

Inclusion of nitriles inside and outside the molecular bowls of tetrabromo calix[4]arene hosts

Felicia Maharaj · Donald C. Craig ·
Marcia L. Scudder · Roger Bishop ·
Naresh Kumar

Received: 17 July 2006 / Accepted: 19 December 2006 / Published online: 25 January 2007
© Springer Science+Business Media B.V. 2007

Abstract New tetrabromo calix[4]arene derivatives **2** and **5a/5b** have been synthesised and found to function as inclusion hosts for nitrile guests. The X-ray structures of (**2**)₂ · (pivalonitrile)₃ and (**5a**) · (acetonitrile)₃ · (water) show that, in each compound, molecular inclusion occurs by a combination of complexation within the calixarene bowl and lattice inclusion outside the bowl. Racemic **5a/5b** crystallises as a conglomerate, with chiral discrimination between these enantiomers being assisted by the propeller-shaped molecular conformation they adopt in the solid state.

Keywords Tetrabromocalix[4]arenes · Inclusion properties · Intermolecular interactions · X-ray crystal structure

Introduction

Organic inclusion compounds generally fall into one of two distinct categories [1, 2]. In many cases, the host molecule contains some type of permanent receptor structure that is capable of binding the guest species. Hosts such as crown ethers, cryptands, and cyclodextrins are familiar examples. Alternatively, stabilisation of a host–guest combination can arise as a result of multiple favourable interactions between the two components in their crystal lattice. These are lattice inclusion compounds or clathrate structures.

Calixarenes are often colourfully described in terms of being container molecules, cups, bowls, or molecular baskets, and the cavities of calixarenes can certainly function as receptors for the complexation of guests. However, many reported calixarene inclusion structures are actually lattice inclusion compounds where the guests occupy spaces between the host molecules [3–5]. There are two reasons for this. First, the bowls of many common calixarenes are relatively small and unable to accept some guest molecules. Secondly, favourable host–guest interactions are required within the bowl for complexation to be competitive with other crystal packing modes. It is also possible for a pendant group of one calixarene to occupy the bowl of a second identical molecule, either with or without additional lattice inclusion [6, 7]. The syntheses of two tetrabromo calix[4]arene derivatives **2** and **5** are described in this paper. Both of these compounds function as host molecules that simultaneously utilise both the bowl receptor and lattice packing modes for their molecular inclusion.

Experimental

Melting points were determined using a Kofler hot stage micromelting apparatus and are uncorrected. ¹H (300 MHz) and ¹³C NMR (75.6 MHz) spectra were obtained on a Bruker AMX300 spectrometer and are reported as chemical shifts (δ) relative to TMS. Infrared spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer, and high resolution ESI mass spectra using a 7 Tesla Bruker BioApex II FTICR mass spectrometer with an electrospray ionisation source.

F. Maharaj · D. C. Craig · M. L. Scudder ·
R. Bishop · N. Kumar (✉)
School of Chemistry, The University of New South Wales,
UNSW Sydney NSW 2052, Australia
e-mail: n.kumar@unsw.edu.au

5,11,17,23-Tetrabromo-25,27-dimethoxy-26,28-dihydroxycalix[4]arene **2**

To an ice cold stirred solution of 5,17-dibromo-25,27-dimethoxy-26,28-dihydroxycalix[4]arene **1** [8, 9] (1.20 g, 1.97 mmol) in dry chloroform (20 mL), was added a solution of bromine (0.94 g, 5.91 mmol) in dry chloroform (10 mL) over 20 minutes. The mixture was stirred for a further 2 h at 0 °C, before it was allowed to warm to room temperature. The precipitated product was collected by filtration and washed with cold methanol. Recrystallisation from chloroform gave a mixture of the tri- and tetrabrominated species as the first crop of crystals. The second crop of crystals was the pure white solid tetrabromide **2** (0.76 g, (50%); mp 283–285 °C (decomp.). HRMS m/z (M+Na)⁺: Calc. for C₃₀H₂₄Br₄O₄Na⁺ 792.82453, 790.82621, 788.82811; Found 792.82530, 790.82663, 788.82917; IR (ν_{\max} , KBr disc) 3310 (s), 1581 (w), 1260 (m), 1245 (m), 1210 (m), 1071 (m), 993 (s), 962 (w), 853 (w) cm⁻¹; ¹H NMR (CDCl₃) δ 7.73 (s, 2H, ArOH), 7.19 (s, 4H, ArH), 7.04 (s, 4H, ArH), 4.21 and 4.17 (d, J_{AB} = 13.2 Hz, 4H, ArCH₂Ar), 3.95 (s, 6H, OCH₃), 3.34 and 3.30 (d, J_{AB} = 13.2 Hz, 4H, ArCH₂Ar); ¹³C NMR (CDCl₃) δ 152.4 (C), 152.2 (C), 134.2 (C), 132.3 (CH), 131.2 (CH), 128.9 (C), 118.1 (C), 111.0 (C), 63.8 (CH₃), 30.8 (CH₂). The inclusion crystals were grown by slow evaporation of a solution of **2** in pivalonitrile.

