A Cage with Fullerene End Caps

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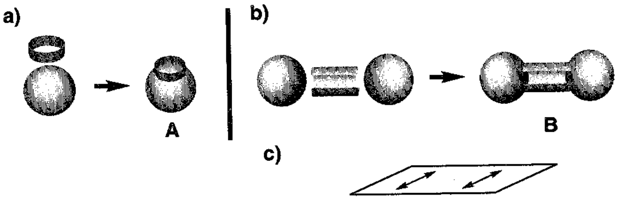
Received August 25, 1999
Revised Manuscript Received January 25, 2000

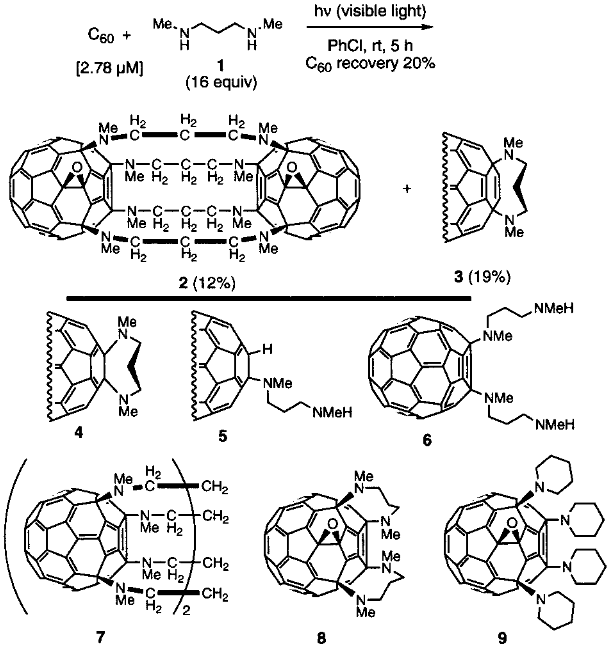
[60]Fullerene is a molecule bearing multiple electrophilic sites, which often generates serious problems of consecutive multiple reactions. This unique property may be exploited, however, as an asset to the rapid construction of large nanoscale structures, if the selectivity of the multiple reaction can be controlled. To this end, we previously developed a synthetic strategy to construct a concave crown-like structure on the fullerene molecule (**A**, the crown here representing five aryl groups) through 5-fold addition of an aryl Grignard reagent to the [5]radialene moiety of [60]-fullerene (Scheme 1a).[1] Execution of such a strategy twice with a bifunctional tethering reagent (represented as a tube in Scheme 1b) would rapidly create a cage structure **B** bearing two fullerene end caps. We report the application of such a strategy to the coupling of four molecules of a 1,3-diaminopropane **1** with two [60]fullerene molecules (Scheme 2). The cage compound **2** thus produced has a longitudinal size as large as 2.1 nm. Although the far-separated fullerene ends have no ground-state electronic interaction with each other, strong hypochromic effect as the result of dipole interaction of parallel transition moments (Scheme 1c) has been observed in the UV/vis spectrum.

We have developed a simple experimental procedure for the synthesis of the cage compound **2** through reexamination of Hirsch's procedure reported for a monomeric congener (**9**).[2] Thus, a mixture of [60]fullerene (100 mg, 0.139 mmol) and 16 equiv of *N,N'*-dimethyl-1,3-diaminopropane **1** (266 μL, 2.22 mmol) in air-saturated[3] chlorobenzene (25 mL) was stirred at 21 °C under visible light irradiation for 5 h (Scheme 2).[4] The reaction mixture was poured onto a silica gel column and eluted with toluene/ethyl acetate (9:1) to obtain only three compounds, the cage **2** (12% isolated yield), the 1,4-diaminoadduct **3** (19%), and recovered [60]fullerene (20%). Notably, in the crude product mixture, we found no other isolable products ($<$1%) which would have been detected with the analytical conditions employed in the present studies.[5] For instance, we could not detect any of the possible intermediates and isomers such as 1,2-diaminoadduct **4**[6] that was previously claimed to form in a similar reaction,[7] monoadduct **5**, bisadduct **6**, nor-epoxide fulvene **7** and monomeric analogue **8**.

Scheme 1



Scheme 2



Only partial structural assignment of **2** was possible by spectral analyses. The ^{1}H NMR spectrum showed two methyl singlets (δ 2.84 and 2.93 ppm) indicating two nonequivalent *N*-methyl groups,[8] and the IR absorption at 860 cm^{-1} suggested the presence of epoxide functionality. The largest positive mass signal detected by the atmospheric pressure chemical ionization (APCI) mass spectroscopy (2-propanol/toluene = 3:7, Figure 1) showed the *m/z* value of 921 (vide infra), which corresponds to $C_{60}[NMe(CH_2)_3NMe]_2\cdot H^+$ (**6**-H). The spectral data suggested the product to be either the monomer **8** or the dimer **2** (or its structural isomer).

