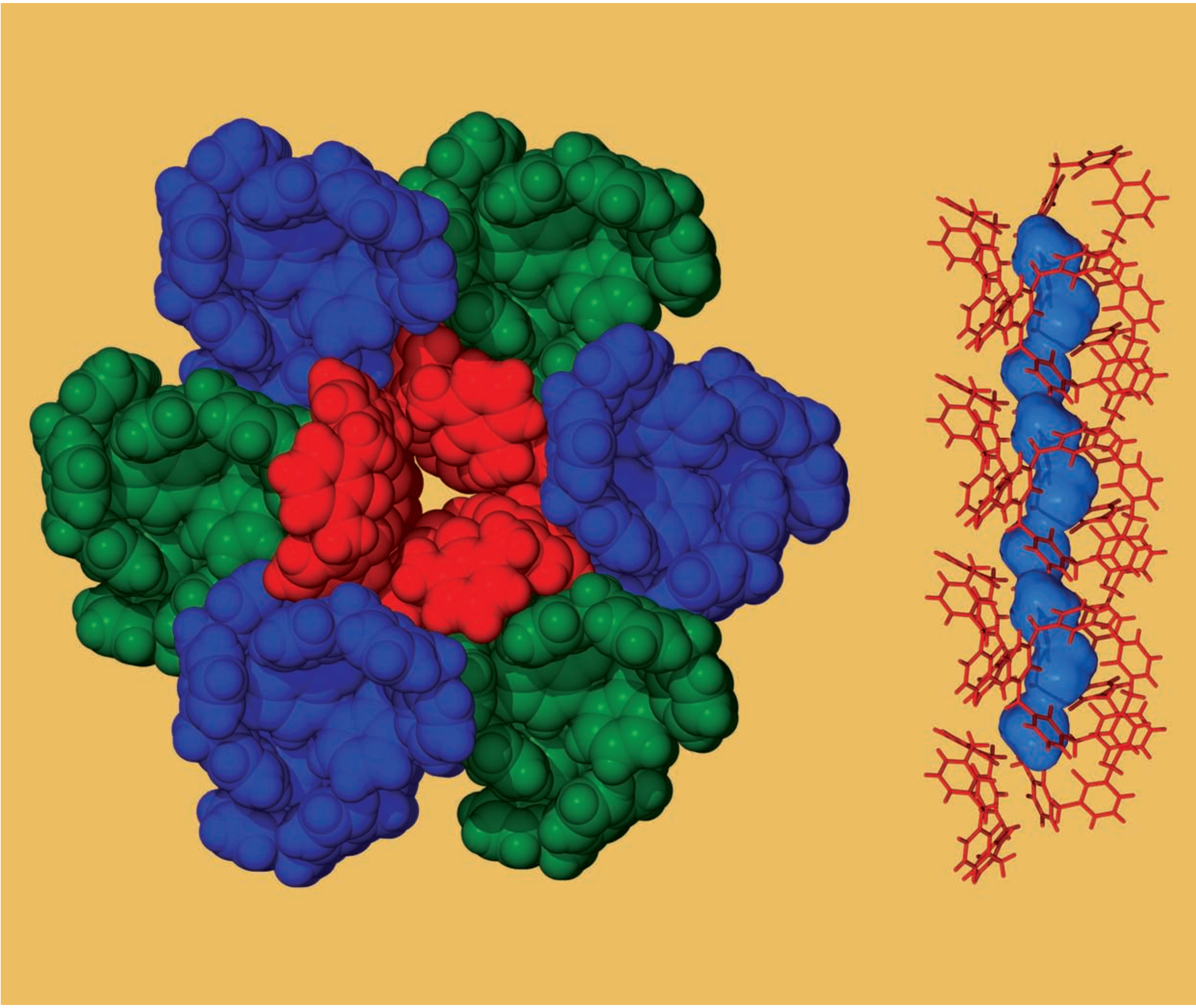
ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 46 | 14 December 2007 | Pages 4821–4960



ISSN 1359-7345

RSC Publishing

COMMUNICATION
Jerry L. Atwood *et al.*
Calix[5]arene: a versatile sublimate that displays gas sorption properties

