COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Inter-digitation approach to encapsulation of C_{60}: [$C_{60} \subset$ (p-phenylcalix[5]arene)$_2$]†

Mohamed Makha, Michaele J. Hardie and Colin L. Raston*
Department of Chemistry, University of Leeds, Leeds, UK LS2 9JT.
E-mail: c.l.raston@chemistry.leeds.ac.uk; Fax: +44 0113 2336401; Tel: +44 0113 233655

Received (in Cambridge, UK) 16th April 2002, Accepted 28th May 2002
First published as an Advance Article on the web 14th June 2002

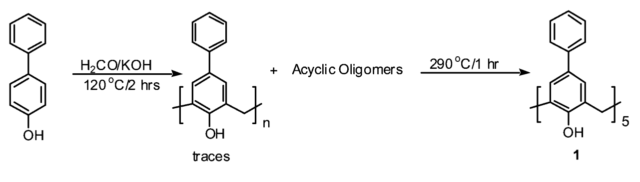
p-Phenylcalix[5]arene shows a strong and selective binding of C_{60} in toluene resulting in crystallisation of a hemi-spherically inter-digitated 2 : 1 complex; the receptor itself crystallises from toluene with self assembly through phenyl group inclusion.

The last decade has seen developments in the host–guest chemistry of fullerenes involving cavitands, especially calixarenes.[1] Initially this was concerned with practical separation techniques of fullerene C_{60}, then crystal engineering and supramolecular chemistry including materials applications such as high temperature superconductivity.[2] Progress in separation of fullerenes deals with retrieval of C_{60} *via* complexation with ^{t}Bu-calix[8]arene[3] and the lower cyclic phenolic oligomers calix[5,6]arenes.[4,5] Calix[5]arenes usually adopt the cone conformation which has dimensional and curvature complementarity for binding a single molecule of C_{60}[6–8] thereby optimising host–guest $\pi\cdots\pi$ interactions,[7] and this has been observed in the solid state for a number of complexes.[6,7,9] We have previously established C_5 symmetry alignment of p-benzylcalix[5]arene with a C_5 symmetry axis of C_{60} in the solid state which manifests itself in high selectivity for binding C_{60} over other fullerenes.[7] In contrast calix[6,8]arenes adopt a double cone conformation with a fullerene in each shallow cavity.[5,10]

As part of our ongoing endeavours in host–guest calixarene–fullerenes chemistry, we recently reported the synthesis of the deep cavity p-phenylcalix[5]arene, **1**, accessible by a direct 'one pot' procedure.[11] Herein we report the improved synthesis of **1** along with its solid state structure and the synthesis and structure of inter-digitated [$C_{60} \subset (\mathbf{1})_2$], and C_{60} binding and separation studies.

The improved synthesis of the receptor, **1**, minimises the use of noxious organic solvents such as tetralin and phenylether, and dispenses with the use of a multiple step process to prepare such compounds.[12] The procedure consists of heating a slurry of p-phenylphenol, KOH and formaldehyde solution for 2 hours at 120 °C, and the resulting solid is transferred to a Kugelrohr and rapidly heated at 290 °C *in vacuo* for 1 hour. Work up of the brown solid then followed the published procedure, affording **1** in 10% yield (*cf.* 5%),[11] Scheme 1.

Crystals of **1** were obtained as a toluene solvate, **1**·(toluene)$_{1.75}$, and the structure determined by X-ray crystallography.‡ The calixarene is in an unsymmetrical cone conformation with centroid···centroid···centroid angles between adjacent inner phenyl groups ranging from 97.5 to 115.3°. One outer rim phenyl group is disordered over two orientations and all are twisted away from the plane of their adjoining inner phenyl ring at torsion angles ranging from 1.4 to 40.2°. The calixarenes show close associations with one another through two modes; a host–guest interaction and phenolic back-to-back stacking. The host–guest association has one arm of a calixarene protruding into the bowl of an adjacent symmetry equivalent host molecule, Fig. 1.



