THE SUPRAMOLECULAR STRUCTURE OF 1,4-BIS(9-FLUORENYL)-1,4-DIHYDRO[60]FULLERENE WITH HEXAHOMOTRIOXACALIX-[3]ARENE IN THE SOLID STATE

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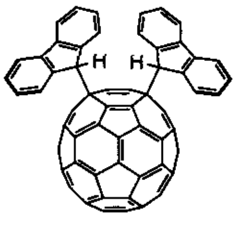
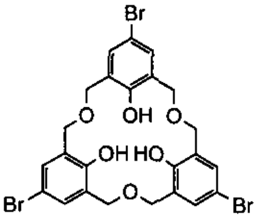
Abstract—The X-Ray analysis disclosed the structure of the supramolecular complex of 1,4-bis(9-fluorenyl)-1,4-dihydro[60]fullerene with *p*-bromohexahomotrioxacalix[3]arene.

Supramolecular complexes of fullerene C_{60} as a guest molecule have evoked a great deal of interest in the field of host-guest chemistry.[1] Recent studies of this complex have focused on the inclusion phenomena of C_{60} with the so-called "dish-shaped" hosts in solutions.[2-5] Among these studies, X-Ray analyses of C_{60} complexes with "dish-shaped" hosts have been reported. Fukazawa reported X-Ray analyses of C_{60} complexes with calix[5]arenes and revealed that a five-membered ring of C_{60} is disposed parallel to the mean plane composed of the five phenolic oxygens of the host.[3] The crystal structures of inclusion complexes of cyclotriveratrylenes with C_{60} have been reported.[6] Recently, we reported complexes of C_{60} with hexahomotrioxacalix[3]arenes and showed that a six-membered ring of C_{60} is oriented parallel to the mean plane composed of the three phenolic oxygens of the host.[4] Based on these results, a fit not just in size and shape but also the symmetry factors of the host and guest appeared to be important. Although crystal structures of the inclusion complexes of C_{60} with various host molecules have been repotred, no X-Ray analysis was reported for the inclusion complexes of C_{60} substituted at any carbon atom(s). In this paper, we report an X-Ray crystal structure of the complex of C_{60} possessing the organic addends, 1,4-bis(9-fluorenyl)-1,4-dihydro[60]fullerene (**1**)[7] with bromohexahomotrioxacalix[3]arene (**2**).[5,8,9]



1



2

In the ^{1}H NMR spectrum of **1**, the signals of the fluorenyl protons are broadened at lower temperature to indicate dynamic behavior of this molecule. The variable temperature ^{1}H NMR (300 MHz) spectra of **1** in CS_2-$CDCl_3$ (1:1) are shown in Figure 1. At 40 °C, a signal corresponding to the methine proton in the fluorenyl group was observed at δ 4.53. This signal broadened and then reappeared as two broad signals at δ 5.59 and 2.89 at -70 °C. This spectral behavior can be ascribed to the hindered rotation of one of the fluorenyl groups, as shown in Figure 2. The free energy of activation for this rotation was estimated to be 49.4±1.3 kJ mol^{-1}. As shown in Figure 3, theoretical calculations by AM1 showed that there are three energetically minimum conformers (**1a**), (**1b**) and (**1c**) in relation to the rotation of the fluorenyl groups. In the ^{1}H NMR at -70 °C, the signal at δ 2.89 can be assigned to the methine proton shielded by another fluorenyl group in conformers (**1b**) and (**1c**) (H_b), while the signal at δ 5.59 would be assigned to another

Figure 1. The variable-temperature ^{1}H NMR spectra of **1** in CS_2-$CDCl_3$ (1:1) at 300 MHz.

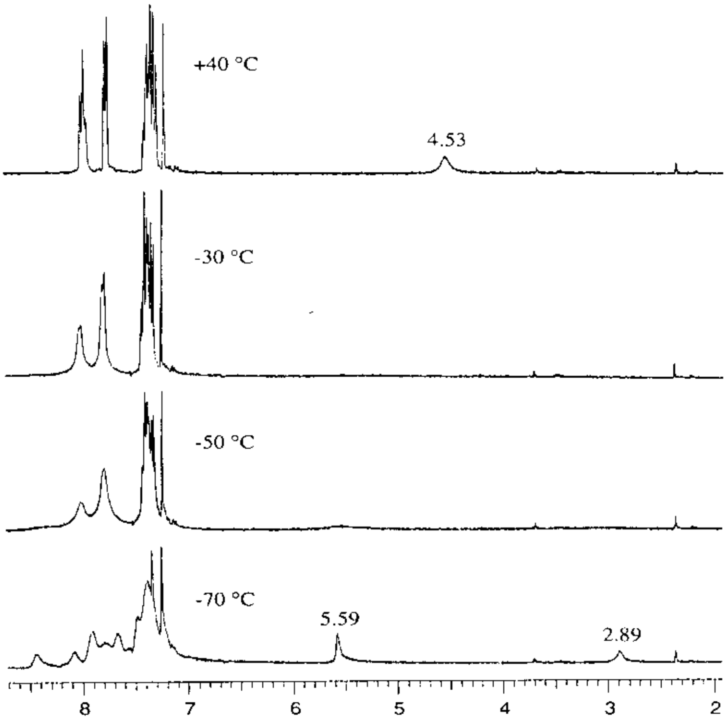
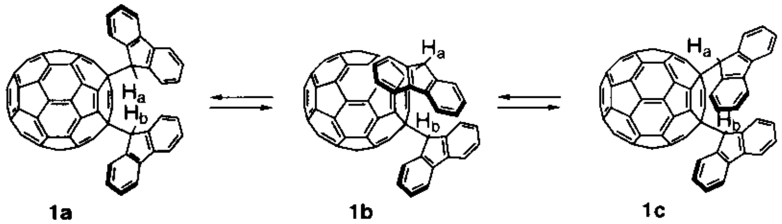


