

Supramolecular intercalation of C₆₀ into a calixarene bilayer—a well-ordered solid-state structure dominated by van der Waals contacts

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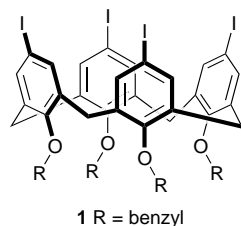
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C₆₀ co-crystallizes with *p*-iodocalix[4]arene benzyl ether to form a layered structure in which the C₆₀ molecule is ordered without the presence of appreciably strong intermolecular interactions.

There has been much interest in the supramolecular complexation of fullerenes, both in solution^{1–4} and in the solid state.^{5–11} Crystallographic characterization of crystals containing C₆₀ is often confounded by twinning¹² and orientational disorder,^{9–11,13,14} the latter being mainly due to the lack of anisotropy of the molecule, and to its inability to interact strongly with other species. It is well-established that important considerations in the design of systems for molecular recognition include shape and size discrimination, as well as the exploitation of relatively weak non-covalent forces¹⁵ (e.g. hydrogen bonding, $\pi\cdots\pi$ interactions). That these criteria are usually complementary makes the prediction of solid-state structures extremely difficult, thus forcing one to produce multicomponent materials by trial and error in order to examine the resulting structures for clues relating to their formation and stability.

Several crystal structures containing ordered C₆₀ molecules have been reported to date.^{6,7,16,17} From these studies we are able to deduce the nature of the weak interactions which can be used to hold the molecule in place. In this context, there have been reports of interactions between six-membered aromatic rings and the electron-poor 6:5 C₆₀ ring fusion,^{16,18} C₅H₅ or C₅Me₅ rings and the electron-rich 6:6 ring fusion,¹⁷ C₅ \cdots C₅ interactions,^{6,19} aromatic C–H \cdots C₆ hydrogen- π bonds¹⁶ and C \cdots I interactions.¹³

We are interested in forming supramolecular complexes between fullerenes and calixarenes and have recently achieved some success in this area.^{1,2} The supramolecular chemistry of calixarenes is mainly associated with a bowl-like cavity which may act as a receptor site for molecular inclusion. Chemical substitution at the lower rim of calix[4]arenes invariably results in a significant reduction in the size of the molecular cavity as the molecule adopts the so-called ‘pinched-cone’ conformation. However, despite the loss of the cavity, such substitution can lead to molecules with interesting solid-state packing properties relating to their shape and functionality. In an effort to gain a better understanding of some of the factors affecting the formation of stable solid-state structures, we are investigating the interaction of C₆₀ with a series of calix[4]arene compounds which have been modified to include both halogen and phenyl moieties. We present here the results of one such structure with a particularly interesting solid-state architecture.



Slow diffusion of propan-2-ol into a solution of **1** and C₆₀ (5:1 molar ratio) in *o*-dichlorobenzene yielded dark red crystals

suitable for single-crystal X-ray diffraction analysis.[†] The asymmetric unit consists of one half of the calixarene molecule, which is situated on a $\bar{4}$ axis, and one quarter of a C₆₀ molecule which is positioned with its centre on the intersection of three mutually orthogonal two-fold rotation axes. No atoms occupy special positions in the unit cell. Although the C₆₀ molecule does not exhibit orientational disorder, the thermal ellipsoids of its atoms have large amplitudes parallel to its surface (Fig. 1). As shown in Fig. 2, the most striking feature of the overall structure is that C₆₀ molecules are intercalated into calixarene bilayers running parallel to (001). The calixarene molecule possesses C₂ symmetry and within each calixarene monolayer there are two distinct molecular orientations. These two orientations are rotated by 90° relative to one another and alternate like the squares on a chess board as shown in Fig. 2(a). The calixarene bilayer consists of two such monolayers associated with one another in a head-to-head fashion, *i.e.* where the upper rim of each calixarene molecule is one layer faces the upper rim of a calixarene molecule of the second layer across a $\bar{4}$ symmetry site. This arrangement gives rise to large intermolecular cavities which are occupied by the C₆₀ molecules. Fig. 2(b) shows a cross-section of the bilayers which are stacked along the crystallographic *c* axis with the calixarene molecules in adjacent bilayers associated with one another in a tail-to-tail arrangement. Thus the calixarene molecules are arranged in . . . a b c d a . . . columns parallel to the *c* axis.

At first glance, it would appear that the head-to-head association of the calixarenes may be facilitated by I \cdots I interactions, while the tail-to-tail association can be attributed to $\pi\cdots\pi$ interactions between the benzyl moieties. However, the closest I \cdots I approach in the structure is 4.26(2) Å. A recent survey²⁰ of halogen \cdots halogen interactions, based on data from the Cambridge Crystallographic Database, suggests that symmetrical I \cdots I distances of ≥ 4.0 Å probably only correspond to van der Waals contacts which occur as a consequence of molecular packing, and thus contribute little to the energy of the crystal. Similarly, the shortest benzyl centroid \cdots centroid dis-