FEATURE ARTICLE
Ramón Martínez-Máñez *et al.*
Chromogenic and fluorogenic reagents for chemical warfare nerve agents' detection

1359-7345(2007)46;1-Y

Calix[5]arene: a versatile sublimate that displays gas sorption properties†

Scott J. Dalgarno,‡[a] Jian Tian,[a] John E. Warren,[b] Thomas E. Clark,[c] Mohamed Makha,[c] Colin L. Raston[c] and Jerry L. Atwood*[a]

Received (in Cambridge, UK) 16th August 2007, Accepted 25th September 2007
First published as an Advance Article on the web 5th October 2007
DOI: 10.1039/b712621b

Varied temperature sublimation of calix[5]arene results in the formation of two distinctly different crystal structures or polymorphs α and β, the latter of which is based on both 'self-included' and 'back-to-back' helical arrangements of the molecule, while also being active towards CO_2 sorption at room temperature and 1 atmosphere pressure.

Gas sorption, storage, separation and transport has come to the fore in recent times as a highly active area of research, which is in part due to the challenges set by the impending energy crisis and continuing fossil fuel usage, for example. Many research groups worldwide are focusing efforts on the generation of new and interesting inorganic materials for such purposes which are often based on key design principles.[1] In this context, significant recent advances in the controlled formation of coordination polymers and metal organic frameworks (MOF's),[1l,m] as well as in the generation of zeolite-like metal organic frameworks (ZMOF's),[1k] have generated numerous new and exciting materials, many of which have interesting gas storage properties and prospects as sensors, for example.

Within this broad research area, we have focused our efforts on the formation and study of porous and non-porous organic solids. A number of our recent studies are based around a key advance: the sublimation of calixarenes as a route to form interesting new organic materials based on these molecular building blocks,[2] two pertinent examples of which are described below. Sublimation of calix[4]arene (**1**, Fig. 1A) affords a 'near-spheroidal' self-included trimer (**1$_3$**) that packs in the solid state in a hexagonal close packed arrangement (Fig. 1B) with lattice voids of approximately 153 Å^3.[2a] The structure of **1$_3$** is identical to a reported acetone solvate (without solvent molecules in the sublimed case), and identification/rationalisation of this behaviour consequently allowed for co-crystallisation of **1$_3$** with volatile freons, halons or methane from toluene solutions. This results in the gases being entrapped in the voids, and this is identifiable from X-ray crystallography and ^{19}F NMR spectroscopy. In the second example, sublimation of the related parent molecule *para-tert*-butylcalix[4]arene (**2**, Fig. 1A) results in the formation of a low density structure in which two molecules of **2** form an offset dimeric capsule that is capable of sorbing a number of different gases under various conditions (Fig. 1C).[2b–d] Notably, this structure is seemingly non-porous, yet it can undergo single-crystal-to-single-crystal phase changes in the presence of vinyl bromide, or allow passage of gas molecules to the ~235 Å^3 void presented by the offset dimer.

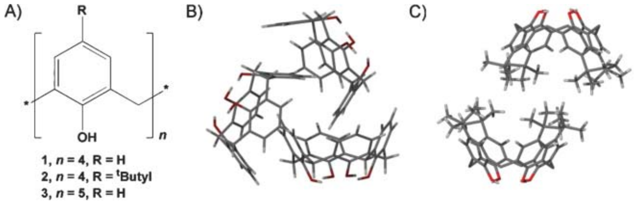


Fig. 1 (A) Compounds **1–3**. (B) The 'self-included' near-spherical trimer formed by subliming calix[4]arene (**1**).[2a] (C) The offset dimeric capsule formed by subliming *para-tert*-butylcalix[4]arene (**2**).[2b] Figures not to scale.