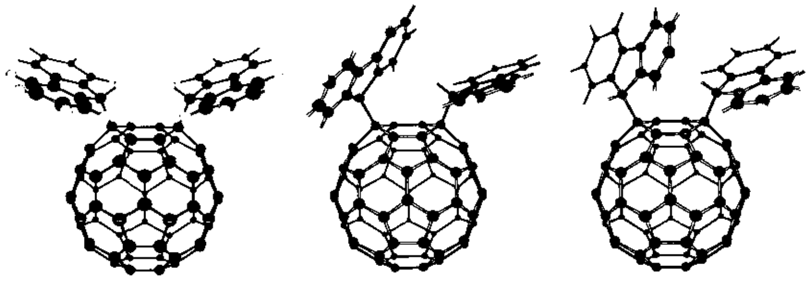
Figure 2.



methine proton in **1b** and **1c** and to two methine protons in **1a**.

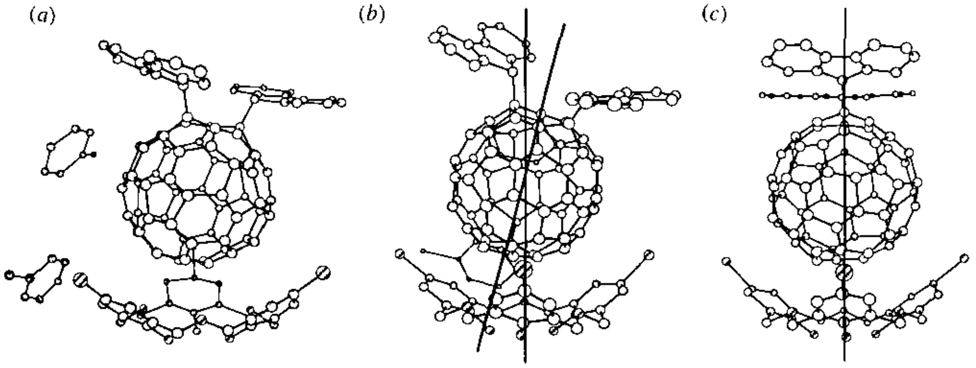
A crop of the inclusion complexes was obtained as yellow-brown crystals by allowing a toluene solution of 1,4-bis(9-fluorenyl)-1,4-dihydro[60]fullerene (**1**) and the bromohexahomotrioxacalix[3]arene (**2**) in a molar ratio of 1:10-20 to stand for a couple of weeks. The crystal structure of the complex of **1** with **2** was clarified by an X-Ray analysis and is shown in Figure 4.[10] While the crystal structure is low in precision, refinement revealed a meaningful aspect of the host-guest complex. With regard to the orientation of two fluorenyl groups, the result is in agreement with the most stable conformer (**1a**), obtained by AM1 calculations. It was quite unexpected that a six-membered ring of **1** at the south pole indicated by the white carbons was shifted from the mean plane composed of the three phenolic oxygens of **2** (Figure 4a). This distortion between **1** and **2** is presumably due to the presence of two toluene molecules in the crystal structure. One of the toluene molecules existing above the equator of **1** is approximately parallel to a six-membered ring of **1**, and the closest contact was observed at a distance of 3.36(6) Å. The fluorenyl groups are tilted from the mean plane of the host **2** (Figure 4b). The complex has a plane of pseudosymmetry (Figure 4c), if the two toluene molecules are not considered. It appears that the toluene molecule and a six-membered ring are in contact with each other by an off-set type π-π interaction. The closest distances from the ethereal oxygen and a carbon atom in the host molecule (**2**) to a carbon atom of the guest molecule (**1**)

Figure 3. Three energetically minimun conformers of **1** calculated by AM1.



