Symmetry-Aligned Supramolecular Encapsulation of C_{60}: $[C_{60} \subset (L)_2]$, L = *p*-Benzylcalix[5]arene or *p*-Benzylhexahomooxacalix[3]arene

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Abstract: *p*-Benzylcalix[5]arene (**1**) or *p*-benzylhexahomooxacalix[3]arene (**2**) form 2:1 complexes with C_{60} in solutions of the fullerene or fullerite in toluene to give $[C_{60} \subset (\mathbf{1})_2] \cdot 8$toluene and $[C_{60} \subset (\mathbf{2})_2]$, respectively. In both structures the fullerene is shrouded by two staggered, *trans*-disposed, host molecules. These host calixarenes adopt a cone conformation and the benzyl groups are either dangling ($[C_{60} \subset (\mathbf{1})_2] \cdot 8$toluene) or they are positioned edge-on to the fullerene ($[C_{60} \subset (\mathbf{2})_2]$). The alignment of the symmetry axis of the calixarene, C_5 or C_3, respectively, with the same symmetry element of C_{60} highlights the importance of symmetry matching in the design of host molecules for fullerenes, as it maximises the number of points of contact and the efficiency of the $\pi \cdots \pi$ interactions. Two host–guest associations for **1** and **2** with C_{60} are evident in solutions in toluene. The new oxacalix[3]arene **2** crystallises with chloroform as the 1:1 complex $[CHCl_3 \subset (\mathbf{2})]$.

Keywords: calixarenes · fullerenes · host–guest chemistry · inclusion compounds · supramolecular chemistry

Introduction

Calix[5]arenes and hexahomooxacalix[3]arenes are polyphenolic bowl-shaped molecules with hydrophilic cavities,[1] and have been recently shown to complex C_{60}.[2–7] This host–guest phenomenon is driven by the $\pi \cdots \pi$ interactions and/or a solvophobic effect, while the complementarity of the curvature of the interacting species maximises the number of intermolecular contacts. In the solid state, smaller calix[4]arenes, including a calix[4]resorcinarene, can result in *exo*-cavity π-cloud interactions with C_{60},[5, 9] whereas the larger calix[6]- and calix[8]arenes include C_{60}[10–14] in double cone conformations with a fullerene in each cavity.[10, 12, 13] The alignment of the C_5 symmetry axis of the calix[5]arene in the cone conformation with a C_5 symmetry axis of C_{60} is favoured energetically as it optimises host–guest $\pi \cdots \pi$ interactions.[2, 3] Symmetry considerations are also important in the complexation of hexahomooxacalix[3]arenes with C_{60}[7] and the related bowl-shaped cyclotriveratrylene (CTV)[15, 17] where alignment with the C_3 symmetry axis is possible.

Calix[5]arenes with *p*-methyl and *p*-iodo substitutents result in the formation of solvated 1:1 host–guest species in toluene and other solutions;[3] however, for di-iodo substitution the 2:1 host–guest complex crystallises from solution with the fullerene shrouded by *trans*-north–south pole opposing calixarenes.[3] This has been extended to C_{60}, and also to C_{70}, encapsulated by two covalently linked calix[5]arenes.[5] Recently we reported the formation of toluene-solvated 1:1 species of C_{60} and *p*-benzylcalix[5]arene (**1**), in which the extended benzyl arms of the calixarene created a deep cavity that shrouded most of the surface of the fullerene.[2] We now report the structure of the 2:1 complex in the solid state. It crystallises as the octa-toluene solvate, $[C_{60} \subset (\mathbf{1})_2] \cdot 8$toluene. Also reported are 1) the synthesis of *p*-benzylhexahomooxacalix[3]arene (**2**), and the structure of its inclusion complex with chloroform, which is significant for the understanding of the role of chloroform in the decomposition of calixarene and CTV complexes of C_{60},[10, 11, 13, 15] 2) the synthesis and structure of the 2:1 complex, $[C_{60} \subset (\mathbf{2})_2]$, in which the fullerene is similarly shrouded by two *trans*-disposed container molecules, and 3) solution studies of **1** and **2** with C_{60} in toluene.

Results and Discussion

Synthesis and solution studies: Compound **2** was prepared by the acid-catalysed condensation of 2,6-bis(hydroxymethyl)-4-benzylphenol, and isolated in 30% yield [Eq. (1)]. This is comparable to the generalised synthesis of hexahomooxacalixerenes,[24] but here the tetramer is usually obtained as a by-product. In the present study only the trimer **2** was obtained