5,17-Bis(3'-phenyl-2'-propen-1'-oyl)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene **4**

A solution of sodium methoxide in methanol (18.88 M, 1.00 mL, 18.88 mmol) was added over a 5 min period to a solution of 5,17-diacetyl-25,27-dimethoxy-26,28-dihydroxycalix[4]arene **3** [10, 11] (1.00 g, 1.88 mmol) and benzaldehyde (2.00 mL, 18.80 mmol) in dry tetrahydrofuran (50 mL). The resulting red solution was then allowed to stir for 24 h at room temperature, before it was quenched with the addition of water (10 mL) and the dropwise addition of glacial acetic acid (20 mL). The resulting solid product was filtered, dissolved in chloroform (200 mL) and washed with saturated sodium metabisulphite solution (2 × 100 mL). The organic phase was dried (Na₂SO₄) and solvent evaporated from the filtrate to yield the crude product as a yellow solid. Recrystallisation from chloroform/methanol gave the bis(chalcone) **4** (1.30 g, 97%) as a pale yellow

powder, mp > 274 °C (decomp.). HRMS m/z (M+Na)⁺: Calc. for C₄₈H₄₀O₆Na⁺ 735.27171, Found 735.27136; IR (ν_{\max} , KBr disc) 3274s, 3058w, 2928w, 2827w, 1655s, 1604s, 1481s, 1469s, 1448m, 1427m, 1334s, 1286w, 1207w, 1191w, 1164m, 1076w, 1057w, 1001m, 976w, 851w, 764m, 685w cm⁻¹; ¹H NMR (CDCl₃) δ 8.51 (s, 2H, ArOH), 7.86 (s, 4H, Ar-H), 7.78 (d, 2H, J = 15.5 Hz, CO-CH=CH-Ph), 7.69–7.66 (m, 4H, Ph-H), 7.56 (d, 2H, J = 15.5 Hz, CO-CH=CH-Ph), 7.43–7.41 (m, 6H, Ph-H), 6.94 (d, 4H, J = 7.5 Hz, Ar-H), 6.77 (t, 2H, J = 7.9 Hz, *p*-Ar-H), 4.33 (d, J_{AB} = 13.2 Hz, 4H, Ar-CH₂-Ar), 4.03 (s, 6H, Ar-OCH₃), 3.57 and 3.52 (d, J_{AB} = 13.2 Hz, 4H, Ar-CH₂-Ar); ¹³C NMR (CDCl₃) δ 189.2 (C), 158.3 (C), 153.4 (C), 143.9 (CH), 135.6 (C), 132.4 (C), 130.5 (CH), 130.2 (CH), 130.0 (C), 129.8 (CH), 129.2 (CH), 128.6 (CH), 128.4 (C), 125.9 (CH), 122.6 (CH), 64.1 (CH₃), 31.5 (CH₂).

5,17-Bis(3'-phenyl-2',3'-dibromopropan-1'-oyl)-25,27-dimethoxy-26,28-dihydroxycalix[4]arene **5**

A solution of bromine (0.47 g, 2.92 mmol) in chloroform (5 mL) was added dropwise over a 30 min period to a stirred solution of the bis(chalcone) **4** (0.26 g, 0.37 mmol) in dry chloroform (20 mL) until the brown colour persisted. The solution was then allowed to stir for a further 2 h at room temperature, before methanol (30 mL) was added to precipitate the crude product. The solid was filtered, washed with cold methanol (2 × 5 mL) giving the tetrabromide **5** (0.22 g, 58%) as colourless fine cubic crystals, mp 196–197 °C. HRMS m/z (M+Na)⁺: Calcd. for (C₄₈H₄₀O₆Br₄Na)⁺ 1054.94158, Found 1054.94245; IR (ν_{\max} , KBr disc) 3274s, 3060w, 3027w, 2927w, 2827w, 1673s, 1588s, 1482m, 1469m, 1455m, 1429m, 1323s, 1281s, 1206s, 1160m, 1003m, 765m, 694m cm⁻¹; ¹H NMR (*d*₆-DMSO) δ 9.11 (s, 2H, Ar-OH), 8.20 (s, 4H, Ar-H), 7.79 (d, 2H, J = 7.2 Hz, Ph-H), 7.46–7.37 (m, 6H, Ph-H), 7.19 (d, 2H, J = 7.5 Hz, Ph-H), 7.09 (d, 2H, J = 7.5 Hz, Ar-H), 6.84 (t, 2H, J = 7.5 Hz, *p*-Ar-H), 6.57 (d, 2H, J = 11.7 Hz, Ar-COCHBr-CHBrPh), 5.71 (d, 2H, J = 10.9 Hz, Ar-CO-CHBr-CHBrPh), 4.26 and 4.22 (d, J_{AB} = 13.0 Hz, 4H, Ar-CH₂-Ar), 3.99 (s, 6H, Ar-OCH₃), 3.73 and 3.68 (d, J_{AB} = 13.0 Hz, 4H, Ar-CH₂-Ar); ¹³C NMR (CDCl₃) δ 189.89 (C), 159.11 (C), 153.51 (C), 139.16 (C), 132.97 (C), 131.01 (CH), 130.95 (CH), 129.85 (CH), 129.69 (CH), 129.42 (CH), 129.21 (CH), 128.94 (CH), 128.75 (C), 128.68 (C), 126.05 (CH), 125.62 (C), 64.40 (CH₃), 51.60 (CH), 46.74 (CH), 30.37

