Complexation of C_{60} with hexahomooxacalix[3]arenes and supramolecular structures of complexes in the solid state

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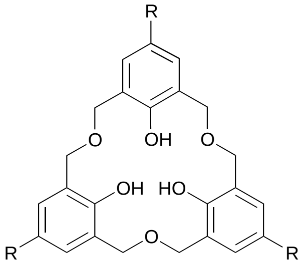
Hexahomooxacalix[3]arenes 1–5, which possess a variety of substituents on their upper rim, have captured fullerene C_{60} in toluene with association constants of K_a = 9.1–35.6 dm^3 mol^{-1}; X-ray analysis of the complex of C_{60} and 4 indicated that a van der Waals attractive interaction is the dominant driving force which brings the hexagonal faces of the C_{60} close to both the aromatic rings and the dibenzyl ether oxygen of 4.

Supramolecular complexes with C_{60} as the guest molecule have provoked a great deal of interest in the field of host–guest chemistry.[1–8] Recent studies on this complexation have focused on the inclusion phenomena of C_{60} with so-called 'dish-shaped' hosts in solution.[9–15] Among these studies, X-ray analyses of the complexes of C_{60} with calix[5]arenes[14,16,17] and with cyclotriveratrylene (CTV)[12,15] have been reported. Quite recently, Shinkai reported the inclusion complex of C_{60} and *tert*-butylhexahomooxacalix[3]arene **2** in organic solution.[11] However, the precise details of the structural features of the inclusion complex are still ambiguous. Here we report the first X-ray analyses of the complexes of C_{60} with hexahomooxacalix[3]arenes **2** and **4**, and the formation of supramolecular complexes of C_{60} with hexahomooxacalix[3]arenes possessing different substituents on their upper rims.



1 R = H
2 R = Bu^t
3 R = OMe
4 R = Br
5 R = $CMe_2C_6H_4$-*p*-OMOM

We have developed a stepwise synthesis for a variety of hexahomooxacalix[3]arenes having different substituents on their upper rim portion, revealing that some hexahomooxacalix[3]arenes adopt a cone conformation owing to an intramolecular hydrogen-bonding network in the solid state.[18] The interaction between hexahomooxacalix[3]arenes **1–5**‡ and C_{60} was examined using UV–VIS spectroscopy. Thus, upon addition of hexahomooxacalix[3]arenes to a solution of C_{60} in toluene, a slight change in color (from purple to pale brown), based on an increase in the absorption band at *ca.* 430 nm, was observed. The UV–VIS titration method allowed us to determine the association constants, which were determined by the Rose–Drago method[19] to be those of a 1 : 1 complex (λ = 425 or 430 nm, 298 K, toluene solution, $[C_{60}]_0 = 5.1 \times 10^{-4}$ M). The composition ratio of C_{60} and **2** has been reported,[11] and that of C_{60} and **5** was determined by Job plot, but this was not effective for the determination of the composition ratios of C_{60} and **1**, **3** and **4** due to both the very small K_a and the change in absorption. These results are shown in Table 1. Generally, neither the magnitude of nor the difference between association constants for the five hosts **1–5** is particularly large. Consequently, it might be concluded that the strength of complexation is not affected by the electron density of the aromatic rings of the host compounds.

Table 1 Association constants for hexahomooxacalixarene–C_{60} complexation in toluene at 298 K[a]

Compound	K_a/dm^3 mol^{-1}
1	9.1 ± 1.0
2	35.6 ± 0.3
3	20.7 ± 0.9
4	14.9 ± 2.0
5	13.3 ± 0.4

[a] Association constants were determined by the Rose–Drago method (ref. 19) for a 1 : 1 complex at 425 or 430 nm.

The inclusion complexes were obtained as dark brown crystals by allowing a toluene solution of C_{60} and the corresponding hexahomooxacalix[3]arenes **2–5** in a molar ratio of 1 : 10–20 to stand for a couple of weeks. The crystal structure of the complex of C_{60} and **4** was clarified by X-ray analysis and is shown in Fig. 1.§ As a result of the suppression of the rotational disorder of C_{60} in the solid state, all the atoms of the inclusion complex can be identified. The inclusion complex has a C_{3d} symmetric structure in the solid state, in which a six-membered ring of C_{60} is disposed parallel to the mean plane composed of the three phenolic oxygens of **4**. In addition, three six-membered rings around the above-mentioned six-membered ring at the bottom position of C_{60} are approximately parallel to three six-membered rings of **4**, where the closest distance [3.615 (6) Å] between two sp^2 carbons is very close to those reported for related complexes (3.51 Å[15] and 3.60–3.62 Å[16]). The inclination angle (θ) of the three phenol rings from the mean plane composed of three phenol oxygens in **4** is 147°, which is consistent with the dihedral angle between the six-membered ring at the bottom and the neighboring five- and six-membered rings of C_{60} (average angle of 145°). The additional striking feature of this complex is that the closest distance from the dibenzyl ether oxygens of **4** to the six-membered ring at the bottom of C_{60} is only 3.290 (5) Å. Taking into account these close contacts, as well as the weak electrostatic effect mentioned above, it can be suggested that van der Waals forces are the predominant attractive forces for complexation. The packing arrangement of C_{60} and **4** is shown in Fig. 2. The closest intermolecular distance of 3.51 (3) Å between carbons of C_{60} suggests some attractive interactions between C_{60} molecules, which is comparable to that observed in graphite (3.35 Å).