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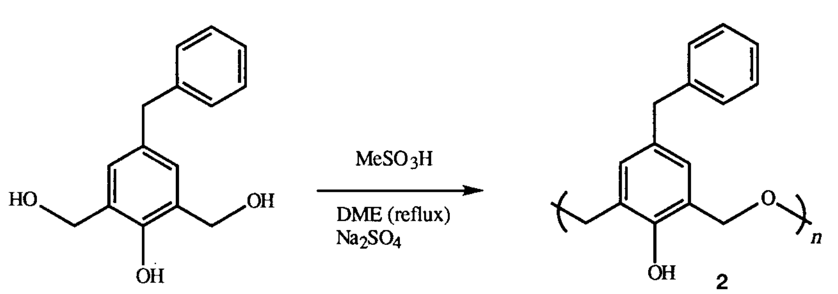
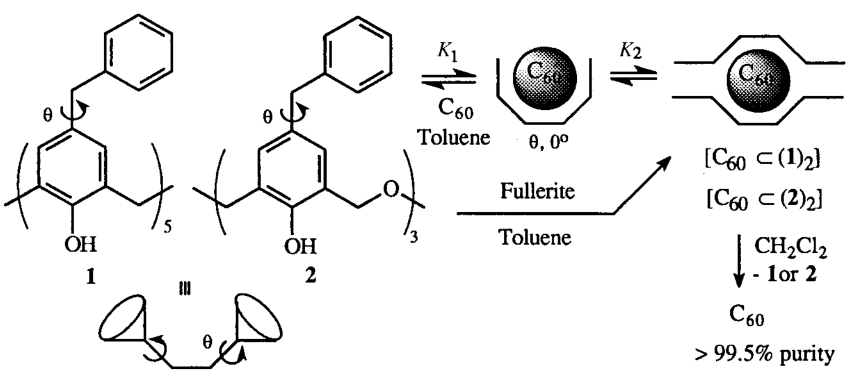


when optimum equivalents of acid were used and there is, therefore, no need to crystallise the mono-Na$^+$ salt in order to separate the mixture of tetramer and trimer.[24]

The syntheses of $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot 8$toluene and $[\mathrm{C}_{60}\subset(\mathbf{2})_2]$ are summarised in Scheme 1. The synthesis of the former was briefly reported elsewhere along with densiometry studies which supported the displacement of two toluene molecules from **1** on complexation with C_{60} in toluene, ($\theta = 0°$, Scheme 1).[2] This work has now been extended to include the determination of the association constants along with the corresponding studies for the complexation of **2** with C_{60}. The 1:1 ratio is prevalent for the corresponding species in toluene solutions of hexahomooxacalix[3]arenes with the groups H, *tert*-butyl, OMe, Br and $\mathrm{CMe_2C_6H_4}$-*p*-OMOM in the *p*-positions of the calixarene, but in these cases only the 1:1 complex crystallises from solution.[7]



Scheme 1. The syntheses of $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot 8$toluene and $[\mathrm{C}_{60}\subset(\mathbf{2})_2]$ as well as the reaction of these complexes with $\mathrm{CH_2Cl_2}$, which represents a one-step purification of C_{60}.

The UV/Vis spectra of solutions of C_{60} (fixed concentration) with **1** in toluene show an isosbestic point only for high concentrations of **1** at $\lambda = 598$ nm (Figure 1b). These findings, along with the values of $K(\mathbf{1})_1 = 2800 \pm 200\ \mathrm{dm^3\,mol^{-1}}$ ($\lambda = 430$ nm, $T = 295$ K)[16] determined at low concentrations of **1** and $K(\mathbf{1})_2 = 230 \pm 50\ \mathrm{dm^3\,mol^{-1}}$ ($\lambda = 430$ nm, $T = 295$ K)[16] determined at higher concentrations suggest the initial formation of the 1:1 complex $[\mathrm{C}_{60}\subset(\mathbf{1})]$, followed by the formation of a 2:1 supermolecule, $[\mathrm{C}_{60}\subset(\mathbf{1})_2]$, on further addition of the host. The formation of a 2:1 complex is consistent with the complex obtained in the solid state. Indeed, crystallisation of the 2:1 complex from solution would drive the equilibrium forward (Scheme 1). Job plots were not consistent with a 1:1 stoichiometry in solution, where, at the concentrations used the second equilibrium would have an impact, notably at a combined concentration of fullerene and calixarene of 3×10^{-3} M (maximum absorption for $[\mathrm{C}_{60}]/\{[\mathrm{C}_{60}] + [\text{calixarene}]\} = 0.65$ compared with 0.5 expected for a 1:1 complex, $\lambda = 430$ nm). Furthermore, molecular mechanics calculations (gas phase) on the minimised structure of two calixarenes with one fullerene, $[\mathrm{C}_{60}\subset(\mathbf{1})_2]$, and a free fullerene is less favoured by only 6 kcal mol^{-1} relative to two $[\mathrm{C}_{60}\subset(\mathbf{1})]$, whereas $[\mathrm{C}_{60}\subset(\mathbf{1})_2]$ is favoured over $[\mathrm{C}_{60}\subset(\mathbf{1})]$

