Supramolecular assembly of well-separated, linear columns of closely-spaced C_{60} molecules facilitated by dipole induction

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Co-crystallization of C_{60} with *p*-bromocalix[4]arene propyl ether results in a remarkably well packed structure; the calixarene molecules pack with their dipole moments aligned unidirectionally and the unusually close van der Waals contact between the C_{60} molecules is most likely a result of an opposing induced dipole.

Solid-state supramolecular systems involving fullerenes are of interest with regard to the development of novel nanostructures with potentially interesting properties.[1] Although the exploitation of non-covalent interactions is an area of especially intense focus in the field of crystal engineering,[2] this approach cannot be applied effectively to the supramolecular manipulation of fullerenes since these molecules simply lack the necessary functionality. Thus, in order to 'engineer' a desired arrangement of C_{60} molecules in the solid state, one needs to consider their size and shape as the principal structure-directing properties. In addition to optimizing their energies of interaction, molecules will tend to arrange in a manner that makes efficient use of the available space and it is because these two mechanisms cooperate in a subtle manner that crystal structures are generally difficult to predict with accuracy.

Pure C_{60} crystallizes in a face centered cubic (fcc) lattice as a cubic close packed (ccp) arrangement of spheres.[3,4] An array of this type results in the formation of large voids in the lattice (the packing efficiency is only *ca* 74 %) and it follows that co-crystallization with small molecules, or even irregularly shaped larger molecules, may lead to more efficiently packed structures of enhanced stability. Indeed, this statement is supported by several crystal structures of supramolecular complexes of C_{60} that have been reported in recent years.[5] In some cases, it appears that the structure entails only a slight modification of the pure C_{60} structure with small molecules or ions occupying the voids between the spheres, while in other cases, the structure bears little or no resemblance to the pure fullerene phase.

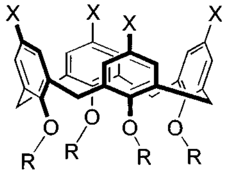
We are currently investigating supramolecular systems composed of co-crystals of calixarenes and fullerenes. The structural chemistry of calixarenes is usually focused on exploitation of their intramolecular cavities for molecular inclusion and in this regard we and other workers have recently reported inclusion complexes of calix[5,6]arene derivatives with C_{60} and C_{70}.[6] In contrast, the calix[4]arenes are not suited to the formation of analogous inclusion complexes with fullerenes because their cavities are relatively small. Moreover the well-known C_{4v} cone conformation of these molecules is usually dependent on the presence of hydroxyl groups at the lower rim (*i.e.* the cone is stabilized by a cyclic hydrogen bonded arrangement), and substitution at this position gives rise to the so-called 'pinched-cone' C_{2v} conformation with an even smaller cavity. Despite the reduced possibilities for the formation of true inclusion compounds, simple calix[4]arene derivatives are similar in dimensions to C_{60} (*ca* 10 Å) and thus co-crystallization of these species may result in interesting and efficiently packed arrangements of the molecules in stoichiometric proportions.

As part of our ongoing study of the interactions between calixarenes and fullerenes, we are currently investigating the effects of substitution at both the upper and lower rims of calix[4]arene (compounds **1**–**4**) on solid-state packing arrangements when co-crystallized with fullerenes.

We now present the results of a remarkably interesting packing mode for a co-crystal of C_{60} with **1**.

Slow diffusion of propan-2-ol into a solution of **1** and C_{60} (5:1 molar ratio) in *o*-dichlorobenzene resulted in the formation of crystals suitable for single-crystal X-ray diffraction analysis.† The molecular structure of the final model is shown in Fig. 1 and the overall packing arrangement of the structure is shown in Fig. 2. The structure is acentric and all the calixarene molecules are arranged in one-dimensional strands (in a head-to-tail arrangement) parallel to [001] such that their dipole moments have the same orientation throughout the crystal. One set of distal propyl groups on each calixarene molecule protrudes down into the small voids between the bromine atoms of the calixarene directly below. The remaining two propyl groups flare out to fill lattice voids associated with the packing of adjacent calixarene strands.

The C_{60} molecules are also arranged in one-dimensional strands running parallel to [001] at $0,0,z$ and $\frac{1}{2},\frac{1}{2},z$. Since the space group symmetry is consistent with an orientationally disordered C_{60} molecule manifesting as a sphere of uniform electron density, the exact positions of the fullerene atoms cannot be determined. However, it is fortuitous that the center···center distance of the fullerenes is represented by the crystallographic *c* axis, which it was possible to determine



	X	R
1	Br	Pr^n
2	Br	CH_2Ph
3	I	CH_2Ph
4	Br	Me

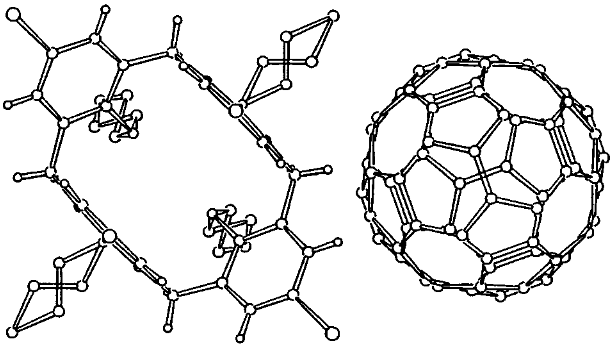


Fig. 1 Projection showing the molecular structure of the calixarene and C_{60} molecules. The calixarene assumes the pinched-cone conformation as a result of substitution at its lower rim. The C_{60} molecule was modeled as being fourfold rotationally disordered with two separate orientations.