Scheme 1

Two inner phenyl rings within this association are coplanar at centroid···centroid separation 4.35 Å. The outer-rim phenyl group sits slightly displaced from the center of the calixarene bowl, the distance between the phenyl centre and centre of the host O_5 plane at 4.07 Å. Calixarene molecules within the extended structure stack back-to-back with intermolecular phenolic O···O separations 2.88–3.30 Å. These distances are consistent with the formation of hydrogen bonds, however the hydrogen atoms were not located and are more likely to be involved in intramolecular hydrogen bonding where the O···O separations are 2.75–2.78 Å. This back-to-back arrangement is similar to that found in the complex of unsubstituted calix[5]arene, (o-carborane)(calix[5]arene)·(CH_2Cl_2).[13] Despite the large number of rigid phenyl groups within the structure, there is only one intermolecular association that could be regarded as a π interaction, notably an edge-to-face interaction from an outer rim phenyl to an inner calixarene phenyl at C–H···π distance 2.76 Å. The solvent toluene molecules are significantly disordered, and hence cannot be commented on with any degree of veracity.

The structure of the complex [$C_{60} \subset (\mathbf{1})_2$] was similarly determined.‡ The asymmetric unit comprises one supermolecule and 1.5 ordered toluene molecules, Fig. 2. The fullerene is entirely disordered, and was treated as a sphere of electron density.‡ The calixarene molecules are ordered and both have a more symmetrical cone conformation than in **1**·(toluene)$_{1.75}$, with centroid···centroid···centroid angles between adjacent inner phenyl groups ranging from 107.0 to 109.0° and 105.1 to 112.7°. As for **1**·(toluene)$_{1.75}$, the outer rim phenyl groups are twisted away from the plane of their adjoining inner phenyl rings.

The two calixarenes form a capsule with C_{60} and are in a staggered arrangement, however, the capsule is considerably skewed, with an angle of 157.5° between the centre of the fullerene and the centres of the phenolic O_5 planes of the calixarenes. Hence the equatorial region of the capsule is unsymmetrical, with a closed arrangement of outer rim phenyl

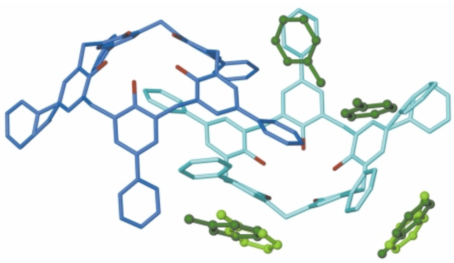


Fig. 1 Structure of p-phenylcalix[5]arene, **1**·(toluene)$_{1.75}$.

DOI: 10.1039/b203688f

---

† Dedicated to Professor Jerry L. Atwood on the occasion of his 60th birthday.

groups at one end, Fig. 2(a), and open at the other, Fig. 2(b). The closed end features inter-digitation of outer rim phenyl groups from the two calixarene molecules with closest C···C separation 3.55 Å. In contrast, the opposite end of the capsule has C···C separations typically > 6.5 Å. The fullerene is slightly closer to one of the two calixarene molecules, with distances from the fullerene centroid to the centres of the phenolic O_5 planes of the calixarenes at 6.87 and 7.01 Å.

The extended structure of $[C_{60} \subset (\mathbf{1})_2]$ features layers of host–guest capsules projected in the *bc* plane and stacking in the *a* direction. Within the layers of capsules there are numerous inter-digitation interactions between adjacent capsules, with C···C separations typically ~ 3.6 Å. As for the structure of the toluene solvate of the host calixarene, there are few obvious π interactions between the phenyl groups. The solvent toluene molecules are located between the layers of capsules.

