





Complexation of a Carbon Nanoring with Fullerenes**

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Dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday

Recently, a variety of layered carbon networks with closed, curved structures, such as carbon nanotubes, [1] bucky onions, [2] and "fullerene peapods"[3] have been discovered and have attracted much attention. Although the nature of the concave-convex interactions between the curved graphene sheets should be important in the formation and properties of these materials, they are yet to be well understood because of the absence of good model compounds. There have been considerable efforts towards the synthesis of belt-shaped conjugated systems.^[4,5] In the accompanying paper,^[6] we reported that the carbon nanorings [6]- and [8]paraphenyleneacetylene (1 and 2) have cavities with diameters of 13.2 and 17.3 Å, respectively (average values determined by X-ray diffraction), and form rather weak inclusion complexes with hexamethylbenzene and toluene, respectively. The size of the cavity in **1** appears to be suitable for the inclusion of C_{60} (7.1 Å in diameter), although it is actually slightly too small when the depth of p orbitals (3.4 Å for benzene) is considered (Figure 1). Therefore, the host-guest chemistry of 1 with fullerenes would give an insight into the concave–convex π - π interactions that are associated with the bucky onion and fullerene peapod. Here, we report on the formation of unusually stable complexes of the carbon nanoring 1 with C₆₀ and bis(ethoxycarbonyl)methanofullerene (3),^[7] and Xray crystallographic analysis of the crystalline 1:1 complex 1:3.

Despite being only sparingly soluble in CHCl₃, [8] C₆₀ was found to be much more soluble (approximately 5 mg per mL) in the presence of 1, to give the 1:1 complex $1 \cdot C_{60}$ as a reddish brown solution, or a dark red-brown solid which precipitated out at higher concentrations. The solid complex could be redissolved completely in CHCl₃, which is in sharp contrast to the behavior of the solid calix[8]arene-C₆₀ complex,^[9,10] where C₆₀ remained undissolved when added to CHCl₃;

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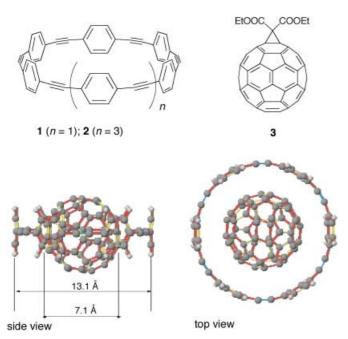


Figure 1. Paraphenyleneacetylenes 1 and 2, fullerene derivative 3, and a possible molecular structure of $1 \cdot C_{60}$.

these results suggest that a much higher association constant exists between 1 and C_{60} in CHCl₃. A similar procedure also afforded the 1:1 complex 1·3. In contrast, the larger carbon nanoring 2 did not show any degree of complexation with either type of fullerene.

The interactions between **1** and C_{60} in solution were examined by absorption spectroscopy. Gradual addition of **1** to a solution of C_{60} in benzene causes a gradual change in the absorption spectrum. The isosbestic point at 583 nm, as well as a continuous-variation (Job's) plot, [11] provides evidence for a 1:1 complex in solution. The association constant (K_a) of the **1**·C₆₀ complex, as determined by Hirose's method, [12] is $(1.6 \pm 0.3) \times 10^4 \, \text{dm}^3 \, \text{mol}^{-1}$. The absorption spectra of **1·3** also showed some variation, but the changes were too small for the measurement of a reliable association constant.

¹H NMR spectroscopy at low temperature afforded further important information (Figure 2). The spectrum of a solution of C₆₀ and **1** (1:2.5) in CD₂Cl₂ exhibits a sharp singlet at 7.36 ppm for the aromatic protons at 30 °C. However, the signal broadens as the temperature is lowered and splits into two singlets which can be assigned to the protons of complex $1 \cdot C_{60}$ (7.37 ppm), and the free host 1 (7.35 ppm) at -100 °C (Figure 2b). This dynamic behavior was not observed in [D₈]toluene. In-and-out motion of C₆₀ against the cavity of 1 in CD₂Cl₂ is thus fast at room temperature and becomes slow enough for the NMR timescale at lower temperatures. Importantly, the ¹H NMR spectrum of the isolated 1·C₆₀ complex, thus an exact 1:1 ratio of two components, exhibits only the signal of the complex at −100 °C (Figure 2a). Taking the concentration of $1 \cdot C_{60}$ (2.2 × 10⁻⁴ mol dm⁻³) and possible detection of the free host 1 (down to 2%) into account, the value for K_a between 1 and C_{60} is estimated to be very large (exceeding 10⁷ dm³ mol⁻¹).^[13] Variable-temperature NMR experiments also reveal that the Gibbs activation energy (ΔG^{\dagger}) for dissociation of 1·C₆₀ is (9.9 ± 0.3) kcal mol⁻¹ $(T_c =$