(CH₂), plus one aryl quaternary obscured. The inclusion crystals were grown by slow evaporation of a solution of **5** in acetonitrile.

Crystal structure determinations

Reflection data for both structures were measured with an Enraf-Nonius CAD-4 diffractometer. Data for the inclusion compound of **2** only were corrected for absorption [12]. The positions of all atoms in the asymmetric unit were determined by direct phasing (SIR92) [13] with hydrogen atoms included in calculated positions. The bromine atoms and the carbon atoms of the methoxy groups were refined anisotropically. A 15 parameter TLX thermal parameter (where T is the translation tensor, L is the libration tensor and X is the origin of libration) was used to assign thermal motion to the remaining atoms of the calixarene molecule, and to each independent guest molecule.

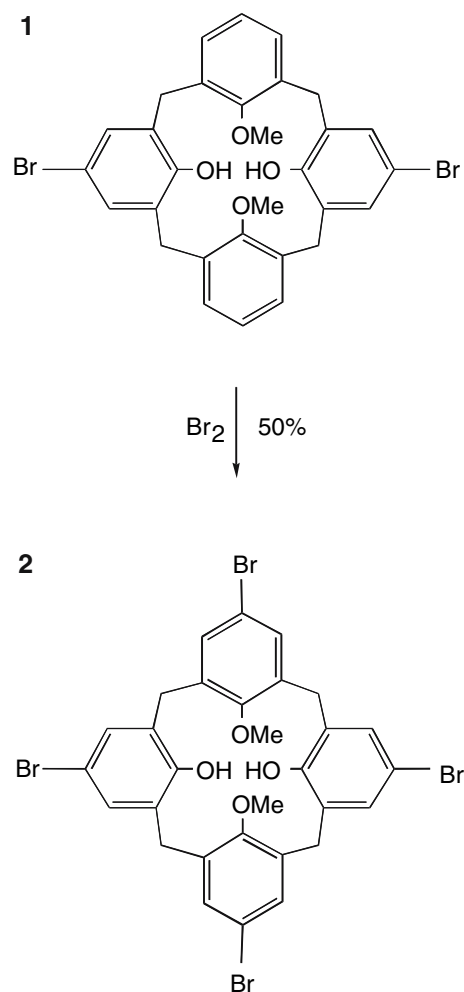
For the inclusion compound of **5**, each independent aryl ring was modelled as a rigid group. Anisotropic thermal parameters were used for the bromine and some carbon atoms, while a single TLX thermal group was used for the remainder. The water molecule in the structure (which is located on a twofold axis) was refined as an individual atom while the remaining guest molecules in both structures were refined as rigid groups with TLX thermal parameters. Full details of refinement for the two structures [14] can be found in the supplementary information.

Crystallographic data (cif) have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 608163–608164). Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

Preparation and crystal structure of (2)₂ · (pivalonitrile)₃

The dibrominated dimethoxycalix[4]arene derivative **1** [8, 9] was reacted with a solution of bromine in chloroform at room temperature. Recrystallisation of the resulting mixture of tri- and tetra-bromo compounds afforded the required product **2** in good yield (Scheme 1).



Scheme 1 Preparation of the tetrabrominated dimethoxycalix[4]arene host **2**

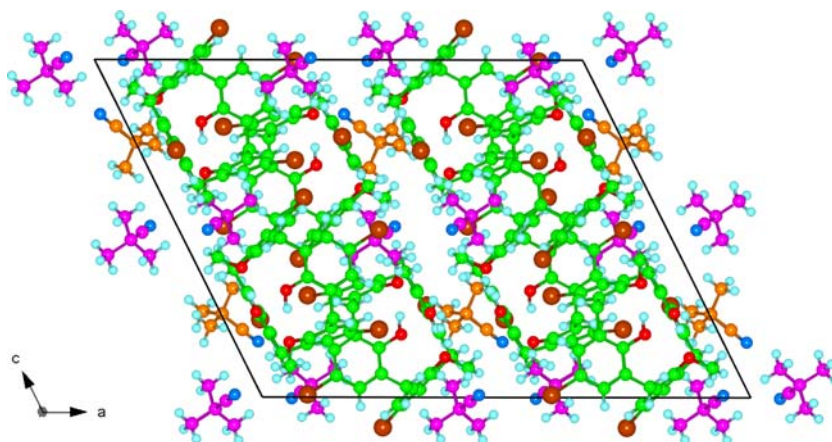
Crystals suitable for single crystal X-ray analysis were obtained by slow concentration of a pivalonitrile (trimethylacetone) solution. The resulting material was found to be the inclusion compound (2)₂ · (pivalonitrile)₃ in space group C2/c. Numerical details of solution and refinement of both crystal structures described in this paper are listed in Table 1.

