

Association and orientation of C₇₀ on complexation with calix[5]areneJerry L. Atwood,^a Leonard J. Barbour,^a Michael W. Heaven^a and Colin L. Raston^{*b}^a Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA^b School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, WA 6009, Australia. E-mail: clraston@chem.uwa.edu.au; Fax: +61 89380 1005; Tel: +61 89380 3045

Received (in Cambridge, UK) 6th June 2003, Accepted 30th July 2003

First published as an Advance Article on the web 13th August 2003

Calix[5]arene and C₇₀ in *p*-xylene form a ball-and-socket supramolecular complex with the C₅ axis of the fullerene tilted 40° relative to the symmetry axis of the calixarene, the extended structure is comprised of well-separated zigzag sheets of C₇₀ molecules.

The supramolecular chemistry of the fullerenes has been extensively investigated with diverse objectives including purification,¹ enzyme mimicry² and magnetic behaviour.³ Owing to its abundance relative to that of its more elusive siblings (*e.g.* C₇₀, C₈₄, *etc.*), the majority of research has focussed on C₆₀. However, with their now commercial availability, the higher fullerenes have also begun to receive considerable attention. For example, it has been reported that C₇₀ can form polymers⁴ and nanowires.⁵

We are interested in the interactions between fullerenes and curved molecular surfaces.⁶ Calix[*n*]arenes have been of particular interest since the latter are bowl-shaped molecules which can act as concave receptors for globular species. Complexation depends primarily on *n* (*i.e.* the size of the cavity) as well as the functional groups at the upper rim of the calixarene. We have shown that, while *p*-Bu⁻-calix[8]arene forms aggregates in solution with both C₆₀ and C₇₀, this compound can be used to extract C₆₀ from fullerite in >99.5% purity.^{1,7} However, derivatives of the cyclic pentamer, Fig. 1, appear to be the most favourable for interactions with the fullerenes, having been shown to bind the latter in both solution^{2,8,9} and the solid state.¹⁰ To date, only two cavitand complexes with C₇₀ have been described. In the first instance, a third component (other than a solvent molecule) was involved: both C₇₀ and *o*-carborane were cocrystallized with cyclotrityrylene.¹¹ In the second case, two C₇₀ molecules were cocrystallized with calix[6]arene to yield a structure which is isostructural to a similar complex with C₆₀.¹² The orientation of the fullerene in the cavitands is of interest in how the interplay of the two components is optimised.

The significance of calix[5]arene/fullerene complexation has been discussed in our recent report which describes how solutions of calix[5]arene/C₆₀/C₇₀ produce crystals with structures that vary, depending on the C₆₀/C₇₀ ratio.¹³ On its own, C₆₀ forms an intricate structure with calix[5]arene and toluene in a 5 : 4 : 2 ratio.¹⁴ Addition of C₇₀ to the solution influences the composition of the resulting crystals, yielding a 1 : 1 : 1

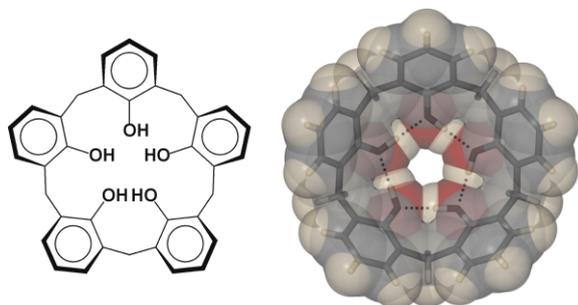


Fig. 1 Calix[5]arene normally assumes a bowl-shaped conformation with a cyclic hydrogen bonded arrangement of the phenolic hydroxy groups.

calix[5]arene : C₆₀ : toluene complex in the solid state. Despite an increase in the C₇₀/C₆₀ ratio, and the superficial similarity in size and shape of the two fullerenes, C₇₀ is not incorporated into the calix[5]arene/C₆₀ structure. Instead, increased concentrations of C₇₀ eventually result in the formation of separate red, needle-like crystals from toluene, the structure of which could not be elucidated owing to their small size. Powder diffraction experiments indicated that the new phase is quite different in structure from either of the two known complexes of calix[5]arene and C₆₀.