UV–vis studies involving **1** and C_{60} in toluene were undertaken. Stoichiometry considerations from the Job plot indicate more than one species present in solution, and the interplay between the two species can be modelled as a two component system, with the formation of 1 : 1 then 2 : 1 supermolecules, eqn. (1).

$$1 + C_{60} \xrightleftharpoons{K_1} [C_{60} \cap (\mathbf{1})] \xrightleftharpoons{K_2} [C_{60} \subset (\mathbf{1})_2] \tag{1}$$

This is analogous to the *p*-benzylcalix[5]arene system, although there the 2 : 1 supermolecules have the *p*-benzyl groups directed away from the centroid of the 2 : 1 supermolecule,[7] at least in the solid state structure, rather than partial inter-digitation in the present study. The binding constants were determined by the Benesi–Hildebrand method and by the procedure outlined by Connors,[14] with $K_1 = 3000 \pm 200$, $K_2 = 250 \pm 50\ M^{-1}$ (*cf.* K_1 of other calix[5]arene and C_{60} systems in toluene, 30 ± 2, 2800 ± 200, 2120 ± 110, 1673 ± 70 and 588 ± 70 M^{-1} respectively for calix[5]arene, *p*-benzylcalix[5]arene, *p*-$(I)_2(Me)_3$-calix[5]arene, *p*-Me-calix[5]arene and *p*-$(H)_2(Me)_3$-calix[5]arene).[5,7] Complex $[C_{60} \subset (\mathbf{1})_2]$ selectively crystallises from a toluene solution of fullerite and the calixarene. However, the separation of C_{60} from the complex is rather difficult. Addition of methylene chloride results in slow dissolution of the complex and, more interestingly, the spontaneous formation of a new crystalline material, possibly the 1 : 1 complex prior to complete dissociation achieved only on evaporation of the solvent.

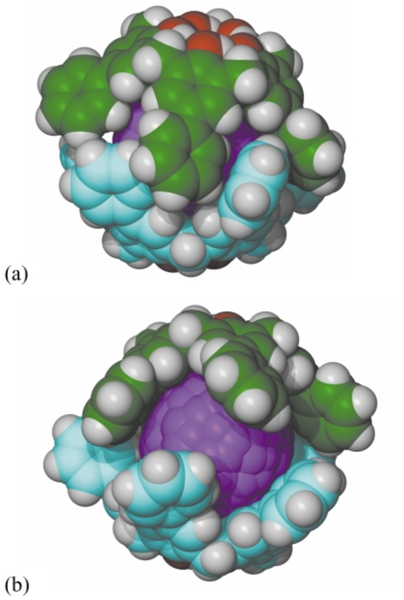


Fig. 2 Space filling projections of the molecular capsules in $[C_{60} \subset (\mathbf{1})_2]$.

In conclusion, we have demonstrated a more facile access to *p*-phenylcalix[5]arene and its high selectivity towards binding C_{60}. The skewed bicapped C_{60} supermolecule with an equatorial gap suggests complexation of mono-derivatised C_{60} is possible. The lack of binding of C_{70} is surprising given that the larger fullerene can in principle be accommodated by two molecules of **1**.

Support of this work by the EPSRC is gratefully acknowledged.

Notes and references

† Dedicated to Professor Jerry L. Atwood on the occasion of his 60th birthday.

‡ Crystal data: All data were collected at 150(1) K on an Enraf–Nonius Kappa CCD diffractometer with Mo-*Kα* radiation. The structures were solved by direct methods (SHELXS-97) and refined with a block matrix least-squares refinement on F^2 (SHELXL-97).

(*p*-phenylcalix[5]arene)(toluene)$_{1.75}$: There was considerable difficulty in locating a suitable crystal with the majority having a mosaicity > 2°. Data was collected on a colorless needle of dimensions 0.20 × 0.12 × 0.10 mm and mosaicity 0.983(2)°. Residual electron density was modelled as 1.75 toluene molecules disordered over 5 positions with rigid body refinement. The methyl group of one such toluene could not be located. $C_{77.25}H_{54}O_5$: $Mr = 1062.20$, monoclinic, $P2_1/c$, $a = 13.7426(4)$, $b = 22.0634(7)$, $c = 21.7546(7)$ Å, $\beta = 99.941(2)°$, $U = 6497.1(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.086$ g mol^{-1}, $\mu = 0.067$ mm^{-1} (no correction), $\theta_{\max} = 25.0°$, 42001 data collected, 11382 unique ($R_{int} = 0.122$), 731 parameters, no restraints, $R_1 = 0.1063$ (5935 data $I > 2\sigma(I)$), $wR_2 = 0.3556$ (all data), $S = 1.056$.