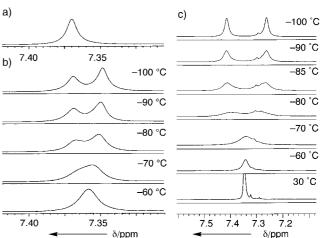


Figure 2. ¹H NMR spectra of a) $1 \cdot C_{60}$ (0.22 mmoldm⁻³; isolated as a solid) at -100 °C; b) a 1:2.5 mixture of 1 and C_{60} ; c) a 1:1 mixture of 1 and 3

 $(-80\pm5)^{\circ}\text{C})$ in CD_2Cl_2 . The appearance of all the protons as a singlet points to near standstill or fast vibration of the C_{60} molecule around the center of the cavity and also its fast rotation inside the cavity, even at -100°C . Moreover, a 1:1 mixture of **1** and **3** in CD_2Cl_2 showed a sharp singlet at 7.38 ppm for the aromatic protons of **1** at room temperature, a broadened singlet as the temperature was lowered, and finally two singlets (7.26 and 7.42 ppm) of equal intensity at -100°C (Figure 2c). The appearance of two singlets is consistent with a lowering in the symmetry of **3**. The value of ΔG^{\pm} for dissociation was calculated to be (9.4 ± 0.2) kcal mol⁻¹ ($T_c = -78\pm3^{\circ}\text{C}$) which is a little lower than that of $1\cdot C_{60}$. Thus, the **1·3** complex is slightly less stable than its $1\cdot C_{60}$ counterpart.

X-ray crystallographic analysis of these crystalline complexes should provide definitive information on their structures. However, attempted X-ray analyses of the 1-C₆₀ complex have so far failed to give adequate diffraction data, probably because of rotation of the guest molecules. Actually, a CP-MAS-NMR spectrum of the 1·C₆₀ complex at 30°C shows a singlet peak (143.2 ppm) for C₆₀ in the solid state. On the other hand, good single crystals of the 1.3 complex, suitable for X-ray analysis, were obtained from a toluene solution by slow evaporation of the solvent.^[14] The molecular structure obtained reveals that each molecule of the complex is associated with two toluene molecules (Figure 3), and that the C_{60} cage of 3 is not deeply embedded in the cavity of 1 but situated at a floating position away from the center of the cavity, which takes on a bowl-shaped conformation. Even in this "ball-on-bowl" structure, all of the benzene rings of 1 are facing the C_{60} cage of 3. The ester groups of 3 lean on the aromatic rings of 1, and therefore the aromatic protons of nanoring 1 act like a gear wheel hindering easy rotation of the

Table 1 lists the structural parameters of **1** in the complex **1·3** compared with those of the complex with hexamethylbenzene (**1·HMB**).^[6] These data are almost identical except for the twist angles of the aromatic rings. The bond lengths and angles of **3** in this complex are also almost identical to those of the known structural data of **3**.^[7c] There are

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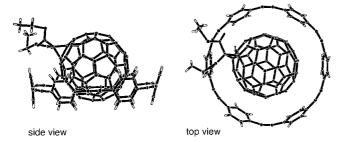


Figure 3. Molecular structure of 1-3. Toluene molecules are omitted for clarity.

Table 1: Structural parameters of 1 in inclusion complexes.