Similarly, X-ray analysis of the crystals of the complex of C_{60} with **2** indicated a complexation pattern with a 1 : 1 ratio, in which **2** is ordered, whereas the packing of the guest C_{60} molecules is rotationally disordered in the solid state. This packing arrangement is shown in Fig. 3.¶

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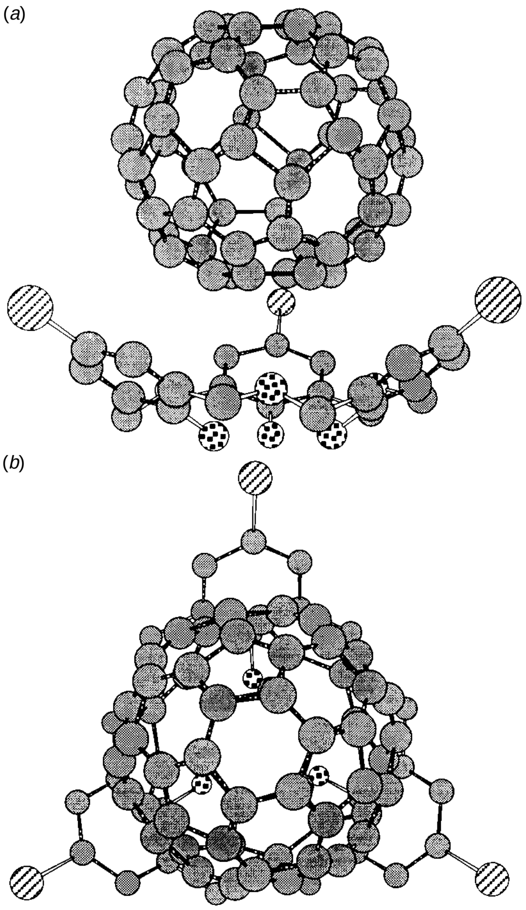

Fig. 1 Crystal structure of C_{60} and **4** generated by CHEM3D; (*a*) side view and (*b*) top view. Hydrogen atoms are excluded for clarity.

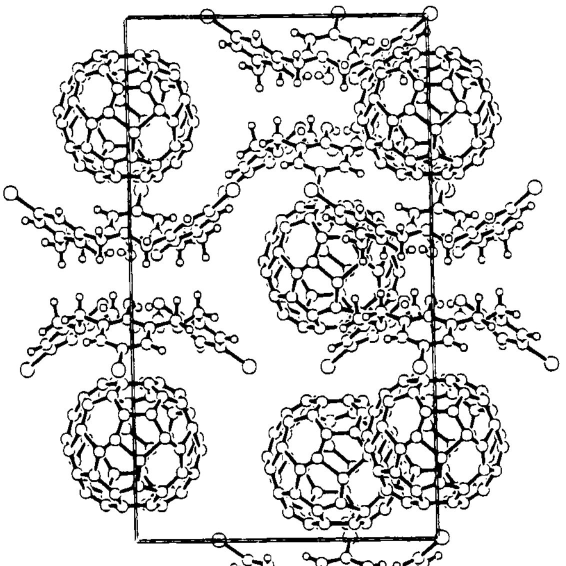

Fig. 2 Packing arrangement for the complex of C_{60} and **4**

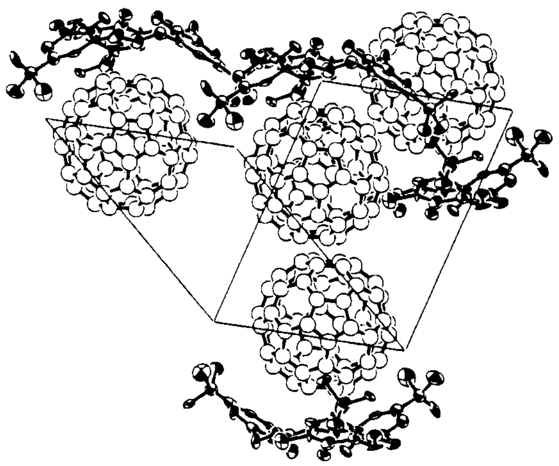

Fig. 3 Packing arrangement for the complex of C_{60} and **2**; the illustrated orientation of C_{60} has been optimized using the information obtained from the X-ray analysis of the complex of C_{60} and **4**

Notes and References

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‡ Syntheses of hexahomooxacalix[3]arenes **1**–**4** have been reported (ref. 18). The hexahomooxacalix[3]arene **5** was prepared by cyclotrimerization according to the procedure of Gutsche (ref. 20).

§ *Crystal data* for **4**·C_{60}; $C_{28}H_7O_2Br$, M = 455.27, trigonal, $a = b = 18.104(1)$, $c = 26.624(2)$ Å, $V = 7556.8(9)$ Å^3, space group $R3$ (#148), $Z = 18$, $D_c = 1.801$ g cm^{-3}, μ(Cu-Kα) = 35.59 cm^{-1}, λ(Cu-Kα) = 1.54178 Å, T = 293 K, R = 0.105, Rw = 0.163 for 3088 reflections.

¶ *Crystal data* for **2**·C_{60}; $C_{96}H_{48}O_6$, M = 1297.43, triclinic, $a = 14.316(4)$, $b = 16.88(1)$, $c = 14.292(6)$ Å, $\alpha = 108.23(5)°$ $\beta = 111.90(2)$, $\gamma = 90.62(5)°$, $V = 3010(3)$ Å^3, space group $P\bar{1}$ (#2), $Z = 2$, $D_c = 1.431$ g cm^{-3}, μ(Cu-Kα) = 6.97 cm^{-1}, λ(Cu-Kα) = 1.54178 Å, T = 293 K, R = 0.205, Rw = 0.198 for 6473 reflections.

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