Supramolecular encapsulation of aggregates of C_{60}

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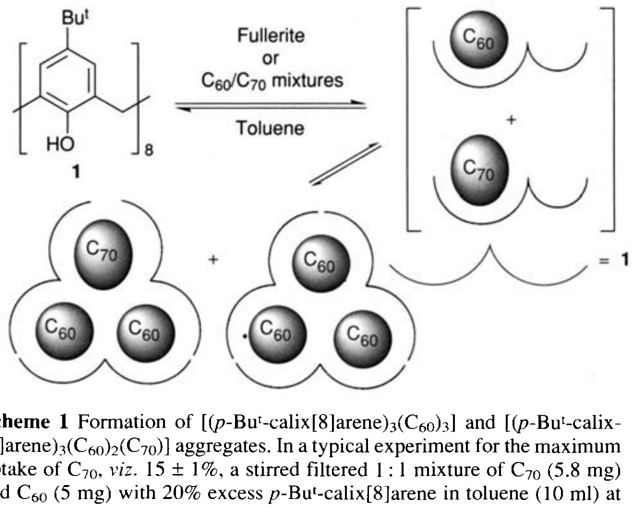
The 1 : 1 *p*-Bu^t-calix[8]arene complex of C_{60} is micelle-like, with a trimeric aggregate of fullerenes surrounded by three host molecules each in the double cone conformation, a structure that can accommodate one C_{70} unit by isomorphous replacement of one C_{60}.

Discrete guest–host complexes involving fullerenes are of interest, in part, in the direct purification of fullerenes from carbon soot.[1–6] Both C_{60} and C_{70} form complexes with a variety of macromolecules, notably calixarenes [**1**, R = H or alkyl, *n* = 6 or 8, (Scheme 1)],[1–5] cyclotriveratrylene (CTV),[6] γ-cyclodextrin,[7] azacrown ethers[8] and a porhyrazine.[9] None of the calixarene complexes have been structurally substantiated, with solid state NMR spectroscopy being inconclusive.[2–4] Herein we show that the 1 : 1 complex between *p*-Bu^t-calix[8]arene and C_{60} is micelle-like with a trimeric aggregate of fullerenes as the core surrounded by three host molecules, each in the double cone conformation and spanning two fullerenes along a triangular edge; the same species forms in C_{60}/C_{70} mixtures, along with a C_{70} containing species, most likely the analogous complex based on [$(C_{60})_2(C_{70})$]. This is based on combining UV–VIS and NMR spectroscopy and X-ray powder diffraction studies, together with the uptake of C_{70} along with C_{60} and molecular mechanics.

Cooling magenta toluene solutions of C_{60} with excess *p*-Bu^t-calix[8]arene below *ca.* 80 °C[1] results in the appearance of a visible absorption band at 470 nm. The band is characteristic of a resonant inter-fullerene molecular transition[5] similar to that observed in thin films of C_{60},[8] rather than a charge transfer transition between the host system and the electron deficient fullerene. The 470 nm absorption band is in fact due to fullerene aggregation in a very finely divided precipitate of the 1 : 1 complex, the filtered solutions at ambient temperature being colourless if excess calixarene is present. Thus, associated fullerenes are present in the solid. A major difficulty in encouraging guest–host complexation of C_{60} is that the fullerene is spherical and non-polarised. Complexation as a monomeric 1 : 1 transient intermediate (Scheme 1) most likely involves distortion of the electron cloud of the fullerene[6] which then favours micelle-like formation featuring fullerene–fullerene interactions in the interior core with the fullerenes encapsulated by the host calixarene molecules.



Scheme 1 Formation of [$(p$-Bu^t-calix[8]arene$)_3(C_{60})_3$] and [$(p$-Bu^t-calix[8]arene$)_3(C_{60})_2(C_{70})$] aggregates. In a typical experiment for the maximum uptake of C_{70}, *viz.* 15 ± 1%, a stirred filtered 1 : 1 mixture of C_{70} (5.8 mg) and C_{60} (5 mg) with 20% excess *p*-Bu^t-calix[8]arene in toluene (10 ml) at *ca.* 100 °C was cooled to room temperature and after *ca.* 12 h the precipitate was collected and washed with a 10% toluene in hexane solution, with the dried product taken up in methylene chloride for HPLC studies.