There are two crystallographically independent guest molecules in (2)₂ · (pivalonitrile)₃. The pivalonitrile coloured purple in Fig. 1 has occupancy one and is located within the calixarene bowl. In contrast, the orange guest is located outside the bowl on a twofold axis, and therefore has half occupancy and is disordered with two overlapping sites. The orange guest occupies a cavity well away from any aromatic ring of the calixarene host, and no significant stabilising interactions are present.

The purple guest molecule is offset to one side of the calixarene bowl in order to maximise host–guest

Table 1 Numerical details of the solution and refinement of the X-ray structures

Compound	(2) ₂ ·(pivalonitrile) ₃	(5a)·(acetonitrile) ₃ ·(water)
Formula	C ₃₀ H ₂₄ Br ₄ O ₄ · 1.5(C ₅ H ₉ N)	C ₄₈ H ₃₈ Br ₄ O ₆ · 3(C ₂ H ₃ N)·H ₂ O
Formula mass	892.8	1171.6
Space group	C2/c	P4 ₃ 2 ₁ 2
<i>a</i> (Å)	25.800(8)	16.091(1)
<i>b</i> (Å)	16.461(5)	16.091(1)
<i>c</i> (Å)	19.913(7)	22.043(4)
β (°)	116.61(2)	90
<i>V</i> (Å) ³	7561(3)	5707(1)
<i>T</i> (K)	294(1)	294(1)
<i>Z</i>	8	4
<i>D</i> _{calc.} (g cm ⁻³)	1.57	1.36
Radiation, λ (Å)	MoK α , 0.7107	MoK α , 0.7107
μ (mm ⁻¹)	4.257	2.842
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{\max}$ (°)	50	50
No. of intensity meas.	6646	4957
Criterion for obs. ref.	$I/\sigma(I) > 2$	$I/\sigma(I) > 2$
No. of indep. obsd. ref.	2675	2015
No. of reflections (<i>m</i>), variables (<i>n</i>) in final ref.	2675/203	2015/239
$R = \sum^m \Delta F / \sum^m F_o $	0.048	0.080
$R_w = [\sum^m w \Delta F ^2 / \sum^m w F_o ^2]^{1/2}$	0.046	0.100
$S = [\sum^m w \Delta F ^2 / (m-n)]^{1/2}$	1.21	1.71
Flack parameter	–	0.00(4)
Crystal decay	17%	19%
<i>R</i> for mult. meas.	0.023	0.025
Min, max transmission coefficients	0.57, 0.68	–
Largest peak in final diff. map (e Å ⁻³)	1.21	1.71

Fig. 1 Crystal structure of (**2**)₂·(pivalonitrile)₃ projected in the *ac* plane. Atom code: H light blue, N dark blue, Br brown, host C green, guest C orange or purple. The purple guest is located inside, and the orange guest outside, the molecular bowl of the calixarene. Only one disorder component of the orange guest is shown

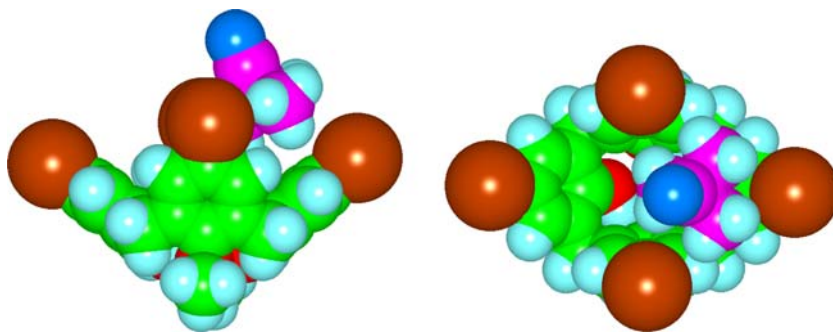
aryl···methyl attractions (Fig. 2), and the calixarene host interacts in two ways with the methyl hydrogen atoms of this pivalonitrile guest (Fig. 3). There are Ar···Br···H interactions of 3.17, 3.18, 3.31 and 3.52 Å, with each of these involving a different hydrogen atom. Furthermore, two other hydrogens interact with one of the calixarene π systems (H··· π approximately 3.7 Å; and H···C 3.11 and 3.18 Å, respectively). The mix of

these attractions provides an effective stabilisation of this host–guest combination.