When *p*-xylene was substituted for toluene, a similar trend in structural composition was inferred from the determination of unit cell parameters with similar parameters obtained to those of the 5 : 4 : 2 and 1 : 1 : 1 C₆₀ : calix[5]arene : solvent complexes. It is presumed that the corresponding crystals are isostructural, and thus changing the solvent from toluene to *p*-xylene affords the same structural types. In contrast, C₇₀ gave a new complex at high relative concentrations of the fullerene as small rectangular crystals which proved to be suitable for X-ray structural determination using synchrotron radiation.[†]

Elucidation of the structure reveals a 1 : 1 complex of C₇₀ and calix[5]arene, with no presence of *p*-xylene. Although each molecular entity possesses a five-fold rotation axis, symmetry matching of these axes does not occur in the complex. Instead, the five-fold axis of the C₇₀ molecule is canted at an angle of approximately 40° relative to that of the calix[5]arene (Fig. 2). A similar tilt of the C₇₀ molecule occurs when complexed by the double cleft of calix[6]arene,¹² and possibly relates to optimising complementarity of curvature of the two components.

In the extended structure, columns of C₇₀ molecules are aligned parallel to [001] (Fig. 3). Adjacent C₇₀ molecules are at the van der Waals limit and are aligned with their major axes at 76° and 104° to the direction of the column. Each column is in close contact with two neighbouring columns of C₇₀ molecules, thus forming a two dimensional zigzag sheet parallel to (100) as

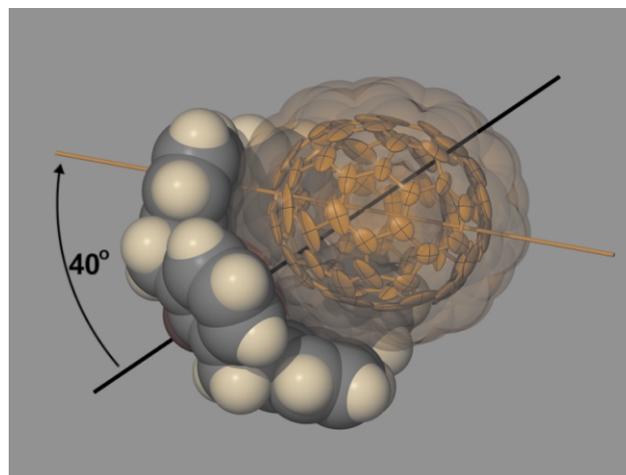


Fig. 2 The asymmetric unit of calix[5]arene : C₇₀. The fullerene is shown in orange as a thermal ellipsoid (50% probability) plot within a semi-transparent van der Waals surface. The five-fold axes of the calix[5]arene and C₇₀ molecules are shown as black and orange lines, respectively.

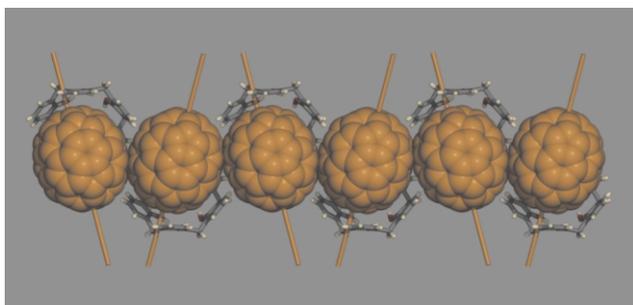


Fig. 3 A single column of calix[5]arene : C_{70} complexes aligned parallel to [001]. The 5-fold axes of the fullerenes are shown in orange.

shown in Fig. 4. Adjacent undulating layers are well-separated by sheaths of calix[5]arene molecules.