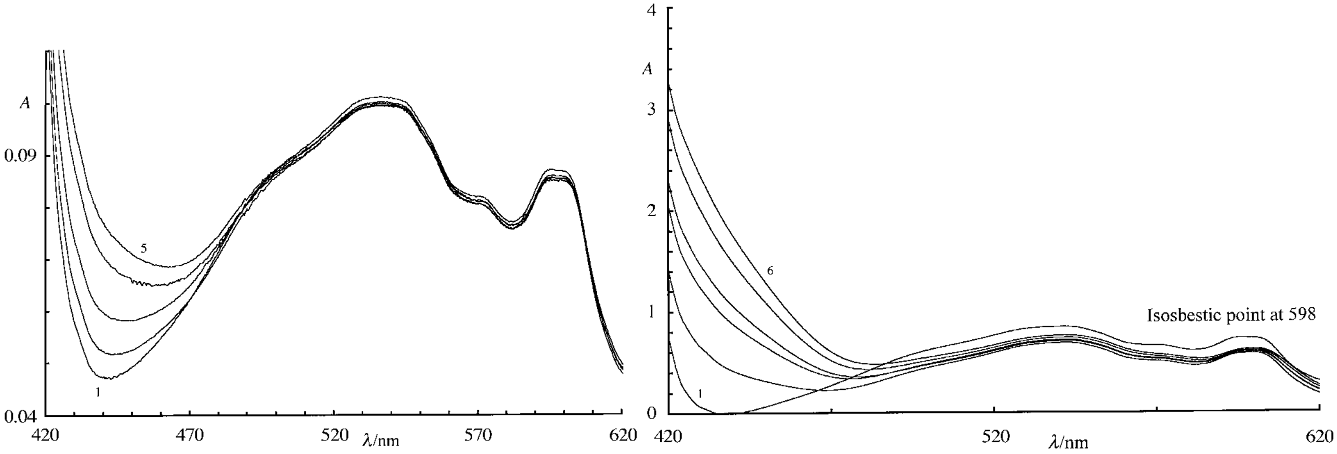


Figure 1. UV/Vis absorption spectra of C_{60} (1.02×10^{-4} M) in the presence of **1** in toluene at 295 K. Concentrations of **1** are: a) from bottom to top (curves 1–5): 0.0, 1.02, 2.02, 3.02, 5.02 ($\times10^{-4}$ M), and b) from bottom to top (curves 1–6) 0.0, 10.03, 20.03, 30.03, 40.03, 50.03 ($\times10^{-4}$ M). The spectra in a) and b) were used for the determination of $K(\mathbf{1})_1$ and $K(\mathbf{1})_2$, respectively.

and a free calixarene by 71 kcal mol^{-1}.[19] The $K(\mathbf{1})_1$ values for the related 1:1 $[\mathrm{C}_{60}\subset(\text{substituted-calix[5]arene})]$ complexes studied by Fukazawa et al. are 2120[3] and $(76\pm5)^{[5]}\times10^3$ dm^{3}mol^{-1} in toluene. There was no mention of a second equilibrium in these studies.

The UV/Vis spectra of solutions of C_{60} (fixed concentration) with **2** in toluene suggest the presence of more than one species in solution (Figure 2). The overall association constant for the 2:1 complex is estimated to be about 100 dm^{3}mol^{-1} ($\lambda = 441$ nm, $T = 295$ K).[16] In contrast, Fuji et al.[7] obtained an association constant of 35.6 dm^{3}mol^{-1} for the 1:1 complex between a related oxacalixarene and C_{60} in toluene, and obtained a 1:1 complex, rather than a 2:1 complex, in the solid state.[7]

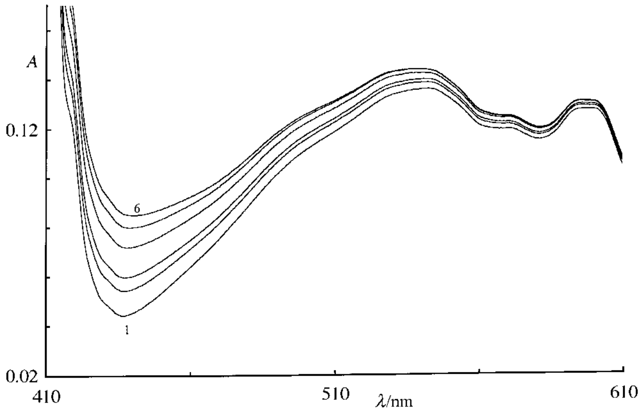


Figure 2. UV/Vis absorption spectra of C_{60} (1.02×10^{-4} M) in the presence of **2** in toluene at 295 K. Concentrations of **2** are: from bottom to top (curves 1–6): 0.0, 10.03, 20.03, 30.03, 40.03 and 60.03 ($\times10^{-4}$ M).

In solution, the 1:1 supermolecule $[\mathrm{C}_{60}\subset(\mathbf{2})]$ the benzyl groups are most likely to be π-bound to the fullerene, which would optimise the number of points of contact between the host molecule and the fullerene, as found in $[\mathrm{C}_{60}\subset(\mathbf{1})]$.[2] This is supported by the minimised structure of $[\mathrm{C}_{60}\subset(\mathbf{2})]$ calculated by molecular mechanics (Figure 3):[19] the structure in which the benzyl arms are π-bound to the fullerene is favoured over side-on C-H···fullerene contacts by 10 kcal mol^{-1}; however, side-on C-H···fullerene contacts are found in the solid-state structure of $[\mathrm{C}_{60}\subset(\mathbf{2})_2]$.

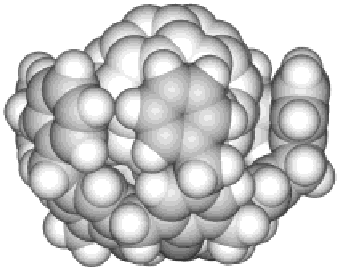


Figure 3. The structure of the $[\mathrm{C}_{60}\subset(\mathbf{2})]$ complex minimised by molecular mechanics which shows the π-bound benzyl arms.