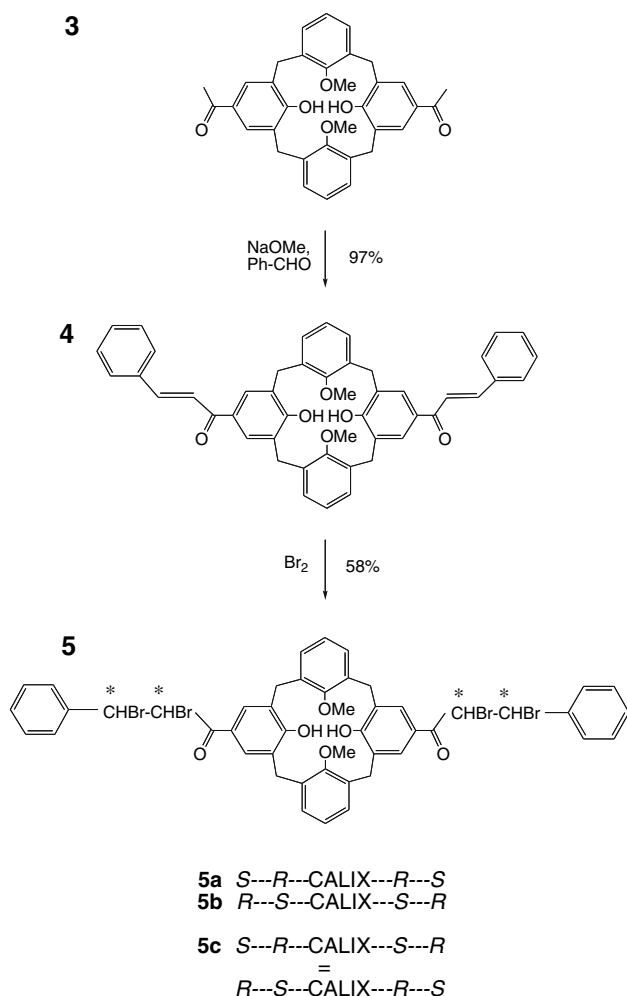
Preparation of **5** and crystal structure of (**5a**) · (acetonitrile)₃ · (water)

5,17-Diacetyl-25,27-dimethoxy-26,28-dihydroxycalix[4]-arene **3** was prepared by the method of Huang and

Fig. 2 Side (left) and top (right) views of one calixarene unit in solid $(2)_2 \cdot (\text{pivalonitrile})_3$, using space-filling representation to illustrate the offset position of the purple guest pivalonitrile molecule within the molecular bowl



Wang [10, 11], and was then subjected to aldol condensation using benzaldehyde and sodium methoxide. The resulting bis(chalcone) adduct **4** was obtained in 97% yield. Finally, reaction with bromine in chloroform solution yielded the target tetrabromide **5**, as shown in Scheme 2.



Scheme. 2 Synthesis of the bis(chalcone) derivatised calix[4]arene **4** and its tetrabromo derivative **5**. The chiral carbon atoms of the latter are indicated by asterisks, and the abbreviated formulae **5a–c** show the isomeric configurations expected from the *erythro*-bromination step

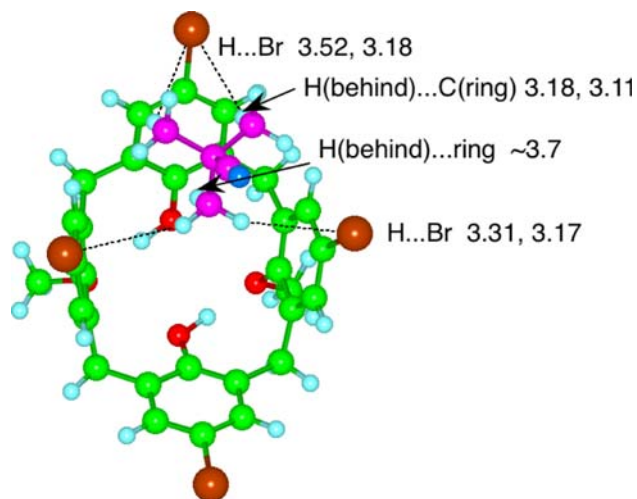


Fig. 3 Structure of one calixarene bowl in $(2)_2 \cdot (\text{pivalonitrile})_3$, indicating the stabilising host-guest interactions (dashed lines) present between the calixarene framework and the purple independent pivalonitrile molecule. Interatomic distances are shown in Å

The ^{13}C NMR spectrum of the bis(chalcone) derivative **4** shows just four aromatic carbon signals for each of the two dissimilar rings of the calixarene core, as is also the case for the compounds **1–3**. However, all six aromatic ring carbons of both ring-types are magnetically non-equivalent in the ^{13}C spectrum of **5**.