In our ongoing studies in this area, we have found that calix[5]arene (**3**) sublimes to form two remarkably different polymorphic crystal structures (**α** and **β**) based on two equally disparate molecular conformations: a stacked arrangement (**α**) and an arrangement based on the interaction of both 'self-included' and 'back-to-back' helices (**β**). Both polymorphs are accessed simultaneously by subliming at a varied rate of heating, a technique that was being employed in order to prevent decomposition of the material.[3] The resulting colourless single crystalline material was isolated and studied using X-ray diffraction studies to generate the two structures described herein.[4–6] In addition, the **β** structure can be isolated in bulk by subliming at higher temperature,[7] and has also been examined for CO_2 and H_2 storage capability.

In **α**, the crystals are in a triclinic cell and the structural solution was performed in space group $P\bar{1}$.[4,5] The asymmetric unit comprises one molecule of **3** within which one of the methylene bridging groups has inverted (Fig. 2A). This causes significant distortion to the typically observed cone conformation of the host,[8] and the structure appears to be unremarkable until the hydrogen-bonding at the lower-rim is examined more closely within the extended structure (Fig. 2B). Expansion of the asymmetric unit shows molecules of **3** forming columnar stacks by nestling one inside the other (Fig. 2B). The hydrogen atoms (located in the difference map) are found to form a helical hydrogen-bonding chain through the core of each stack with

---

[a] *Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA. E-mail: AtwoodJ@missouri.edu;*
Fax: 001-573-882-2754; Tel: 001-573-882-8374
[b] *Station 9.8, Daresbury Laboratory, Daresbury, Warrington, UK WA4 4AD*
[c] *School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, Crawley, Perth WA 6909, Australia*

† Electronic supplementary information (ESI) available: X-Ray powder diffraction data relating to the isolation of **β** in bulk scale; large versions of Fig. 2 and Fig. 3 (Fig. S2 and S3, respectively). See DOI: 10.1039/b712621b

‡ Current address: School of Engineering and Physical Sciences – Chemistry, Heriot-Watt University, Edinburgh, UK EH14 4AS.

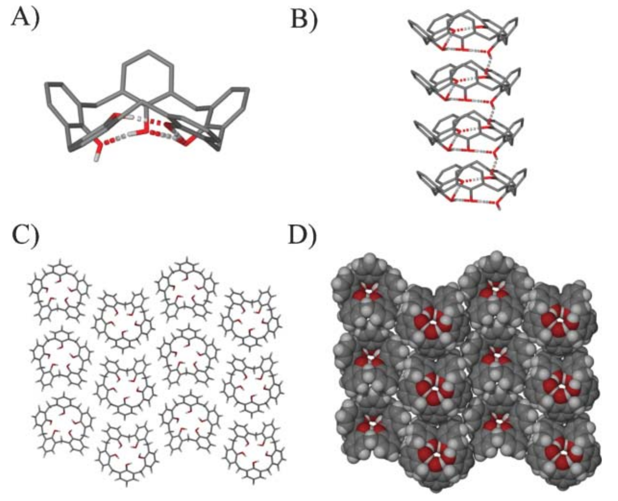


Fig. 2 Different views (not to scale) of polymorph **α**. (A) The asymmetric unit showing the distortion to the cone conformation of **3**. (B) A stack of **3** showing the hydrogen-bond helix running through the core of the stack. (C) Packing of stacks of **3** along the *a* axis: layers of stacks running in alternating directions form a wave-like arrangement along the *c* axis. (D) Space filling representation of the packing diagram in C. In A and B, some hydrogen atoms have been omitted for clarity.†

$\mathrm{OH\cdots O}$ distances ranging from 1.747–2.063 Å (corresponding $\mathrm{O\cdots O}$ distances ranging from 2.641–2.781 Å). These stacks are found to pack in layers of unidirectional H-bonded helices that form a wave-like pattern along the *c* axis, interacting through van der Waals contacts (Fig. 2C–D). Space filling rendering shows this arrangement of stacks to be non-porous (Fig. 2D), which combined with the stacking nature suggests that **3** in the **α** polymorph would not be useful as an organic solid for gas sorption purposes as there are no apparent lattice voids for guest molecules to reside in.[2b]