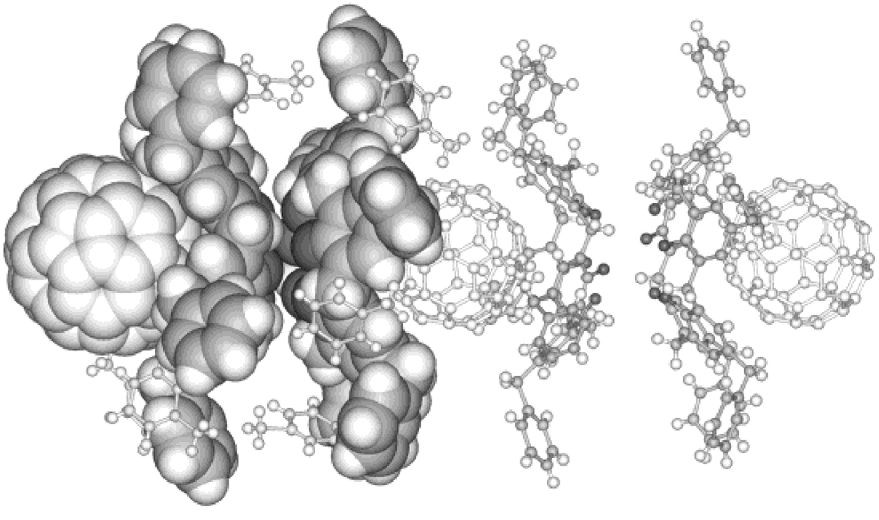


Figure 4. Columnar structure for successive $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot8$ toluene entities; for clarity the toluene molecules are shown for only half the column.

Solid-state structures: The structure of $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot8$ toluene and $[\mathrm{C}_{60}\subset(\mathbf{2})_2]$ at $-100\,^{\circ}$C show two calixarenes bound to a single fullerene in a *trans*-arrangement. In this regard we note that the compound which analyses as a 2:1 complex of CTV with icosahedral *o*-carborane in fact comprises the 1:1 host–guest species with the second CTV self-assembled into a π-stacked array.[21] Formation of $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot8$ toluene and $[\mathrm{C}_{60}\subset(\mathbf{2})_2]$ precludes π···π interaction between the fullerenes with the benzyl groups of the calixarenes either directed away from the fullerene, $\theta = 180^{\circ}$, or oriented so that there are C-H···fullerene interactions, $\theta = 90^{\circ}$ (Scheme 1). There is only one other authenticated structure based on the encapsulation of C_{60} by two container molecules, that is calix[5]arene with three methyl and two iodo groups (1,3-disposition) in the *p*-positions of the upper rim.[3] Other structures are based on supramolecular arrays of host–guest species built up by fullerene–fullerene interactions.[13, 15]

Figure 4 shows the inter-calixarene and calixarene–solvent architecture, and the staggered arrangement of the two calixarenes on each fullerene for $[\mathrm{C}_{60}\subset(\mathbf{1})_2]\cdot8$ toluene. While there is a crystallographically imposed centre of inversion and thus the angle subtended by the centroid of the fullerene and the two centroids of the five oxygen atoms of each calixarene is 180°, the symmetry of the supermolecule is $D_{5\mathrm{d}}$, if the orientation of the benzyl groups is ignored. Thus, one of the five-membered rings of the fullerene is positioned over the lower rim of the calixarene (Figure 5). The closest interactions between the fullerene and the calixarene are at the van der Waals limit, and most of the C···C distances are about 3.5 Å. The closest $\mathrm{O}\cdots\mathrm{C}_{\mathrm{fullerene}}$ contacts are longer (3.81 Å), which is

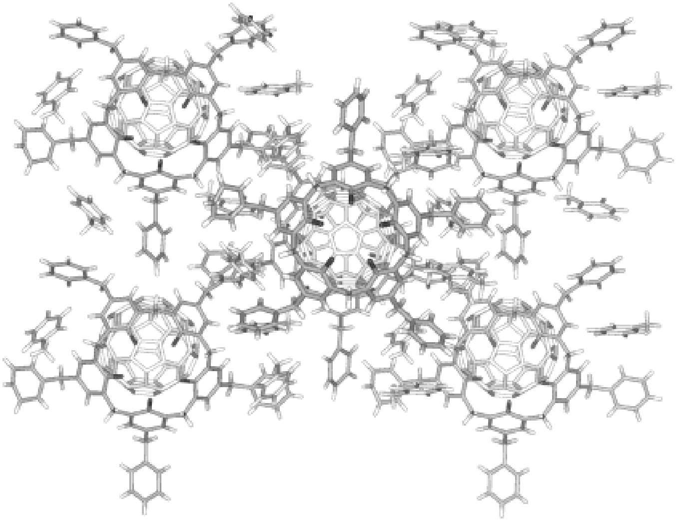


Figure 5. Packing diagram for $[C_{60}\subset(\mathbf{1})_2]\cdot 8$toluene projected down a C_5 axis of the central fullerene; for clarity only this fullerene is shown with its two associated calixarenes.