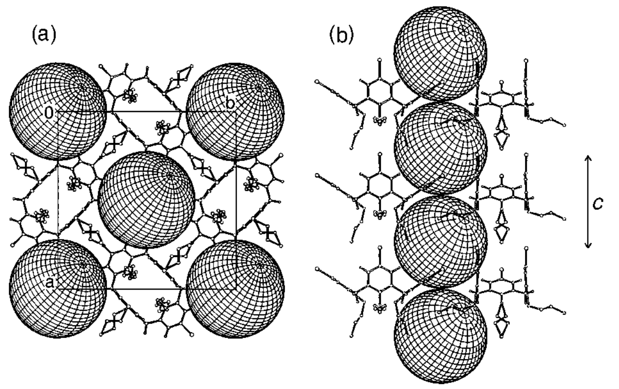


Fig. 2 Packing diagrams (hydrogen atoms omitted) viewed along (a) [001] looking down the linear columns of calixarene and C_{60} molecules, and (b) [−110] showing a side view of the columns and the space-optimization of the calixarene propyl groups.

accurately as 9.8782(5) Å at −100 °C [9.9231(6) Å at room temperature]. In contrast to the close spacing of the C_{60} molecules within the linear strands, the individual nearest-neighbor strands are separated by 12.81 Å (half the diagonal distance of the *ab* unit cell face). Within the linear strands, the $C_{60}\cdots C_{60}$ separation is 0.05 Å shorter than in the structure of pure C_{60}.[3] Taking the mean atom-to-atom diameter of the C_{60} molecule as being approximately 7.07 Å,[3,7] the short $C_{60}\cdots C_{60}$ separation along [001] implies that the shortest possible intermolecular C_{60} C···C distance for a spherically disordered molecule ranges from 2.81 to 3.15 Å. The upper limit compares favorably with previously reported values.[8,9]

The present structure is a striking example of the size–shape complementarity between **1** and C_{60} that allows the formation of an efficiently packed two-component system. This is evidenced by the observation that the crystallographic *c* axis is the repeat distance for both the calixarenes and fullerenes within their respective linear strands as shown schematically in Fig. 3. Although one-dimensional arrangements of C_{60} molecules have been observed in previously reported structures,[10] the complete structural isolation of such strands is unprecedented. Perhaps the most interesting and surprising aspect of the structure is that all the calixarene molecules align themselves in the same direction rather than adopting an overall centrosymmetric arrangement. As a consequence of this polar arrangement, the C_{60} molecules undergo dipole induction and this phenomenon satisfactorily accounts for the rather close spacing of the fullerenes within their linear strands.

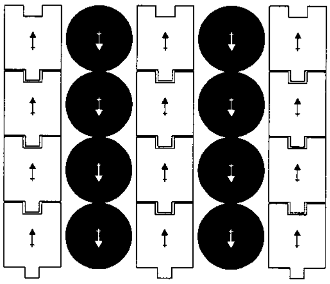


Fig. 3 Schematic representation of the packing arrangement between the calixarene and C_{60} molecules. The view is perpendicular to the *c* axis and the C_{60} molecules are represented by shaded circles. The calixarenes stack in a modular fashion with their dipoles all aligned in the same direction. The calixarene repeat distance exactly matches that for the C_{60} molecules while an opposing polarity is induced in the latter.

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Notes and References

† *Crystal data* for $C_{100}H_{44}Br_4O_4$: M = 1628.99, dark red needle-shaped crystal, 0.40 × 0.20 × 0.20 mm, tetragonal, space group *P4bm* (no. 100), $a = b$ = 18.1160(6), c = 9.8782(5) Å, Z = 2, V = 3241.9(2) Å^3, D_c = 1.669 g cm^3, Siemens SMART CCD diffractometer, Mo-Kα radiation, λ = 0.7107 Å, T = −100 °C, $2\theta_{max}$ = 54.3°, 19179 reflections collected, 3735 unique (R_{int} = 0.0327), μ = 2.548 mm^{-1}. SHELX-TL structure solution and refinement software, final GOF = 1.179, $R1$ = 0. 1174, $wR2$ = 0.3472, R indices based on 3111 reflections with $I > 2\sigma(I)$ (refinement on F^2), L_p and absorption corrections applied, μ = 2.548 mm^{-1}, min. transmission factor = 0.621. The structure was solved by direct methods and expanded by difference electron density synthesis. The asymmetric unit consists of a quarter each of a calixarene and a spherically disordered C_{60} molecule. The calixarene molecule is situated on the intersection of two mutually perpendicular mirror planes running along $x,x+\frac{1}{2},z$ and $\frac{1}{2}-x,x,z$. The propyl groups are disordered across the mirror planes and their hydrogen atoms were not placed. The fullerene molecules are positioned on the fourfold rotation axes at 0,0,z and $\frac{1}{2},\frac{1}{2},z$. CCDC 182/952.

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