In **β**, the crystals are in a rhombohedral cell and the structural solution was performed in the space group *P*31.[4,6,9] The asymmetric unit comprises three independent molecules of **3** (Fig. 3A), all of which adopt the typical cone conformation observed for the host,[8] and that pack in the extended structure to form an interesting and complicated combination of helical arrangements. There are limited examples of purely organic helical, tubular, or helical and tubular assemblies based on calixarenes in general, although a handful of examples exist in the literature (in the presence of other molecular components).[10] This is also true for other types of molecule, and a limited number of organic nanotubes based on cyclic oligomers composed of peptides,[11a,b] ureas[11b] or carbohydrates[11c] have also been documented. More recently, helical tubular arrangements based on *N*,*N*′-dimethylnaphthalenediimide with pendant carboxylic acids have also been reported.[12] Given the complexity of polymorph **β**, it will be described in parts and then as an integral structure to show how these helical arrangements interact in concert.

Symmetry expansion of the asymmetric unit shows that two of the three independent molecules of **3** form two very similar 'self-included' helical arrangements (one of which is shown in Fig. 3B). These two independent helical arrangements are stabilised by a number of $\mathrm{CH\cdots\pi}$ interactions as one molecule of **3** nestles within an adjacent symmetry equivalent.[13] For the remaining molecule of

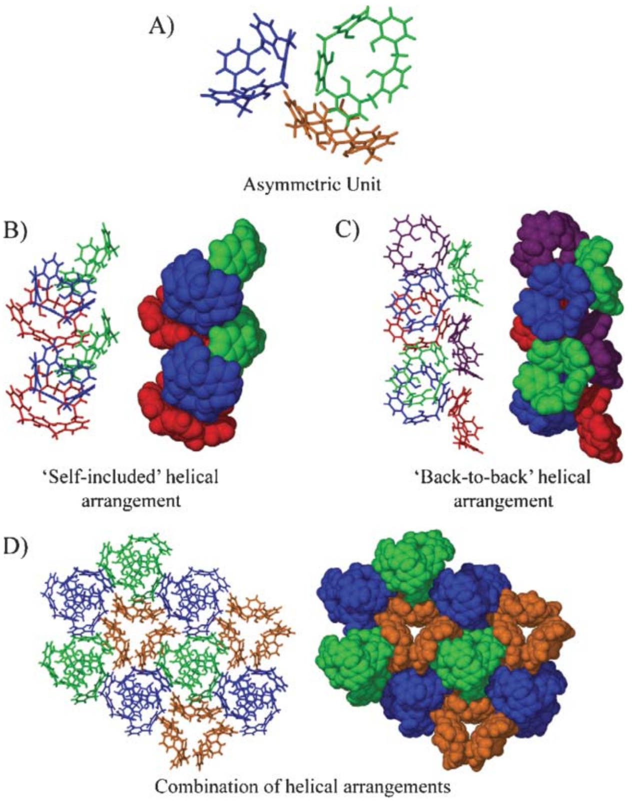


Fig. 3 Stick and space filling views (not to scale) of crystal structure **β**. (A) The asymmetric unit showing three independent molecules of **3** (coloured individually). (B) A 'self-included' helical arrangement. (C) The 'back-to-back' helical arrangement. (D) The extended structure showing the packing of 'self-included' (green and blue) and 'back-to-back' (orange) helical arrangements, as well as the small pores present in the latter. Colours of **3** in (B) and (C) are not relative to (A) but have been used to show the helical nature of the arrangements. Colours of molecules of **3** in (D) are relative to those in (A).†

3, symmetry expansion shows this to form a 'back-to-back' helical arrangement (Fig. 3C) through two unique intermolecular interactions (one $\mathrm{CH\cdots\pi}$ and one π-stacking interaction).[14]

Large non-covalent structures incorporating helical arrangements of molecules are generally rare,[10–12] and although there are limited examples in the literature, there are (to our knowledge) no examples where two different types of helical arrangement interact directly with each other in such a fashion as that observed in **β**. Examination of the extended structure in both stick and space filling representation (Fig. 3D) shows that each 'back-to-back' helical arrangement is surrounded by six 'self-included' helices, all of which run with the same handedness. This interaction between neighboring helical arrangements occurs through numerous van der Waals interactions through inter-digitation, and the space filling view (Fig. 3D) also shows that the only apparent void space in the structure is that which is observable in the core of the 'back-to-back' helical arrangement, therefore making **β** desirable for gas sorption studies.