The single-crystal X-ray analysis of orange crystals (recrystallized from CHCl$_3$) unequivocally established the dimeric structure **2** (Figure 2)[9,10] which has a near C_{2v} symmetric structure. The ORTEP diagram shows that two fullerene moieties are connected by four diamine tethers, which are not fully aligned to achieve perfect C_{2v} symmetry due to steric reasons.[11] The solvent accessible surface of **2** (Figure 3 inset) indicates that the cage

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(1) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850−12851; Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912−7913; Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285−8286.

(2) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023−2024.

(3) Bubbling of molecular oxygen (1 mL/min) to the reaction lowered the yield.

(4) The presence of both light and molecular oxygen is absolutely necessary for the reaction. Thus, the reaction of **1** with [60]fullerene in chlorobenzene under air in total darkness resulted in 87% recovery of fullerene even after 6 days, and the same reaction in the absence of oxygen (several freeze/thaw cycles) under visible light irradiation resulted in 95% recovery of the fullerene after 20 h.

(5) The progress of the reaction was monitored by HPLC equipped with a BuckyPrep column (eluted: toluene/hexane = 8/2 with anthracene internal standard), and the whole product mixture was chromatographically separated and scrutinized.

(6) The structure assignment of **3** relied upon the symmetry assignment by ^{13}C NMR spectrum which shows C_S symmetry as expected for **3** (and not for **4**, which should show C_{2v} symmetry).

(7) We found the 1,4-diaminoadduct **3** exhibits the same ^{1}H NMR spectra previously reported for **4** (the key ^{13}C NMR was not recorded in this previous work). Kampe, K. -D.; Egger, N. *Liebigs Ann.* **1995**, 115−124.

(8) The very low solubility of **2** prevented the ^{13}C NMR measurement.

(9) Diffraction study was carried out by an imaging plate method with MacScience DIP-2030 diffractometer. Crystal data of $\mathbf{2}\cdot 2CHCl_3$: monoclinic, $P2_1/a$: $a = 19.827$ Å, $b = 21.768$ Å, and $c = 21.155$ Å, $\beta = 100.26°$, $V = 8984.6$ Å^3; $Z = 4$; μ(Mo Kα) = 2.65 mm^{-1}; λ(Mo Kα) = 0.7107 Å; $T = 298$ K; 15881 reflections measured, 7790 observed ($I > 3.00\,\sigma(I)$); $\theta_{\max} = 24.76°$; 1387 parameters; $R = 0.198$; $Rw = 0.214$. The structure was solved by direct method (maXus). The high *R* value is due to disorder of solvent molecules and insufficiency of the number of wide-range reflections. See Supporting Information for details of the crystallographic data.

(10) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583−586; Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J.-F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925−4947.

(11) Molecular mechanics study (MM2*) on the cage fullerene showed that the steric trans-annular effect disturbs parallel alignment of all four methylene tethers.

10.1021/ja993091c CCC: $19.00

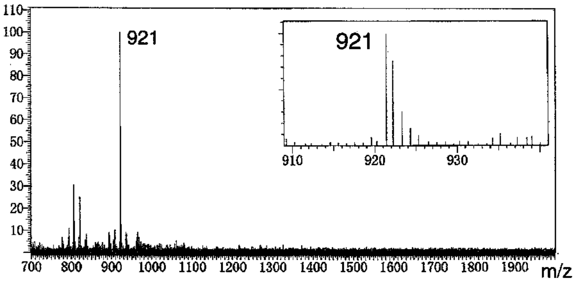

Figure 1. APCI mass spectra of **2**, showing a predominant signal corresponding to (**6**-H)$^+$.

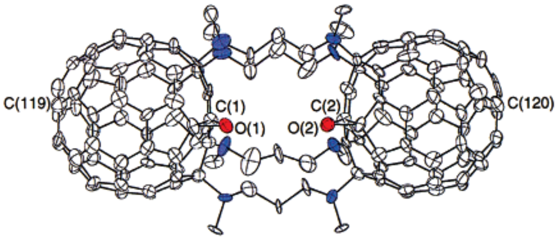

Figure 2. Crystal structure of **2** (ORTEP diagram). Thermal ellipsoids are drawn at the 50% level. Sovent molecules in the unit cell are omitted for clarity. Nitrogen atoms and oxygen atoms are colored in blue and red, respectively. Selected atom distances (Å) and dihedral angle: O(1)−O(2) 4.47(3); C(1)−C(2) 5.82(3); C(119)−C(120) 19.27(3): O(1)−C(1)−C(2)−O(2) = −0.9°.