The calculated¹⁵ powder diffraction pattern for the structure does not comport with that measured for the crystals grown from a solution of calix[5]arene and C_{70} in toluene. It is therefore reasonable to assume that the solid-state complexes of C_{70} obtained from *p*-xylene and toluene are not isostructural. This is an interesting observation since, as stated above, it is possible to obtain isostructural complexes for calix[5]arene and C_{60} from either solvent, even though one of the two known calix[5]arene : C_{60} structures incorporates solvent molecules into its lattice. Furthermore, thermogravimetric analysis of calix[5]arene : C_{70} crystals grown from toluene does not indicate the presence of solvent in that structure. We therefore conclude that, while neither toluene nor *p*-xylene plays a structural role in the solid state complexes of calix[5]arene with C_{70} , the choice of solvent certainly influences the form of the resultant structure, possibly in the way the fullerenes aggregate, *cf.* complexation of C_{60} .¹³ Indeed, if the complex isolated from toluene proves also to consist of an exact 1 : 1 molar ratio of calix[5]arene and C_{70} , this would be the first known instance of true polymorphism in fullerene complexation.

Although difficult to predict, the ability to control the close arrangement of fullerenes in the solid state is highly relevant to their subsequent covalent linking, *inter alia*. Izuoka and coworkers reported a solid state structure of [bis(ethylenedithio)tetrathiafulvalene]₂ C_{60} in which the fullerene molecules are in van der Waals contact with one another,¹⁶ and this arrangement can be exploited to effect a [2 + 2] cycloaddition reaction to form the C_{60} dimer, C_{120} .¹⁷ We have reported structures containing calix[4]arene derivatives cocrystallized with C_{60} molecules where the latter are either arranged in columnar arrays,^{18,19} or intercalated into a calixarene bilayer.²⁰ Our speculation, based on the results of Izuoka *et al.*, that such controlled frameworks could be utilized to form linear C_{60} polymers was confirmed by Sun and Reed.²¹ With the limited

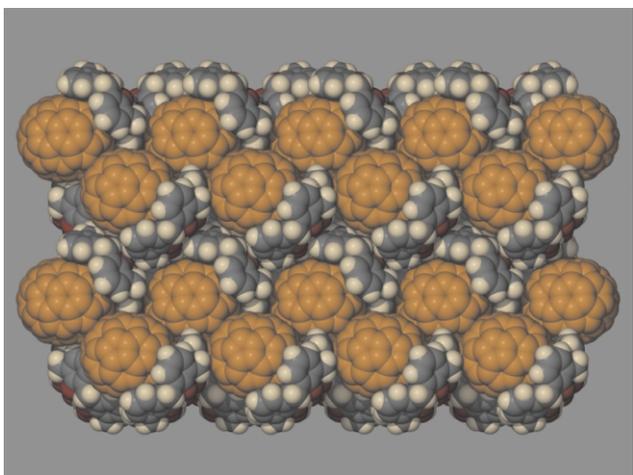


Fig. 4 Perspective view along [001] showing two zigzag layers of C_{70} molecules enshrouded by calix[5]arenes.

number of authenticated van der Waals complexes of C_{70} greatly enhanced by the above structure, the scene is now set for covalently linking these fullerenes in a controlled fashion.

We thank the NSF and the EPSRC for financial support of this work, and Professor William Clegg for data collection.

Notes and references

† Crystal data for calix[5]arene : C_{70} : $C_{105}H_{30}O_5$, $M = 1371.29$, dark red prism, $0.08 \times 0.05 \times 0.05$ mm³, monoclinic, space group $P2_1/c$ (No. 14), $a = 19.710(3)$, $b = 14.582(2)$, $c = 20.427(3)$ Å, $\beta = 104.525(2)^\circ$, $V = 5683.3(14)$ Å³, $Z = 4$, $D_c = 1.603$ g cm⁻³, $F_{000} = 2800$, synchrotron radiation, $\lambda = 0.68600$ Å, $T = 120(2)$ K, $2\theta_{max} = 58.8^\circ$, 37334 reflections collected, 15903 unique ($R_{int} = 0.0448$). Final $Goof = 1.695$, $R1 = 0.1492$, $wR2 = 0.4027$, R indices based on 11230 reflections with $I > 2\sigma(I)$ (refinement on F^2), 788 parameters, 10 restraints. Lp and absorption corrections applied, $\mu = 0.098$ mm⁻¹. O-Hydrogen atoms were included in a 50 : 50 disorder model for a cyclic array of hydrogen bonding. Molecular graphics were generated using X-Seed and POV-Ray.²² CCDC 212392. See <http://www.rsc.org/suppdata/cc/b3/b306411p/> for crystallographic data in CIF or other electronic format.