	1a	**1b**	**1c**
$\Delta\Delta H_f$(AM1)	0	3.14 kJ mol^{-1}	3.51 kJ mol^{-1}

Figure 4. Crystal structure of the complex of **1** and **2** generated by CHEM3D. Hydrogen atoms are excluded for clarity. (*a*) Whole structure including two molecules of toluene. (*b*) Side view showing a tilt of the fluorenyl moieties form the mean plane of the host molecule (**2**). (*c*) Side view to visualize existence of the plane of peudosymmetry. The six-membered rings at the north and the south poles are indicated with the white color in each figure.



are 2.94(3) Å and 3.29(4) Å, respectively. These two distances are shorter than those of the inclusion complex of fullerene C_{60} with **2**,[4] and indicate that **1** is deeply embedded in the cavity of **2**.

REFERENCES AND NOTES

1. (a) Z. Yoshida, H. Takekuma, S. Takekuma, and Y. Matsubara, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1597. (b) T. Andersson, G. Westman, G. Stenhagen, M. Sundahl, and O. Wennerström, *Tetrahedron Lett.*, 1995, **36**, 597. (c) T. Suzuki, K. Nakashima, and S. Shinkai, *Chem. Lett.*, 1994, 699. (d) J. L. Atwood, G. A. Koutsantonis, and C. L. Raston, *Nature*, 1994, **368**, 229. (e) F. Diederich, J. Effing, U. Jonas, L. Jullien, T. Plesnivy, H. Ringsdorf, C. Thilgen, and D. Weinstein, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1599. (f) J. D. Crane, P. B. Hitchcoch, H. W. Kroto, R. Taylor, and D. M. R. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764. (g) J. D. Crane and P. B. Hitchcoch, *J. Chem. Soc., Dalton Trans.*, 1993, 2537. (h) D. M. Eichhorn, S. Yang, W. Jarrell, T. F. Baumann, L. S. Beall, A. J. P. White, D. J. Williams, A. G. M. Barrett, and B. M. Hoffman, *J. Chem. Soc., Chem. Commun.*, 1995, 1703.
2. (a) C. L. Raston, J. L. Atwood, P. J. Nichols, and I. B. N. Sudria, *Chem. Commun.*, 1996, 2615. (b) K. Araki, K. Akao, A. Ikeda, T. Suzuki, and S. Shinkai, *Tetrahedron Lett.*, 1996, **37**, 73. (c) A. Ikeda, M. Yoshimura, and S. Shinkai, *Tetrahedron Lett.*, 1997, **38**, 2107. (d) J. L. Atwood, M. Barnes, M. G. Gardiner, and C. L. Raston, *Chem. Commun.*, 1996, 1449. (e) N. S. Isaacs, P. J. Nichols, C. L. Raston, C. A. Sandova, and D. J. Young, *Chem. Commun.*, 1997, 1839. (f) J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston, and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1994, **116**, 10346. (g) T. Haino, M. Yanase, and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 997.
3. (a) T. Haino, M. Yanase, and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259. (b) T. Haino, M. Yanase, and Y. Fukazawa, *Tetrahedron Lett.*, 1997, **38**, 3739.
4. K. Tsubaki, K. Tanaka, T. Kinoshita, and K. Fuji, *Chem. Commun.*, 1998, 895.
5. A. Ikeda, Y. Suzuki, M. Yoshimura, and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497.
6. (a) H. Matsubara, T. Shimura, A. Hasegawa, M. Semba, K. Asanao, and K. Yamamoto, *Chem. Lett.*, 1998, 1099. (b) H. Matsubara, A. Hasegawa, K. Shiwaku, K. Asanao, M. Uno, S. Takahashi, and K. Yamamoto, *Chem. Lett.*, 1998, 923.
7. Y. Murata, K. Komatsu, and T. M. S. Wan, *Tetrahedron Lett.*, 1996, **37**, 7061.
8. K. Tsubaki, T. Otsubo, K. Tanaka, K. Fuji, and T. Kinoshita, *J. Org. Chem.*, 1998, **63**, 3260.
9. (a) B. Dhawan and C. D. Gutsche, *J. Org. Chem.*, 1983, **48**, 1536. (b) P. Zerr, M. Mussrabi, and J. Vicens, *Tetrahedron Lett.*, 1991, **32**, 1879.
10. Crystal data for **1**•**2**•(toluene)$_2$; $C_{124}H_{55}O_6Br_3$, M = 1880.51, monoclinic, a = 14.155(1) Å, b = 22.038(1) Å, c = 14.260(1) Å, β = 115.553(5)°, V = 4013.1(5) Å^3, space group $P2_1$ (#4), z = 2, D_c = 1.556 g cm^{-3}, μ(Cu-Kα) = 24.14 cm^{-1}, Rigaku AFC7R diffractometer with graphite-monochlomated Cu-Kα (λ = 1.54178 Å, T = 293 K), No. of measured reflections: 6988. Structure solution by direct method (SHELX86), refinement by full-matrix least-squares using all reflections, R = 0.081 ($|F_0| > 4\sigma(F_0)$), Rw = 0.124 (all reflections), GOF = 2.58. Further details of the crystal structural investigation are available on request from the director of the Cambridge Crystallographic Data Centre.

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