The bromination of a *trans*-chalcone creates two chiral carbon atoms in the resulting product. There is a very strong preference, however, for formation of the *erythro*-diastereomer [15, 16]. This is because it is energetically favourable for bromide ion to attack *anti* to the intermediate bromonium ion at the carbon atom that is distal to the carbonyl group. Since bromination can take place equally on either face of the alkene group, the major product is a 1:1 racemic mixture of enantiomers (*S,R* and *R,S*) of just one of the two possible diastereoisomers.

The situation for the reaction of **4** is slightly different due the presence of two identical chalcone substituents, but both brominations will predominantly yield *erythro*-isomers. Despite the bowl-shaped nature

of the substrate and questions about cone conformational inversion rates, there is free rotation of both arms about the calixarene core and therefore addition is expected to occur on both faces of each alkene group. Hence two diastereoisomers of **5** are expected, as indicated in Scheme 2. The first is a racemic mixture of the enantiomers **5a** and **5b**. Because the two arms of **5** involve the same substituents on each, the two configurations shown for **5c** in Scheme 2 are related by twofold rotation. These arrangements are identical and only one structure exists. This second diastereoisomer has a mirror plane and therefore is an achiral *meso*-compound. Recrystallisation of the crude tetrabromide from our reaction afforded a 58% yield of just one diastereoisomer from consideration of either its ^1H or ^{13}C NMR spectra. It was not possible to tell whether this was **5a/5b** or **5c** from these data.

Crystallisation of **5** from acetonitrile, and subsequent single crystal X-ray determination, revealed that the major product from the synthetic work was the racemic mixture of **5a** and **5b**. However, this material underwent spontaneous self-resolution during crystallisation to produce a conglomerate [17, 18] in the enantiomorphous tetragonal space groups $P4_12_12$ and $P4_32_12$. The crystal studied here belonged to space group $P4_32_12$ as indicated by the value of the Flack parameter listed in Table 1, and had the composition (**5a**).(*acetonitrile*)₃.(*water*). The crystal structure of one calixarene bowl of this compound, which is arranged around a twofold axis, is illustrated in Fig. 4.

There are two crystallographically independent acetonitrile guest molecules in this structure, both of which are outside the calixarene bowl. One is ordered

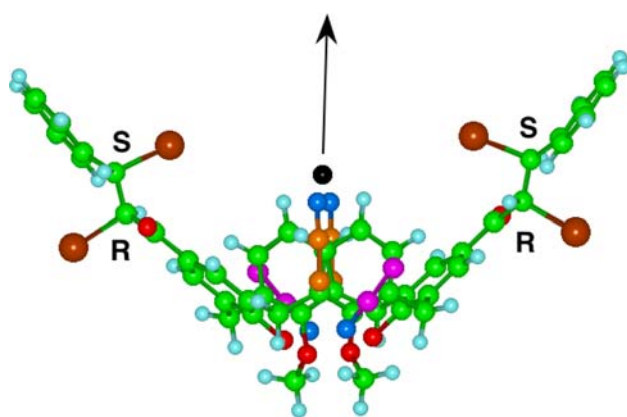


Fig. 4 Side view of one molecular bowl of the crystal structure of (**5a**).(*acetonitrile*)₃.(*water*), showing the configurations of the brominated carbon atoms. The twofold rotation axis is indicated by the arrow, and guest hydrogen atoms are omitted. The water molecule (black sphere) is situated near the top of the bowl and the carbon atoms of the two independent acetonitrile molecules are coloured purple or orange

(coloured purple), while the second (coloured orange) is disordered over two positions and, additionally, lies near a twofold axis. Hence this site is fourfold disordered but, for simplicity, only one component is shown in the accompanying figures. Two of these disorder components lie parallel to each other and the remaining two are orientated anti-parallel.

The disordered acetonitrile molecule is not close to any aromatic system, but there is a range of $\text{N}\cdots\text{Br}(1)$ contacts present (depending on the disorder component) which range between 3.35 and 4.10 Å. The ordered acetonitrile molecule lies almost parallel to the outer surface of an aromatic ring of the calixarene, at a distance of around 4 Å from it. This suggests that a weak host–guest $\pi\cdots\pi$ stabilisation exists. There is also a $\text{N}\cdots\text{Br}(2)$ contact of 4.13 Å to a second calixarene molecule.

In contrast to the behaviour of the acetonitrile guests, the water molecule is located within and near the top of the calixarene bowl. This guest is positioned closer to the two unsubstituted aromatic rings of the calixarene, rather than those bearing the brominated arms. The shortest aryl $\text{C}\cdots\text{O}$ distance is 3.82 Å, followed by 4.22 and 4.23 Å, whereas the $\text{C}\cdots\text{O}$ distances involving the substituted rings are all > 5 Å. The $\text{Br}\cdots\text{O}$ distance across the bowl is 5.18 Å. The latter two separations are too large to provide host–guest attractions of any significance.