It is evident from ^{13}C CP-MAS NMR data[10] that no well-ordered structure of the Bu^t-calix[8]arene complex of C_{60} exists, and a variety of modifications are possible in the solid state depending on the solvent system and thermal treatment (heating to *ca.* 180 °C for several hours). X-Ray powder diffraction data show that the material crystallising from solution does not have long range order. Thermal treatment results in more extensive diffraction and thus more ordering on heating. Nevertheless all the NMR data is consistent with a ratio of *ca.* 2 : 6^3 for two different types of Bu^t-phenyl groups. A local structure in agreement with this ratio has each calixarene spanning two fullerenes such that three of these *tert*-butylphenyl groups wrap around each fullerene with a fourth *tert*-butylphenyl group also associated with each fullerene, yet astride both fullerenes. Thus each calixarene is in a double cone conformation which would require minimal perturbation of the H-bonded phenol network relative to uncomplexed *p*-Bu^t-calix[8]arene,[11] as concluded from earlier IR studies.[1,2]

Fullerene C_{70} alone does not form a precipitate with *p*-Bu^t-calix[8]arene in toluene, although some complexation occurs in the presence of C_{60}. This is consistent with an aggregate of fullerenes with at least one of the C_{60}'s replaced by C_{70}. However, the maximum molar incorporation of C_{70} in the complex is only 15 ± 1.0% as established by HPLC[12] calibrated with standardised solutions of C_{60} and C_{70}. This maximum is for solutions with an excess of calixarene relative to C_{60} and C_{70} and for an excess of C_{70} relative to C_{60}; beyond a *ca.* 1 : 4 ratio for C_{60} : C_{70} no precipitate is obtained, possibly at the expense of forming complex toluene soluble species. Analysis of the mixed C_{60} : C_{70} complex for the highest uptake of C_{70} gives an overall calixarene to fullerene ratio of 1 : 1 as for the complex based exclusively on C_{60}. Comparison of the X-ray powder diffraction patterns of the C_{60} complex freshly prepared and after heat treatment (see above) with that containing some C_{70}[10] is consistent with some isomorphous replacement of C_{60} by C_{70}. The most likely model is that based on two C_{60} units and one C_{70} in a micelle-like structure similar to that for the pure C_{60} complex. Incorporating more than one molecule of C_{70} per fullerene trimer may be too disruptive to the tight fullerene–calixarene meshing as identified by molecular mechanics (see below). Interestingly pure C_{70} forms a 2 : 1 fullerene rich complex in benzene and not toluene and the solid state NMR data,[4] which indicates the fullerenes are symmetrical, can now be interpreted as being representative of a complex with two C_{70}'s at the van der Waals limit residing in each cavity of the calixarene in a double cone conformation. This is a reasonable structure using molecular mechanics, with the overall structure dominated by fullerene–fullerene interactions.

The determination of the number of fullerenes in the clusters rests on consideration of molecular mechanics. These were performed using BIOSYM[13] for the two aggregates [(*p*-Bu^t-

calix[8]arene)$_3$(C_{60})$_3$] and [(*p*-Bu^t-calix[8]arene)$_3$(C_{60})$_2$(C_{70})], and the minimised structures are shown in Fig. 1. In both structures the calixarenes are in the double cone conformation with two *tert*-butylphenyl groups distinct from the other six in lying astride two fullerenes, consistent with NMR studies (see above).[3,10] These two groups are directed towards the centre of the triangle of fullerenes and in the (C_{60})$_3$ aggregate this approximates to a C_3 symmetry axis. The calixarenes are chiral with individual C_2 symmetry, the principle axis of the envelope of hydrogen bonded hydroxy groups being *ca.* 45° away from the plane of the fullerenes. The (C_{60})$_3$ aggregates have overall D_3 symmetry.