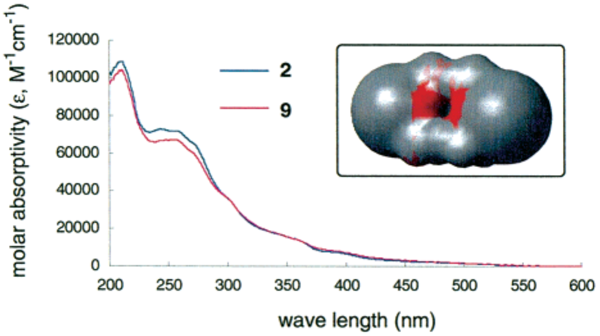

Figure 3. UV−visible spectra of dimeric compound **2** and monomeric **9** in cyclohexane ($c = 9.98 \pm 0.02$ and 9.97 ± 0.04 μM, respectively). Two spectra (including molar absorptivity) are almost identical throughout the measured range (200−800 nm). **2**: ϵ_{max} (λ_{max}) 1.1×10^5 (210 nm), 7.2×10^4 (255 nm) M^{-1}•cm^{-1}, **9**: ϵ_{max} (λ_{max}) 1.0×10^5 (210 nm), 6.7×10^4 (255 nm) M^{-1}•cm^{-1}. Inset: Crystal structure of **2** presented with solvent accessible surface showing a small opening of the cavity.

has an opening on the side of the epoxide and a cavity large enough to hold a small molecule.[12]

The present reaction must involve a series of complicated reversible and irreversible steps involving light, oxygen, amine, and fullerene. The notable feature of the present reaction is the formation of only two products, **2** and **3,** without giving traces of any isomers or intermediates (cf. Scheme 2). Molecular mechanics analysis of the strain energy[13] of the tether of intramolecular diamination products **3** and **4** indicated that **3** suffers more from ring strain than **4**, suggesting, in turn, that the formation of the 1,4-diaminoadducts (**3**) is a kinetically favored process. The strain associated with the formation of **3** also gives a reasonable rationale for the competitive formation of the intermolecular aminations leading to an intermediate **6**. The facile formation of $C_{60}[NMe(CH_2)_3NMe]_2 \cdot H^+$ (**6**-H) in an APCI mass spectrometer (Figure 1) provides reasonable evidence that the monomer **6** serves as a key precursor to the fulvene dimer **7**, which will be finally oxidized to the epoxide **2**.[14] The formation of **3** could be eliminated by lowering the reaction temperature (i.e., smaller $-T\Delta S$ term for an intermolecular reaction). Thus, when the reaction was carried out at 0 °C, **2** was isolated in 13% yield as the sole isolable product. We did not detect **6** in the reaction mixture, which suggested that either dimerization of **6** or further addition of **1** to **6** is fast.

The new cage compound **2** exhibits unusual electronic properties, owing to its highly symmetrical and rigid molecular structure as revealed through comparison of the UV−visible spectrum of **2** with that of the monomer **9**[15] (Figure 3). The two spectra were virtually identical, indicating two facts. First, there is no ground-state interaction between the end cap fullerenes connected through σ-bonded tethers. Second, the molar absorptivity of **2** is not twice that of the monomer **9**, but almost the same (i.e., 96%).[16] To our knowledge, such a large magnitude of hypochromicity[17] has seldom been described in the literature. Theory tells us that hypochromism will be observed for a rigid molecule with two isolated chromophores, whose transition moments due to the chromophores are parallel to each other. The degree of the hypochoromism depends on the oscillator strengths (i.e., total molar absorptivity) of each chromophore, the degree of parallelism of the transition moments, and the distance between the transition moments.[18] The large hypochromicity for **2** is due to the inflexible symmetric structure[19] and to the very large molar absorptivity of the fullerene moiety.

In summary, a new cage structure composed of an aliphatic side wall and two fullerene end caps has been synthesized through creation of twelve new σ bonds in a single step. Strong hypochromic effect in the UV/vis spectrum indicated that there is a high degree of parallelism of the transition moments in the molecule. The size and the electronic properties of the cage may be modified further, since the organic tether is amenable to modification as to size, constitution, and stereochemistry.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research from Monbusho. We thank Professors K. Yamanouchi and K. Iwata for discussion.

Supporting Information Available: Physical properties of **2** and **3**, and the X-ray crystal data of $\mathbf{2} \cdot 2CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

JA993091C

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[12] Preliminary attempts so far failed to detect inclusion of a small molecule such as methane.

[13] Isobe, H.; Tokuyama, H.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 5034−5041.

[14] We found that the 1,4-diaminoadduct **3** is a dead-end product since it reacts only very slowly with **1** under the reaction conditions.

[15] Prepared as described in ref 2.

[16] As has been known for the compounds in our hand (and in others as informed by a reviewer), the molar absorptivity of a dimer tethered with a flexible side chain is expectedly nearly twice as large as that of a monomer.

[17] Lipsett, M. N.; Happel, L. A.; Bradley, D. F. *J. Biol. Chem.* **1961**, *236*, 857−863.

[18] Tinoco, I., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 4785−4790; **1961**, *83*, 5047; Rhodes, W. Chase, M. *Rev. Mod. Phys.* **1967**, *39*, 348−361.

[19] Stochastic dynamics analysis (300.0 K, 10 ps, 1.5 fs time step; MM2*, MacroModel v6.0) of the cage **2** (Figure 2) showed only ±1% displacement of the C(119)−C(120) atom distance and ±12° change of the dihedral angle O(1)−C(1)−C(2)−O(2).