As the presence of two different crystal types is not useful for gas sorption studies (given the lack of sample purity for example), sublimation of **3** was performed directly at 290 °C overnight, also affording colourless single crystals.[7] Comparison of X-ray powder patterns of this material and the calculated patterns from the

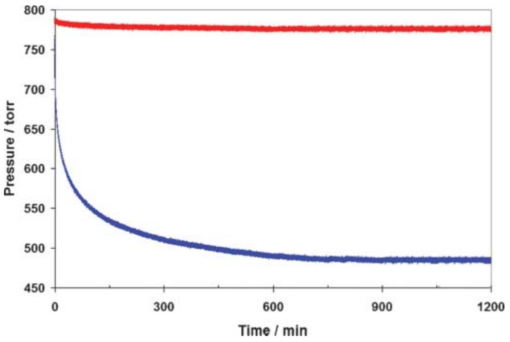


Fig. 4 Gas sorption isotherms obtained for CO_2 (blue) and H_2 (red) when **β** is exposed to 1 atm pressure of each gas at room temperature.

crystal structures of **α** and **β** shows that higher temperature sublimation affords **β** in high purity (Fig. S1, ESI†).[15] Once obtained in the pure form, freshly sublimed **β** was finely ground and studied using apparatus previously described in the literature.[16] This material was studied under 1 atmosphere pressure of either CO_2 or H_2, and was found to be active for sorption of only CO_2 (Fig. 4). The pores/channels in **β** are therefore favorable for interaction with CO_2, and the material was found to store 1.1 wt% under these conditions.

In conclusion, **3** sublimes under different conditions to form two very different polymorphs based on two molecular conformations. The **α** polymorph is based on an inverted cone conformation of **3**, molecules of which stack to form hydrogen-bonded helices through the 'OH core'. The **β** polymorph is based on **3** adopting the common bowl conformation and shows the molecules to pack in both 'self-included' and 'back-to-back' helices. The **β** structure contains small pores/channels through the centre of the 'back-to-back' helix and was examined for gas sorption capability with CO_2 and H_2, showing selective sorption of the former over the latter. Further studies will focus on studying the sorption of other gases within **β**, as well as attempting to isolate the **α** form in bulk to confirm whether the columnar stacks are capable of gas sorption.§

Notes and references

§ We would like to thank the NSF and CCLRC for financial support of this work.

1 For selected reviews and independent articles, see: (*a*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*b*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*c*) M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2000, **39**, 3052; (*d*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*e*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*f*) D. Braga, *Chem. Commun.*, 2003, 2751; (*g*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*h*) D. N. Dybstev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033; (*i*) M. J. Rosseinsky, *Microporous Mesoporous Mater.*, 2004, **73**, 15; (*j*) J. L. C. Roswell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670; (*k*) Y. Liu, V. Ch. Kravstov, R. Larsen and M. Eddaoudi, *Chem. Commun.*, 2006, 1488; (*l*) X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schröder, *Angew. Chem., Int. Ed.*, 2006, **45**, 7358; (*m*) D. Bradshaw, J. E. Warren and M. J. Rosseinsky, *Science*, 2007, **315**, 977.

2 (*a*) J. L. Atwood, L. J. Barbour and A. Jerga, *Science*, 2002, **296**, 2367; (*b*) J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, *Science*, 2002, **298**, 1000; (*c*) J. L. Atwood, L. J. Barbour and A. Jerga, *Angew. Chem., Int. Ed.*, 2004, **43**, 2948; (*d*) S. J. Dalgarno, P. K. Thallapally, L. J. Barbour and J. L. Atwood, *Chem. Soc. Rev.*, 2007, **36**, 236.

3 Under reduced pressure, **3** was heated at 150 °C and the temperature increased at a rate of 10 °C per 2–3 h period to afford colourless single crystals that were suitable for X-ray diffraction studies.

4 CCDC 637165–637166 contains the crystallographic data for polymorphs **α** and **β**. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712621b.