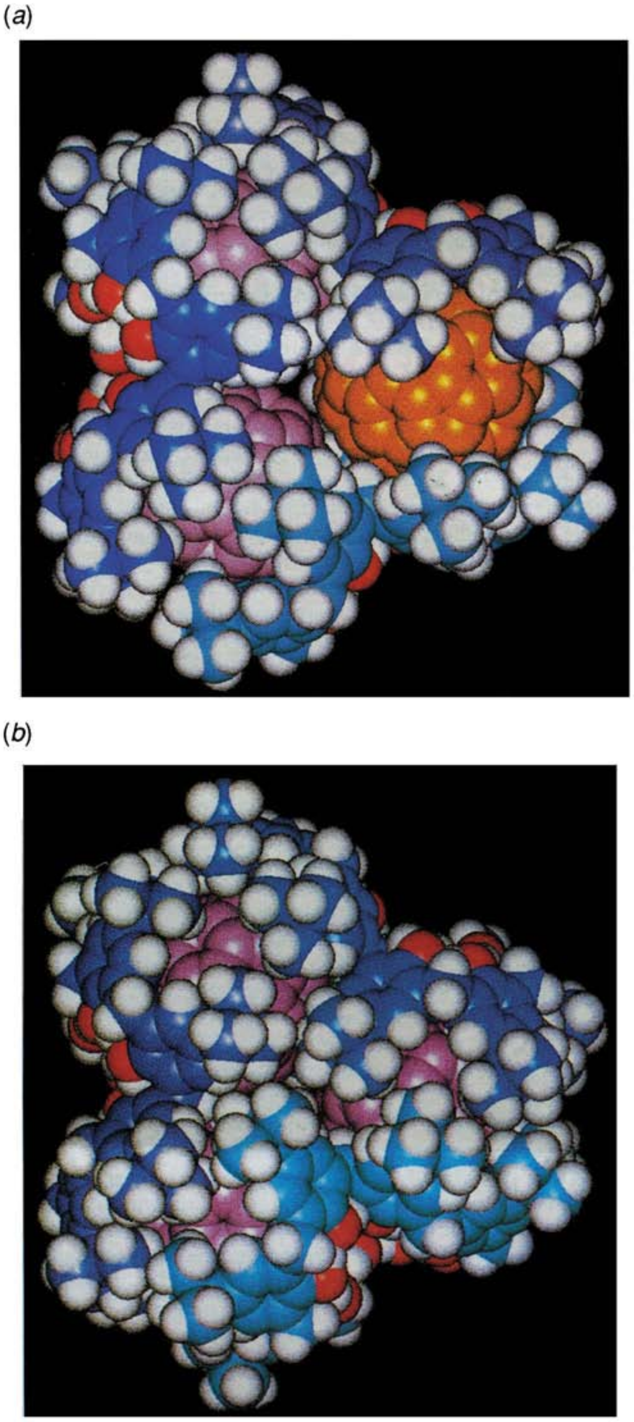


Fig. 1 Space filling molecular mechanics structure of (*a*) [(*p*-Bu^t-calix[8]arene)$_3$(C_{60})$_3$] and (*b*) [(*p*-Bu^t-calix[8]arene)$_3$(C_{60})$_2$(C_{70})]; standard CVFF forcefields were employed and the structure minimised using the conjugate gradients algorithm with a convergence criterion of the average derivative being less than 0.001 kcal mol^{-1} (1 cal = 4.184 J)

The calixarene molecules of the minimised trimers have four aromatic rings orientated for π–π cloud interaction with each fullerene. Incorporating one C_{70} results in a more open structure yet still retaining this interaction. A second C_{70} disrupts the otherwise encapsulating structure even further, and this would possibly be at the expense of any precipitation–complexation. The presence of aggregates of fullerene complexes rather than monomeric species explains why the so called size specific nature of the calixarene complexing C_{60} is associated with some complexation of C_{70}, since pure C_{70} fails to form a complex under the same conditions.

A dimeric structure has been ruled out on several grounds, including the fact that the structure with each of the two calixarenes in a similar double cone conformation has considerable surface area of the fullerenes exposed at that ends of the dimer, such that additional fullerene–fullerene interactions are possible. Aggregates based on more than three fullerenes would be at odds with molecular mechanics. Notably, the van der Waals contact of more than two calixarenes on a fullerene while maintaining maximum π–π interaction is not possible, and also there is insufficient surface to accommodate the calixarenes while maintaining a 1 : 1 ratio of fullerene to calixarene. Molecular mechanics on the monomeric 1 : 1 [(*p*-Bu^t-calix[8]-arene)(C_{60})] (and the C_{70} analogue) gives a minimum corresponding to five of the aromatic rings of the calixarene forming a shallow cavity associated with docking of the fullerene, the other three aromatic rings in a smaller cone with the phenolic protons forming a closed hydrogen bonded loop.[11] Such species for both C_{60} and C_{70} analogue are likely to be intermediates in the formation of the micelle-like structures (Scheme 1).

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