in accordance with the fullerene facing the π-cloud of the aromatic rings. The supermolecules are stacked back-to-back, which is possibly associated with H-bonding; the closest intercalixarene $O\cdots O$ distances are 3.10 Å. This type of back-to-back interaction is also found in the structure of [tetralin $\subset$ *p-tert*-butylcalix[5]arene] · ethanol, its closest intercalixarene $O\cdots O$ distance is 2.79 Å.[22]

There is no back-to-back stacking of the supermolecules in the structure of $[C_{60}\subset(\mathbf{2})_2]$ (Figure 6). Here there is a crystallographically imposed D_{3d} symmetry and again the angle subtended by the centroid of the fullerene and the two centroids of the two sets of three phenolic oxygen atoms of each calixarene is 180°. Symmetry requires a six-membered ring of the fullerene to reside symmetrically over the lower rim of the calixarene (Figure 7), which is also found in the 1:1 complex of C_{60} with bromohexaoxacalix[3]arene.[7] It is noteworthy that this complex exhibits intermolecular, back-to-back phenolic H-bonding ($O\cdots O = 3.01$ Å), as observed in $[C_{60}\subset(\mathbf{1})_2]$.[7] The greater flexibility of the host allows both π-cloud interactions of the phenolic groups with the fullerene as well as interactions with the dibenzyl oxygen centres. Nearest host–guest contacts are at the van der Waals limit; most of the $C\cdots C$ distances are ≈3.83 Å, and nearest $O\cdots C_{\text{fullerene}}$ contacts are 3.14 (ether oxygen atoms) and 3.64 (phenolic oxygen atoms) Å.

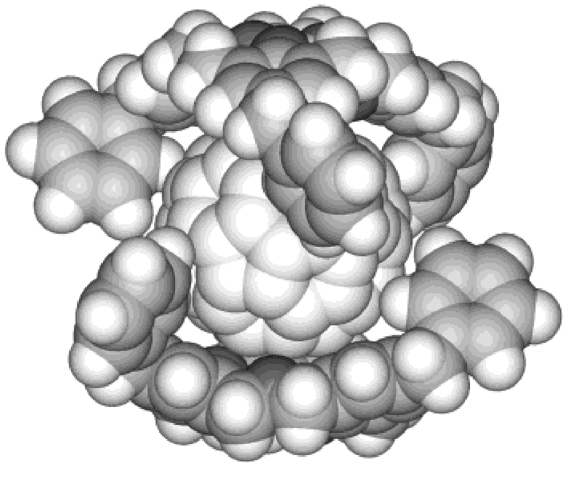


Figure 6. Supermolecule of $[C_{60}\subset(\mathbf{2})_2]$.

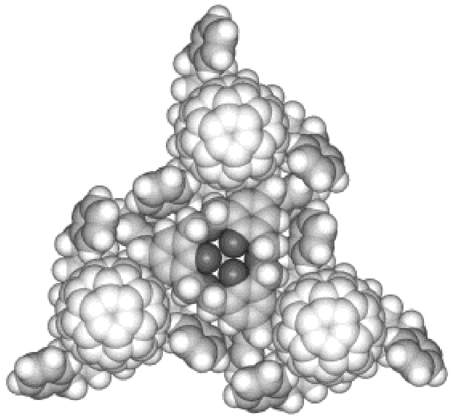


Figure 7. Packing diagram for $[C_{60}\subset(\mathbf{2})_2]$, projected along a C_3 axis of the central fullerene.

The curvature complementarity of calix[5]arenes and hexahomooxacalix[3]arenes for the phenolic residues with the curvature of C_{60} in the two host–guest structures is noteworthy. The pitch angle, defined by the inclination of the planes of the phenol rings relative to the plane of the five oxygen atoms, shows that the empty[23] or solvent-occupied[22, 24] cavity of the calixarene has an oval shape with respect to the phenolic oxygen atoms. In $[C_{60}\subset(\mathbf{1})_2]$ there is a circular arrangement of the oxygen atoms with pitch angles 132–142°, as found in other calix[5]arenes complexes of C_{60}: 134–138° for $[C_{60}\subset(I_2Me_3\text{calix[5]arene})_2]$, 133–137° for $[C_{60}\subset(Me_5\text{calix[5]arene})_2]$ and 132–144° for $[C_{60}\subset(Me_3H_2\text{-calix[5]arene})_2]$.[3] This rearrangement is also evident in the phenolic hydrogen-bonded network. Note that on the NMR time scale all hydroxy protons are equivalent in solution. Upon complexation, a downfield shift of $\Delta\delta = +0.23$ ppm is observed in the ^1H NMR spectrum in $[D_8]$toluene, while there is a corresponding upfield shift in the ^{13}C NMR spectrum for C_{60} of $\Delta\delta = -0.26$ ppm (cf. $\Delta\delta = -0.35$ ppm) spectrum.[3] Similarly, in the IR spectra (KBr) there is a shift in ν_{O-H} from 3229 to 3198 cm^{-1}, while the intramolecular $O\cdots O$ distances, 2.72–2.80 Å (cf. 2.90 Å in [tetralin $\subset$ *p-tert*-butylcalix[5]arene] · ethanol[21] and 2.84 Å in [acetone $\subset$ *p-tert*-butylcalix[5]arene][23]) also suggest an induced fit.