- J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229.
- T. Haino, Y. Yamanaka, H. Araki and Y. Fukazawa, *Chem. Commun.*, 2002, 402.
- E.g. R. E. Dinnebier, O. Gunnarsson, H. Brumm, E. Koch, P. W. Stephens, A. Huq and M. Jansen, *Science*, 2002, **296**, 109.
- A. V. Soldatov, G. Roth, A. Dzabchenko, D. Johnels, S. Lebedkin, C. Meingast, B. Sundqvist, M. Haluska and H. Kuzmany, *Science*, 2001, **293**, 680.
- H. Cao, Z. Xu, X. Wei, X. Ma and Z. Xue, *Chem. Commun.*, 2001, 541.
- J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston and R. S. Burkharter, *J. Am. Chem. Soc.*, 1994, **116**, 10346; P. C. Andrews, J. L. Atwood, L. J. Barbour, P. J. Nichols and C. L. Raston, *Chem. Eur. J.*, 1998, **4**, 1384; P. C. Andrews, J. L. Atwood, L. J. Barbour, P. D. Croucher, P. J. Nichols, N. O. Smith, B. W. Skelton, A. H. White and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1999, 2927.
- C. L. Raston, J. L. Atwood, P. J. Nichols and I. B. N. Sudria, *Chem. Commun.*, 1996, 2615.
- J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston and C. A. Sandoval, *Chem. Eur. J.*, 1999, **5**, 990 and references therein.
- T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed.*, 1998, **37**, 997; M. Yanase, T. Haino and Y. Fukazawa, *Tetrahedron Lett.*, 1999, **40**, 2781; M. Yanase, M. Matsuoka, Y. Tatsumi, M. Suzuki, H. Iwamoto, T. Haino and Y. Fukazawa, *Tetrahedron Lett.*, 2000, **41**, 493; T. Haino, H. Araki, Y. Yamanaka and Y. Fukazawa, *Tetrahedron Lett.*, 2001, **42**, 3203; T. Haino, Y. Yamanaka, H. Araki and Y. Fukazawa, *Chem. Commun.*, 2002, 402; J. Wang and C. D. Gutsche, *J. Org. Chem.*, 2002, **67**, 4423.
- M. Makha, M. J. Hardie and C. L. Raston, *Chem. Commun.*, 2002, 1446; T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259.
- M. J. Hardie, P. D. Godfrey and C. L. Raston, *Chem. Eur. J.*, 1999, **5**, 1828.
- J. L. Atwood, L. J. Barbour, C. L. Raston and I. B. N. Sudria, *Angew. Chem., Int. Ed.*, 1998, **37**, 981.
- J. L. Atwood, L. J. Barbour, M. W. Heaven and C. L. Raston, *Angew. Chem., Int. Ed.*, 2003, **42**, 3254.
- J. L. Atwood, L. J. Barbour and C. L. Raston, *Cryst. Growth Des.*, 2002, **2**, 3.
- K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr.*, 1977, **10**, 73.
- A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.
- Y. Iwasa, K. Tanoue, T. Mitani, A. Izuoka, T. Sugawara and T. Yagi, *Chem. Commun.*, 1998, 1411.
- K. N. Rose, L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1998, 407.
- L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1998, 1901.
- L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 1997, 1439.
- D. Sun and C. A. Reed, *Chem. Commun.*, 2000, 2391.
- L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189; J. L. Atwood and L. J. Barbour, *Cryst. Growth Des.*, 2003, **3**, 3; <http://www.povray.org>.