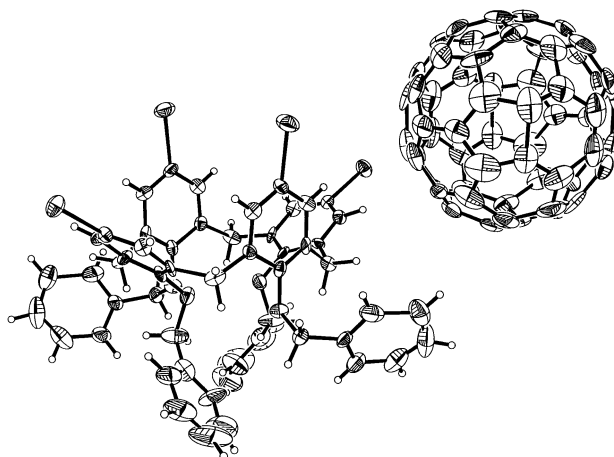


Fig. 1 ORTEP diagram showing 30% thermal ellipsoids

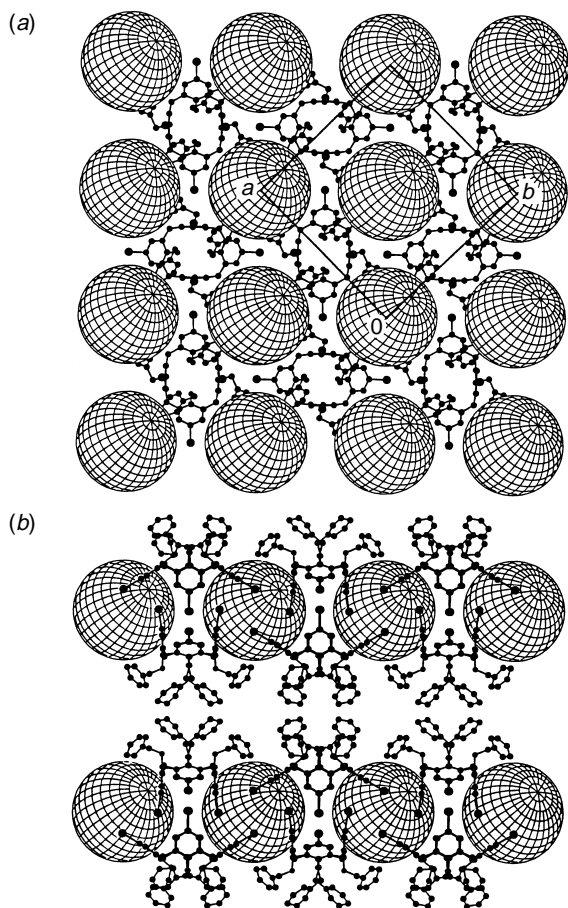


Fig. 2 Packing diagrams (hydrogen atoms omitted) viewed along (a) [001], looking down the calixarene cavities and showing the C_{60} molecules resting on a 2-dimensional calixarene monolayer, and (b) $[-110]$, showing a cross-section of two adjacent C_{60} -intercalated calixarene bilayers centred at x, y, z , and $x, y, z + \frac{1}{2}$

tance of 5.28(3) Å is much too long to be attributed to an appreciably strong aromatic $\pi \cdots \pi$ interaction.²¹

The shortest $C_{60} \cdots I$ distance of 3.67(3) Å is comparable to the sum of the van der Waals radii²² (3.68 Å) and is considerably longer than the value of 3.09 Å reported for the solvated structure $C_{60} \cdot I_2 \cdot \text{toluene}$.¹³ In an earlier study, $C_{60} \cdots I$ values of 3.29 and 3.54 Å were reported for the solvate $C_{60} \cdot C_6H_6 \cdot CH_2I_2$,²³ implying that these interactions contribute to ordering of the C_{60} molecule. Furthermore, in the present structure, the closest approach of iodine to any centroid of the fullerene rings is 3.84(4) Å. There are no calixarene aromatic centroids within 5 Å of any 6 : 5 bond of the C_{60} and all fullerene ring centroids are > 3.8 Å from any calixarene atoms or ring centroids. The closest calixarene–fullerene $C \cdots C$ contact of 3.55 Å compares favourably with the sum of their van der Waals radii (3.54 Å). It therefore appears that the only contact between the calixarene and C_{60} which may feasibly be construed as an interaction is that between an aromatic hydrogen atom (*ortho* to the iodine) of the calixarene and a carbon atom of the fullerene. This distance is 2.63(2) Å while the $C-H \cdots C$ angle is 168(1)°.

The closest $C_{60} \cdots C_{60}$ approach is 13.46 Å within the intercalated layers and 21.18 Å between layers. The average 5 : 6 and 6 : 6 bond lengths [1.46(8) and 1.31(8) Å respectively] are in good agreement with values reported in the literature. Despite the apparent absence of any appreciable interactions between the C_{60} and calixarene, it is intriguing that the structure has yielded such a well-ordered C_{60} molecule.

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Footnotes

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† *Crystal data* for $2(C_{56}H_{44}I_4O_4) \cdot C_{60}$: $M = 3297.62$, tetragonal, $a = b = 19.0353(7)$, $c = 42.372(2)$ Å, $V = 15353(1)$ Å³, space group $I4c2$, $Z = 4$, $D_c = 1.427$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 16.71$ cm⁻¹, $F(000) = 6423$. A dark red crystal of dimensions $0.45 \times 0.25 \times 0.20$ mm was used. Intensity data were collected on a Siemens SMART CDD diffractometer using the omega scan mode. Data were corrected for absorption using the program SADABS which is based on the method of Blessing (ref. 24). The positions of the iodine atoms were located by the Patterson method and the structure was expanded by difference synthesis. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in calculated positions. A peak of $1.93 \text{ e} \text{ \AA}^{-3}$ in the final difference Fourier map was unaccounted for. NMR analysis of the crystals did not reveal the presence of *o*-dichlorobenzene or propan-2-ol, and the peak was thus attributed to being an artifact of the structure. Final refinement converged with $R_1 = 0.089$ for 4522 unique reflections [$I > 2\sigma(I)$, $2\theta \leq 46^\circ$], 425 parameters and 12 restraints. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/471.

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