The hexahomooxacalix[3]arene is more flexible than the calix[5]arenes and can reorganise for C_{60} inclusion. Upon complexation, the ^1H NMR downfield shift for the hydroxy group is only $\Delta\delta = +0.004$ ppm, while there is a corresponding ^{13}C NMR upfield shift for C_{60} of $\Delta\delta = -0.03$ ppm (cf. -0.002 for complexation with *tert*-butyl-hexahomooxacalix[3]arene),[4] while the ν_{O-H} (KBr) for the free ligand changes from 3357 to 3344 cm^{-1}. The intramolecular $O\cdots O$ distance of 2.71 Å (cf. 3.00, 3.09 Å in *tert*-butyl-hexahomooxacalix[3]arene,[18] 2.93 Å in [$C_{60} \subset$ (bromooxacalix[3]arene)] and 2.86 – 2.93 Å in [$C_{60} \subset$ (*tert*-butyloxacalix[3]arene)]),[7] and the symmetrical pitch angle of 157° (cf. 141.5°, 148.0° for *t*-butyl-hexahomooxacalix[3]arene,[18] 147° in [$C_{60} \subset$ (bromooxacalix[3]arene)] and 144 – 153° in [$C_{60} \subset$ (*tert*-butyloxacalix[3]arene)][7]) provide evidence of structural flexibility and subtle rearrangement during crystallisation.

Even for a 1:1 mixture of **1** or **2** with C_{60} in toluene, the 2:1 complexes precipitate. In the case of **1** it is also the only complex formed by the treatment of a fullerite mixture in toluene with **1**. The addition of dichloromethane to these 2:1 complexes liberates the starting C_{60} [>99.5 % (HPLC)], which can be readily isolated [30 % recovery of the fullerene, based on the change in the C_{60}:C_{70} ratio (HPLC)] and thus represents an effective one-step purification of C_{60} (Scheme 1). There is no evidence for complexation of C_{70} or any of the higher fullerenes in the solid state, so that this finding represents a major advance in the use of selectivity in host – guest chemistry as a means of purifying C_{60}. Earlier studies centred on the use of *p*-butyl-calix[8]arene; however, here some C_{70} is incorporated into the micelle-like structure which requires two recrystallisations in order to obtain C_{60} with >99.5 % purity.[10, 11] Interestingly, the complexation of C_{60} with the mixture of calixarenes formed from the condensation of *p*-benzylphenol with paraformaldehyde[2, 20] is effective for the retrieval of **1** from other products, including the *p*-benzylcalix[6]- and *p*-benzylcalix[8]arenes. Similar studies with **2** and fullerite did not give any selective extraction of C_{60}.

For a 1:1 species, and in the absence of solvent effects, the minimised structure, in which the five benzyl rings are π-bound to the fullerene, [$C_{60} \subset$ (**1**)], is favoured by ≈40 kcal mol^{-1} relative to the structure with the benzyl groups directed away from the fullerene, as observed in the crystal structure of [$C_{60} \subset$ (**1**)$_2$] · 8 toluene.[19] Little change in the overall structure of [$C_{60} \subset$ (**1**)$_2$] · 8 toluene is observed, however, on the minimisation which starts from the crystallographic coordinates and includes the solvent molecules. Minimised [$C_{60} \subset$ (**1**)$_2$], in the absence of the toluene molecules, rearranges to a structure which contains three benzyl groups of each calix[5]arene π-bound to the C_{60}. There is insufficient space for the remaining benzyl groups to approach C_{60}. In the crystal structure, the back-to-back stacking of the calixarenes which involves H-bonding coupled with the interplay of the benzyl groups of other stacked columns, in addition to the effect of the occluded toluene, (Figure 3) collectively stabilise the 2:1 species in the solid state. The 2:1 structure of a mixed methyl-/iodo-substituted calix[5]arene with C_{60}[3] does not have back-to-back stacking of the supermolecules. Here interactions involving polarisable iodine atoms may predetermine the 2:1 ratio in the solid state.[3]

Energy minimisation of [$C_{60} \subset$ (**2**)$_2$], which starts with the geometry of the supermolecule in the crystal structure, results in the rotation of the benzyl groups to enable π-bonding to the fullerene (energy difference of ≈40 kcal mol^{-1}). However, there is insufficient space for the six benzyl groups and, as a consequence, one molecule of **2** slides off to one side to allow only two of its benzyl groups to π-bond while the other is too distant from the C_{60}. In the solid-state structure of [$C_{60} \subset$ (**2**)$_2$], the edge-on benzyl groups are presumably stabilised by crystal packing, in which benzyl groups on one molecule interact strongly with benzyl groups of neighbouring molecules.