5 **Polymorph α**: $C_{35}H_{30}O_5$, $M = 530.59$, triclinic, $a = 4.7324(14)$, $b = 11.924(4)$, $c = 22.876(7)$ Å, $\alpha = 90.517(4)$, $\beta = 92.792(4)$, $\gamma = 94.965(4)°$, $U = 1284.4(7)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, synchrotron radiation (wavelength $\lambda = 0.6907$ Å), GOF = 1.139, agreement index $R_1 = 0.1257$, 13 714 reflections measured, 7670 unique ($R_{int} = 0.0469$) which were used in all calculations. The final w$R(F^2)$ was 0.3297 (all data).

6 **Polymorph β**: $C_{105}H_{90}O_{15}$, $M = 1591.77$, rhombohedral, $a = 24.2871(9)$, $c = 12.1358(6)$ Å, $U = 1284.4(10)$ Å^3, $T = 150(2)$ K, space group $P31$, $Z = 3$, synchrotron radiation (wavelength $\lambda = 0.6907$ Å), GOF = 1.044, agreement index $R_1 = 0.1225$, 60 966 reflections measured, 20 352 unique ($R_{int} = 0.0877$) which were used in all calculations. The final w$R(F^2)$ was 0.3309 (all data).

7 Sublimation of **3** was performed at 290 °C overnight under reduced pressure to afford colourless single crystals, the purity of which was checked by X-ray powder diffraction studies.

8 M. Coruzzi, G. D. Andreetti, V. Bocchi, A. Pochini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1982(9), 1133. An 'organic only' CCDC search of discrete pentahydroxycalix[5]arenes with methylene bridges, correct as of 7th March 2007 (CSD version 1.9), returns 24 results all of which have the calixarene in a bowl conformation. For an example of a distorted calix[5]arene with similar conformation to that in polymorph **α**, see: S. Usui, K. Deyama, Y. Odagaki and Y. Fukazawa, *Tetrahedron Lett.*, 1993, **34**, 8127.

9 The structure could also be solved in the space group $P32$.

10 (*a*) B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong and K. S. Kim, *Science*, 2001, **294**, 348; (*b*) H. Mansikkamäki, M. Nissinen and K. Rissanen, *Angew. Chem., Int. Ed.*, 2004, **43**, 1243; (*c*) F. Perret, A. N. Lazar, O. Shkurenko, K. Suwinska, N. Dupont, A. Navaza and A. W. Coleman, *CrystEngComm*, 2006, **8**, 890.

11 (*a*) M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. McRee and N. Khazanovich, *Nature*, 1993, **366**, 324; J. D. Hartgerink, J. R. Granja, R. A. Milligan and M. R. Ghadiri, *J. Am. Chem. Soc.*, 1996, **118**, 43; (*b*) C. Valéry, M. Paternostre, B. Robert, T. Gulik-Krzywicki, T. Narayanan, J.-C. Dedieu, M.-L. Torres, R. Cherif-Cheikh, P. Calvo and F. Artzner, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 10258; (*c*) V. Semetey, C. Didierjean, J.-P. Briand, A. Aubry and G. Guichard, *Angew. Chem., Int. Ed.*, 2002, **41**, 1895; (*d*) G. Gattuso, S. Menzer, S. A. Nepogodiev, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1451.

12 G. D. Pantoş, P. Pengo and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2007, **46**, 194.

13 For each 'self-included' arrangement, two CH···π interactions from methylene bridges (four CH···aryl centroid distances in the range of 2.714–3.340 Å) and three CH···π interactions from aryl hydrogen atoms were observed (six ArH···aryl centroid distances ranging from 2.960–3.340 Å).

14 For the 'back-to-back' helical arrangement, the unique ArH···aryl centroid and aryl centroid···centroid interactions have distances of 2.824 and 3.977 Å, respectively.

15 It has subsequently been found that the **β** polymorph can also be isolated in bulk by crystallisation from isopropyl alcohol.

16 J. L. Atwood, L. J. Barbour, P. K. Thallapally and T. B. Wirsig, *Chem. Commun.*, 2005, 51. Note that the sample holder volume on the instrumentation has been altered from this report.