial intensity by cooling back to ambient temperature. The water content of the NMR solvent also affected the signal intensity. It decreased to 0.8 when using distilled deuterium solvent from P_2O_5 . Furthermore, irradiation of the signal at $\delta -11.4$ ppm in the differential NOE measurement resulted in the irradiation transfer and the appearance of the signal at $\delta 1.5$ ppm assigned to the residual water in the solvent. In the ES mass spectrum, on the other hand, the molecular ion peak corresponding to the monohydrate was not detected. These results indicate that, in solution and a gas phase, water can escape from **4** and is in equilibrium with the molecules outside the cage.

Taking into account the strong shielding effects of fullerenes,^{1,3,4} the signal might be reasonably assigned to the endohedral structure ($\text{H}_2\text{O}@4$) as shown in Figure 1b. To date, there is no experimental example of the endohedral water complex of C_{60} ,⁹ although the inside cavity of C_{60} (4 Å in diameter) is wide enough to encapsulate one molecule of water. Further, the calculated ^1H NMR chemical shifts for $\text{H}_2\text{O}@4\text{b}$ by using the GIAO method at the B3LYP/6-31G(d) level accurately reproduced the observed value ($\delta -11.59$ and -11.51 ppm), while the other structure, an exohedral complex with the hydrogen bonding to the functionalized moieties, could not computationally emulate it at all.⁷

In summary, we demonstrated that the novel bowl-shaped fullerene derivative prepared by the regioselective multiple cage scissions of C_{60} forms the first endohedral water complex. Although the conversion of $\text{H}_2\text{O}@4$ to $\text{H}_2\text{O}@C_{60}$ seems far from easy according to the initial concept,² these derivatives allow reversible molecular storage unlike the formal endohedral fullerenes. Further investigations regarding the limitations and mechanism of the encapsulation, and the properties of the molecule inside the open-cage fullerene derivatives, are now in progress.

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Supporting Information Available: Experimental procedures, characterization data, copies of ^1H , ^{13}C NMR spectra, and molecular modeling coordinates (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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