The 1:1 complex [$CHCl_3 \subset$ (**2**)] (Figure 8) crystallises from a toluene/$CHCl_3$ solution. Here, the symmetry-imposed uniform pitch angle (151.3°) and the O ··· O distance (2.82 Å), further demonstrate the ability of **2** to adapt to the available guest. The nature of the chloroform – host interactions is noteworthy. The chloroform hydrogen atom is hydrogen-bonded to the three phenolic oxygen atoms of **2** with a $Cl_3C–H \cdots O$ distance of 2.73 Å, while the nearest distance between the same chloroform and a second oxacalix ($HC(Cl)_2Cl \cdots$ oxacalix) is 3.71 Å (Figure 8). This type of interaction between chloroform and calixarenes may effectively cause competition for such molecules and favour chloroform molecules at the expense of fullerenes, thereby resulting in decomposition of calixarene – fullerene complexes formed in toluene.[10, 11, 13, 15] However, non-classical $Cl_3C–H \cdots$ π-aromatic hydrogen interactions are also possible[6, 26, 27] and may effectively compete against fullerene complexation.

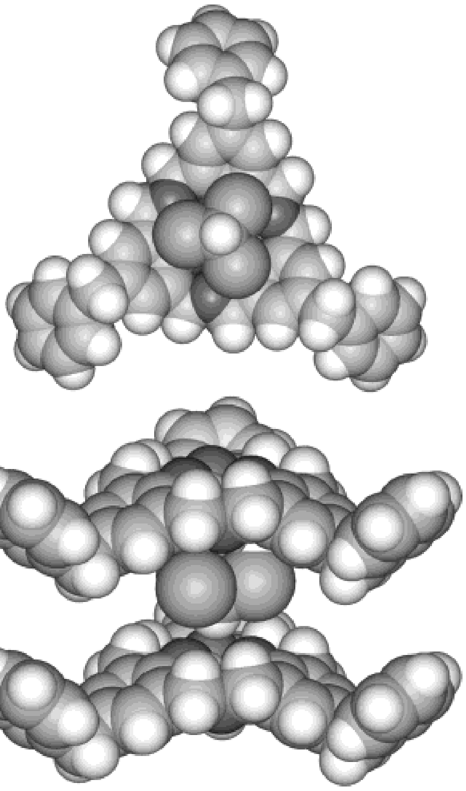


Figure 8. Structure of the [$CHCl_3 \subset$ (**2**)] complex: top) projected along a C_3 axis and bottom) a side-on view.

Conclusions

Our findings provide further insight into the construction of supramolecular assemblies of fullerenes and the rational design of container molecules for selective complexation of C_{60} over C_{70} and higher fullerenes. We note that *p*-benzylcalix[6]-and *p*-benzylcalix[8]arenes show complexation in toluene (change in electronic spectra at $\lambda \approx 420-480$ nm);[4, 15] however, they do not form discrete host–guest complexes in the solid state. Alignment of the C_3 or C_5 symmetry axis with the same symmetry axis of a fullerene is noteworthy; this maximises the number of points of contact within the supermolecules and thereby enhances the overall van der Waals interaction energy.

Experimental Section

General: All solvents and starting materials were obtained from Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker DRX400 spectrometer referenced relative to partially deuterated solvent and carbon signals. The IR spectra were recorded on a Perkin–Elmer1610 FTIR (4000–400 cm^{-1}) as KBr discs. Mass spectra were recorded on a Bruker BioApex47e FTMS (4.7 Tesla) fitted with an Analytica electrospray source. Elemental analysis were performed by Chemical and Micro Analytical Services. HPLC were performed on a Varian5000 liquid chromatograph fitted with a Varian UV-50 UV/Vis detector operating at 254 nm with a Waters DeltaPak C18 100 Å (PN#11797) column. X-ray data was recorded on an Enraf–Nonius Kappa CCD or a Siemens SMART CCD diffractometer.

***p*-Benzylcalix[5]arene (1)**: This synthesis is a modification of the method reported by Vincens et al.[20] and was carried out under an inert N_2 atmosphere: *p*-benzylphenol (19.45 g, 106.8 mmol) and paraformaldehyde (9.0 g, 300 mmol) were suspended in tetralin (130 mL) and heated to 80 °C. A solution of aqueous KOH (1.4 mL, 14 M) was added and the temperature quickly raised (<5 min) to 200 °C. The mixture was kept at 200 °C for 4 h, and then worked up according to the literature procedure.[20]