	1 ·HMB	1.3
long axis [Å] short axis [Å]	13.3 13.0	13.3 13.0
average bond angles of sp carbon atoms [°]	162.5 ≈ 165.6 (164.4)	162.2 ≈166.2 (164.5)
twist angles of benzene rings [°][a]	-9, 1, 17	20.3, 14.8, 16.9, 19.6, 16.5, 5.1
bend angles of benzene rings [°][b]	151.9, 149.2, 149.5	153.0, 151.6, 150.9, 149.0, 148.4, 148.1

[a] Evaluated from dihedral angles between least-square planes. [b] The angles between the two *para*-benzyl bonds of each boat-form benzene ring.

altogether 41 short interatomic distances (< 3.6 Å) and eight particularly short contacts (< 3.4 Å) between the host and guest (Figure 4). There are, however, no short contacts between the C_{60} cage and the outer surface of 1. Most of the carbon atoms of 1 (37 out of 48) are in close contact with the C_{60} cage of 3. The average distance between the host and guest is roughly estimated to be 3.4 Å, which is almost equal to the interlayer distance of multiwall carbon nanotubes. Taking into account the van der Waals distance between sp² carbon atoms (3.4 Å), the diameter of 1 (13.2 Å) seems a little too small to allow C_{60} to be fully embedded, and therefore the

floating position of 3 would be a consequence of energetic favoring. Therefore, the singlet signal of $1 \cdot C_{60}$ and the two singlets of $1 \cdot 3$ in their NMR spectra at -100 °C suggest that fast vibrational motion of the C_{60} molecule around the center of the cavity is evident, even at such a low temperature.

The short contacts seem to bear little correlation with the molecular orbital interaction between the HOMO of $\bf 1$ and the LUMO of $\bf 3$.^[7b] For example, although the C(103)···C(19) separation is the shortest contact of its type (3.26 Å), C(103) has no coefficient in the LUMO orbital. It is noteworthy that all the benzene rings of $\bf 1$ lie over the [5:6] ring fusions of the C₆₀ cage, which represent centers of positive charge on the C₆₀ surface.^[15,16]

According to many studies, [17-20] noncovalent interactions between aromatic rings have been explained in terms of van der Waals (dispersion force) and polar electrostatic (PE) interactions rather than as charge-transfer interactions. The high affinity between 1 and C₆₀ cannot be explained in terms of dispersion forces alone because the complex of 1 and hexamethylbenzene described before, [6] where the dispersion force would be expected to play a greater role, is almost dissociated in nonpolar solvents. Charge-transfer effects would also be negligible because 1 has poor electron-donating properties (the first electrochemical oxidation potential is over +1.0 V in CH₂Cl₂), and only a slight change is observed in the charge-transfer absorption band (450–650 nm) in every case. In contrast, the complex of C_{60} with N,N-dimethylaniline exhibits a rather intense charge-transfer absorption band.^[21] Thus, the PE interaction remains the most probable driving force for complexation.

Theoretical studies have predicted that curved aromatic hydrocarbons should be polarized with regard to their convex and concave faces because π systems on a curved surface suffer an anisotropic distribution of π electrons, which results in the segregation of electrostatic charge. However, the results of theoretical calculations have been controversial as to the direction of polarization. The significantly strong complexation found here between 1 and fullerenes, as well as the good face-to-face solvating ability of benzene and

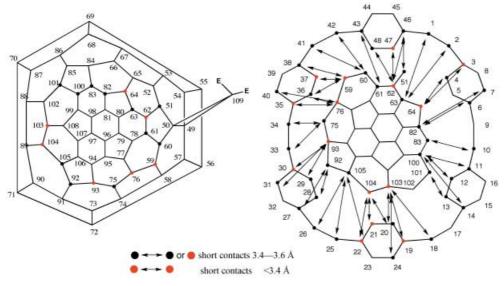


Figure 4. The short contacts between the host and guest in the 1.3 complex.

alkylbenzenes, may be understood by assuming the electronic potential of the convex surface of the fullerenes to be positive. [16a] An electrostatic attractive force, namely, a quadrupolar–quadrupolar interaction between the electrostatically opposite concave and convex surfaces, as well as the dispersion force, would play an important role in the formation of complexes between 1 and fullerenes, [23] and hence the spontaneous formation of layered carbon nanotubes, bucky onions, and fullerene peapods.

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