The relative arrangement of the molecular components can also be gauged from Fig. 5, which shows the structure as a projection in the *ab* plane. This perspective shows that there is significant edge-face $\text{Ar}\cdots\text{H}\cdots\pi$ interaction present between neighbouring host molecules, as was found earlier in the crystal structure of the simpler dibromochalcone 2,3-dibromo-1,3-diphenylpropan-1-one [19]. The $\text{C}\cdots\text{C}$ distances are standard for this type of motif at around 3.6 Å.

The *S-R*—CALIX—*R-S* configuration of **5a** is present in the $P4_32_12$ crystals, and the *R-S*—CALIX—*S-R* configuration of **5b** in the $P4_12_12$ crystals. Each molecule in a given crystal adopts an identical conformation. These involve propeller-shaped arrangements of the two brominated side arms of the molecules of **5**, as shown in Fig. 6. The two opposite screw directions of the propellers thus lead to the generation of either $P4_1$ or $P4_3$ part-symmetry, and help drive the self-resolution process.

Conclusions

This investigation has shown that tetrabrominated calix[4]arene derivatives can act as host molecules that

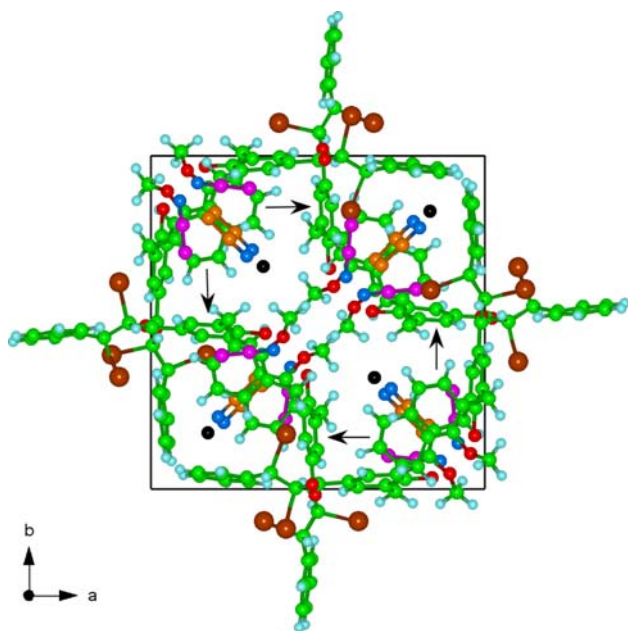


Fig. 5 Projection in the *ab* plane of the crystal structure of **(5a)**.(acetonitrile)₃.(water). Atom code: H light blue, N dark blue, Br brown, host O red, guest acetonitrile C purple or orange, guest water O black. All guest hydrogen atoms have been omitted for clarity. The two independent acetonitrile guests (purple or orange) lie outside, and the water molecule lies inside, the molecular bowl. The interhost edge-face Ar–H... π interactions are indicated by the black arrows

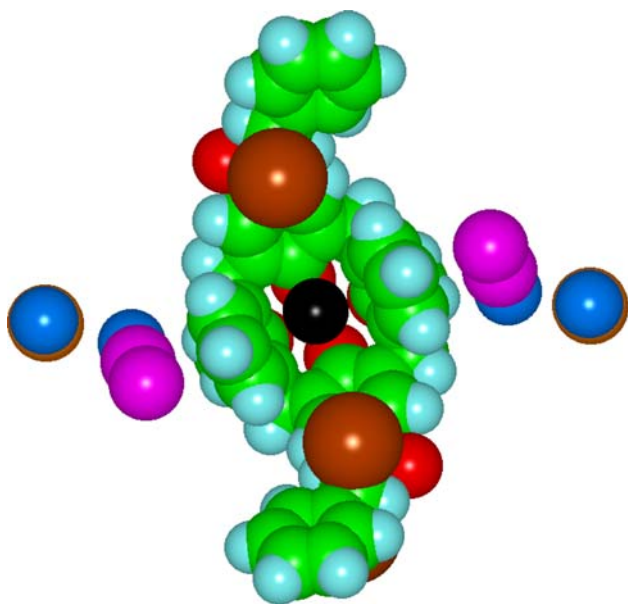


Fig. 6 Top view of one molecular bowl of the crystal structure of **(5a)**.(acetonitrile)₃.(water) using space-filling representation. The position of the guest water molecule within the bowl, and the propeller-shaped conformation of the two brominated arms, are readily apparent. All the guest hydrogen atoms are omitted in this diagram

enclose guests by both the receptor and lattice inclusion modes. For the former inclusion type to operate, it is essential that the guest molecule is capable of interacting effectively with the internal surfaces of the molecular bowl. For **(2)**₂.(pivalonitrile)₃ this was achieved by means of a mix of host–guest Ar–Br...H and π ...H–C interactions. In the **(5a)**.(acetonitrile)₃.(water) structure it was the host–water π ...H–O attractions that performed this role.