$[C_{60} \subset (\mathbf{1})_2]$(toluene)$_{1.5}$: Data was collected on a dark red needle of dimensions 0.15 × 0.10 × 0.08 mm. Crystals were small and weakly diffracting with subsequent problems with the data:parameter ratio. The disordered fullerene was modelled with 60 C atoms over 120 sites each at 50% occupancy and with all *U*ij values restrained to be approximately equal to those of neighbouring atoms. $C_{200.5}H_{112}O_{10}$: $Mr = 2680.90$, monoclinic, $C2/c$, $a = 30.4539(2)$, $b = 17.3036(1)$, $c = 50.3034(5)$ Å, $\beta = 96.676(1)°$, $U = 26328.2(3)$ Å^3, $Z = 8$, $\rho_{calc} = 1.353$ g mol^{-1}, $\mu = 0.082$ mm^{-1} (no correction), $\theta_{\max} = 25.0°$, 71483 data collected, 22692 unique ($R_{int} = 0.085$), 2469 parameters, 2230 restraints, $R_1 = 0.0642$ (12507 data $I > 2\sigma(I)$), $wR_2 = 0.1961$ (all data), GoF = 1.037, restrained $S = 1.013$. CCDC 184114 and 184115. See http://www.rsc.org/suppdata/cc/b2/b203688f/ for crystallographic files in .cif or other electronic format.

1 S. Shinkai and A. Ikeda, *Pure Appl. Chem.*, 1999, **71**, 275; M. J. Hardie and C. L. Raston, *Chem. Commun.*, 1999, 1150; F. Diederich and M. Gomez-Lopez, *Chem. Soc. Rev.*, 1999, **28**, 263; C. L. Raston, Complexation of Fullerenes, in *Comprehensive Supramolecular Chemistry*, ed. G. W. Gokel, Pergamon Press, 1996, vol. 1, p. 777.
2 J. H. Schon, C. Kloc and B. Bratlogg, *Science*, 2001, **293**, 2432.
3 J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229; S. K. Nakashima and S. Shinkai, *Chem. Lett.*, 1994, 699; E. C. Constable, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2269.
4 A. Ikeda, T. Suzuki and S. Shinkai, *Tetrahedron Lett.*, 1996, **37**, 73; K. N. Rose, L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1998, 407; A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497.
5 (*a*) J. L. Atwood, L. J. Barbour, C. L. Raston and I. B. N. Sudria, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 981; (*b*) T. Haino, M. Yanase and Y. Fukazawa, *Tetrahedron Lett.*, 1997, **38**, 3739; (*c*) J. Wang and C. D. Gutsche, *J. Am. Chem. Soc.*, 1998, **120**, 12226.
6 T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259.
7 J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston and C. A. Sandoval, *Chem. Eur. J.*, 1999, **5**, 990.
8 T. Haino, Y. Yamanaka, H. Araki and Y. Fukusawa, *Chem. Commun.*, 2002, 402.
9 J. L. Atwood, L. J. Barbour and C. L. Raston, *Cryst. Growth Design*, 2002, **2**, 3.
10 C. L. Raston, J. L. Atwood, P. J. Nichols and I. B. N. Sudria, *Chem. Commun.*, 1996, 2615.
11 M. Makha and C. L. Raston, *Tetrahedron Lett.*, 2001, **42**, 6215.
12 K. No, K. M. Kwon and B. H. Kim., *Bull. Korean Chem. Soc.*, 1997, **18**, 1034.
13 M. J. Hardie and C. L. Raston, *Eur. J. Inorg. Chem.*, 1999, 195–200.
14 K. A. Connors, *Binding Constants*, John Wiley, New York, 1987.