***p*-Benzylhexahomooxacalix[3]arene** (**2**): Sodium sulfate (4 g) and methanesulfonic acid (0.67 mL) were suspended in DME (200 mL). This mixture was brought to reflux, at which point 2,6-bis(hydroxymethyl)-4-benzylphenol (1.22 g) was added. The mixture was refluxed for 5 h and then the reaction was quenched by the addition of a saturated solution of sodium bicarbonate (50 mL). The solvent was removed in a vacuum. $CHCl_3$ (50 mL) and H_2O (100 mL) were added and the water layer washed with a further $CHCl_3$ (50 mL). The organic fractions were combined, dried with $MgSO_4$ and evaporated to dryness. Isopropyl alcohol (25 mL) was added and the suspension refluxed for 1 h and then allowed to cool which afforded a white powder. M.p. 300 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.84$ (s, 2H; Ar-CH_2-Ar), 4.64 (s, 4H; Ar-CH_2-O), 6.92 (s, 2H; Ar-H), 7.21 (m, 5H; Ar-H), 8.62 (s, 1H; OH); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 34.2$ (Ar-CH_2-Ar), 62.5 (Ar-CH_2-O), 115.4 (Ar), 117.2 (Ar), 119.6 (Ar), 121.0 (Ar), 122.4 (Ar), 124.0 (Ar), 132.6 (Ar), 145.2 (Ar-OH); IR (KBr): $\tilde{\nu} = 3358$ (s, br), 3024 (w), 2963 (w), 2863 (w), 1611 (m), 1486 (s), 1357 (m), 1260 (s), 1153 (s), 1075 (s), 1018 (m), 978 (m), 880 (m), 798 (m), 701 (m) cm^{-1}; MS (ESI): m/z (%): 701 (60) [M+Na$^+$]; $C_{45}H_{42}O_6$ (678.8): calcd C 79.62, H 62.37, O 14.14; found C 79.45, H 6.31, O 14.24. Crystals for X-ray studies were grown from a solution of toluene/$CHCl_3$ (10:1).

[$C_{60} \subset (1)_2$] · 8toluene: Synthesis from fullerite is similar to the method that used C_{60}.[2] Analytical HPLC performed on a standard solution of C_{60}:C_{70} (1:1, 1 mg mL^{-1}) with 100% hexane as eluent gave a satisfactory separation ($R_f = 5.31$ and 7.28 for C_{60} and C_{70}, respectively, at a flow rate of 1 mL min^{-1}; detector wavelength: $\lambda = 254$ nm). Under the same conditions [$C_{60} \subset (\mathbf{1})_2$] · 8toluene was found to have a retention time of 5.32, with no evidence of any higher fullerenes.

[$C_{60} \subset (2)_2$]: To a solution of C_{60} (5 mg) in toluene (1 mL) was added **2** (10 mg). When the mixture was allowed to stand for 12 h, reddish crystals were obtained. Yield: 6 mg (42%); IR (KBr): $\tilde{\nu} = 3344$ (m, br), 3022 (w), 2851 (w), 1604 (m), 1485 (s), 1429 (m), 1357 (m), 1252 (m), 1182 (m), 1151 (m), 1075 (s), 1027 (m), 978 (m), 877 (m), 795 (m), 700 (m), 576 (m), 527 (m) cm^{-1}; $C_{150}H_{84}O_{12}$ (2078.3): calcd C 86.69, H 4.07, O 9.24; found C 86.71, H 4.10,O 9.21.

Crystallographic data:

[$C_{60} \subset (\mathbf{1})_2$] · 8toluene: Siemens SMART CCD diffractometer; $T = 173(2)$ K; $C_{214}H_{136}O_5$; monoclinic, $P2_1/n$ (No. 14); $a = 17.1656(8)$, $b = 17.5663(8)$, $c = 28.3785(11)$ Å, $\beta = 105.7750(10)°$; $V = 8234.8(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.124$ mg m^{-3}; $\mu = 0.066$ mm^{-1} (no correction), Mo$_{K\alpha}$ radiation, 16867 unique reflections, $2\theta = 1.38-27.28°$ (38061 observed, $I > 2\sigma(I)$), $R_1 = 0.1763$, $wR_2 = 0.3517$.

[$C_{60} \subset (\mathbf{2})_2$]: Enraf-Nonius Kappa CCD diffractometer; $C_{150}H_{84}O_{36}$; trigonal (hexagonal setting); $R\bar{3}$ (No. 148), $a = 18.546(1)$, $c = 24.643(1)$ Å; $V = 7340.4(5)$ Å^3, $Z = 3$, $\rho_{calc} = 1.671$ mg m^{-3}; $\mu = 0.12$ mm^{-1} (no correction), Mo$_{K\alpha}$ radiation, 4064 unique reflections, $2\theta = 3.32-28.34°$ (10819 observed, $I > 2\sigma(I)$), $T = 173(2)$ K, $R_1 = 0.1393$, $wR_2 = 0.1362$.

[$CHCl_3 \subset (\mathbf{2})$]: Enraf-Nonius Kappa CCD diffractometer; $C_{46}H_{43}Cl_3O_6$; trigonal (hexanonal setting), $R\bar{3}$ (No. 148); $a = 16.939(2)$, $c = 7.946(2)$ Å; $V = 1974.5(6)$ Å^3, $Z = 2$, $\rho_{calc} = 1.342$ mg m^{-3}; $\mu = 0.282$ mm^{-1} (no correction), Mo$_{K\alpha}$ radiation, 1391 unique reflections, $2\theta = 2.92-28.25°$ (2709 observed, $I > 2\sigma(I)$), $T = 173(2)$ K, $R_1 = 0.0709$, $wR_2 = 0.1664$. All structure solutions and refinements were performed with SHELXTL[28] and teXsan.[29]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Data Centre as supplementary publication nos. CCDC-102743 for [$C_{60} \subset (\mathbf{2})_2$], CCDC-102472 for [$CHCl_3 \subset (\mathbf{2})$], and CCDC-102443 for [$C_{60} \subset (\mathbf{1})_2$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21E2, UK (fax: (+ 44)1223-336-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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