2,3-Dibromo-1,3-diphenylpropan-1-one was noted in earlier work to crystallise in a non-centrosymmetric structure and to exhibit a significant non-linear optical response to red light [16]. In the case of our dibromochalcone a chiral crystal was obtained simply by self-resolution during crystallisation. This finding supports the comments made by Harrison et al. that dibromochalcones are an interesting class of compounds for the investigation of second harmonic generation properties [19].

References

- (a) Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.): Inclusion Compounds, vols. 1–3, Academic Press, London (1984); (b) Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.), Inclusion Compounds, vols. 4–5, Oxford University Press, Oxford (1991)
- Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Vögtle, F. (eds.): Comprehensive Supramolecular Chemistry, vols. 1–11, Pergamon, Oxford (1996)
- Perrin, M., Dehler, O.: Topics in inclusion science. In: Vicens, J., Böhmer, V. (eds.), Calixarenes: A Versatile Class of Macrocyclic Compounds, pp. 65–85. Kluwer, Dordrecht (1991)
- Pochini, A., Ungaro, R.: Calixarenes and related hosts. In: Vögtle, F. (ed.), Comprehensive Supramolecular Chemistry, vol. 2, pp. 103–142. Pergamon, Oxford (1996) ch. 4
- Gutsche, C.D.: Calixarenes revisited, The Royal Society of Chemistry, Cambridge (1998)
- Cecillon, S., Lazar, A., Danylyuk, O., Suwinska, K., Rather, B., Zaworotko, M.J., Coleman, A.W.: Head-to-tail self-assembly of a calix[4]arene inclusion polymer controlled by a pendant arm. Chem. Commun. 2442–2444 (2005)
- Maharaj, F., Craig, D.C., Scudder, M.L., Bishop, R., Kumar, N.: Crystallographic and inclusion properties of some diacetylated calix[4]arenes. J. Incl. Phenom. Macrocycl. Chem. **55**, 315–324 (2006)
- Van Loon, J.D., Arduini, A., Verboom, W., Ungaro, R., Van Hummel, G.J., Harkema, S., Reinhoudt, D.N.: Selective functionalisation of calix[4]arenes at the upper rim. Tetrahedron Lett. **30**, 2681–2684 (1989)
- Van Loon, J.D., Arduini, A., Coppi, L., Verboom, W., Pochini, A., Ungaro, R., Harkema, S., Reinhoudt, D.N.: Selective functionalisation of calix[4]arenes at the upper rim. J. Org. Chem. **55**, 5639–5646 (1990)
- Huang, Z.-T., Wang G.-Q.: Selective Friedel-Crafts reaction of 26,28-dimethoxycalix[4]arene. J. Chem. Soc., Perkin Trans. **1**, 167–168 (1993)
- Huang, Z.-T., Wang G.-Q.: Study of calixarenes. V. Friedel-Crafts reaction of calixarenes. Chem. Ber. **127**, 519–523 (1994)

12. De Meulenaer, J., Tompa, M.: The absorption correction in crystal structure analysis. *Acta Crystallogr.* **19**, 1014–1018 (1965)
13. Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C., Polidori, G., Camalli, M.: SIR92 – a program for automatic solution of crystal structures by direct methods. *J. Appl. Cryst.* **27**, 435 (1994)
14. Rae, A.D.: RAELS. A comprehensive constrained least squares refinement program. Australian National University, Canberra, Australia (2000)
15. Tanaka, K., Shiraishi, R., Toda, F.: A new method for stereoselective bromination of stilbene and chalcone in a water suspension medium. *J. Chem. Soc., Perkin Trans.* **1**, 3069–3070 (1999)
16. Nakamatsu, S., Toyota, S., Jones, W., Toda, F.: The important role of solvent vapour in an organic solid state reaction. *Chem. Commun.* 3808–3810 (2005)
17. Jacques, J., Collet, A., Wilen, S.H.: *Enantiomers, racemates, and resolutions*. Wiley, New York (1981)
18. Collet, A., Brienne, M.-J., Jacques, J.: Optical resolution by direct crystallisation of enantiomeric mixtures. *Chem. Rev.* **80**, 215–230 (1980)
19. Harrison, W.T.A., Yathirajan, H.S., Sarojini, B.K., Narayana, B., Anilkumar, H.G.: Do C-H...O and C-H... π interactions help to stabilise a non-centrosymmetric structure for racemic 2,3-dibromo-1,3-diphenylpropan-1-one? *Acta Crystallogr. Sect. C* **61**, o728–o730 (2005)