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Structures and properties of solvated and unsolvated isopropyl functionalised calix[4]arenes

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The tetra-isopropyl ethers of calix[4]arene and *p-t*-butylcalix[4]arene have been isolated in the cone conformation, and structurally characterised as chloroform solvates. Thermogravimetric analysis demonstrated that the parent isopropylcalix[4]arene solvate is significantly more stable than the *p-t*-butylcalix[4]arene analogue, retaining the solvent up to a temperature of 125°C. It was found that the calix[4]arene ether sublimes at atmospheric pressure, and solvent-free crystals appropriate for structure determination were produced at reduced pressure. The *p-t*-butylcalix[4]arene ether was also isolated without solvent in the lattice, but in this case the calixarene was crystallised from acetone, as sublimation did not produce crystals of sufficient quality.

Keywords: crystal structure; calixarene; thermogravimetric analysis

Introduction

The structural chemistry of the calixarenes, and, in particular, the incorporation of guests into the calixarene cavity and/or interstitial sites in the crystal, has been of interest from the earliest work on these widely studied macrocycles (*1*). Despite this activity, research into the solid-state behaviour of even the simple calix[4]arene and *p-t*-butylcalix[4]arene continues, with recent developments including the studies of the solvent-free crystal structures produced by sublimation, as well as crystallisation from solvents that do not incorporate into the structure (*2*, *3*). As well as providing fundamental information on the formation of crystalline structures, additional interest has been generated by the discovery that such matrices can form remarkable stable clathrates with gases and volatile liquids, despite the fact that the systems are stabilised by van der Waals interactions only (*2*, *4*). For example, *p-t*-butylcalix[4]arene can be sublimed to form a low-density, but non-porous, structure that absorbs a range of gases under ambient conditions. Some selectivity in the absorption has been reported, such that separation of gases is possible. It has been proposed that the disordered *t*-butyl groups in the non-porous structure of sublimed *p-t*-butylcalix[4]arene serve as 'turnstiles', allowing admission of gas molecules into the crystal (*5*). It should be noted that absorption of guests into non-porous structures has also been observed in hydrogen-bonded host lattices (*6*), suggesting that this may be a phenomenon that can occur in a range of weakly bound host lattices. This area of calixarene chemistry has been reviewed very recently, and is of particular interest, given the huge effort being invested in the development of materials for gas storage (*5*, *7*).

We have been developing pinched cone calix[4]arene receptors for soft metal cations (*8*), and as part of this programme tetra-isopropoxy derivatives of calix[4]arene and *p-t*-butylcalix[4]arene (**1**, **2**) were synthesised. The observation that the calix[4]arene derivative sublimed at atmospheric pressure prompted us to investigate the structures of these molecules in the presence and absence of solvent, and to test the stability of the solvates formed. We report here the crystal structures of **1** and **2**, and their chloroform solvates, as well as thermogravimetric investigation of the latter.

Experimental

Synthesis

The calixarene derivatives **1** and **2** were synthesised using a modification of the literature procedure (*9*). All NMR spectra were recorded in $CDCl_3$, and referenced to residual chloroform.

*Synthesis of 1,2,3,4-tetra-isopropylcalix[4]arene (**1**)*

Calix[4]arene (5.0 g, 12 mmol) was added to clean sodium hydride (8.0 g, 0.33 mol) and imidazole (50 mg, 0.073 mmol) in DMF (60 ml) and stirred under nitrogen for 30 min. An excess of 2-bromopropane (30 ml, 0.32 mol) was then added dropwise to the reaction mixture with stirring. The reaction progress was monitored by thin

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layer chromatography (1:1 petroleum spirit:toluene) and additional portions of sodium hydride and 2-bromopropane were administered when required (2 g, 0.08 mol and 15 ml, 0.16 mol at 48 and 120 h, respectively). The reaction was quenched after 160 h with the careful addition of methanol to the mixture. Water was added to precipitate the calixarene, which was collected and washed with further aliquots of water. The product was purified by flash chromatography (1:1 petroleum spirit:toluene) to yield a white powder (2.13 g, 30%) m.p. 268°C (sub). Found: C 81.0; H 7.9%, $C_{40}H_{48}O_4$, required: C 81.0; H 8.2%.

IR: 2958 cm^{-1} (ν_{as} CH_3); 1654 and 1481 cm^{-1} (aromatic C═C); 1362 cm^{-1} (δ_s CH_3); 1200 cm^{-1} (Ar—O—C antisymmetric stretch). ^{1}H NMR: δ 1.37 [d, $J = 5.86$ Hz, 24H, CH_3CH]; 3.08 [d, $J = 13.0$ Hz, 4H, Ar—CH_2—Ar (equatorial)]; 4.47 [m, 4H, CH(CH_3)$_2$]; 4.50 [d, $J = 13.0$ Hz, —CH_2—Ar (axial)]; 6.52–6.67 [m, 12H, Ar—H]. ^{13}C NMR: δ 23.46 (CH(*C*H_3)$_2$); 31.79 (Ar—*C*H_2—Ar); 77.32 (O*C*H); 122.23, 128.65, 136.44, 154.92 (aromatic).

Synthesis of 1,2,3,4-tetra-isopropyl-p-t-*butylcalix[4]arene (**2**)*

p-t-Butylcalix[4]arene (5.13 g, 7.7 mmol) was added to clean sodium hydride (2.96 g, 123 mmol) and imidazole (50 mg, 0.073 mmol) in dried DMF (125 ml) and stirred for 30 min under nitrogen. A large excess of 2-bromopropane (15 ml, 0.16 mol) was then added dropwise and stirred under nitrogen for 24 h. Additional aliquots of 2-bromopropane (10 ml, 0.11 mol and 7.0 ml, 0.074 mol) were added to the reaction flask at 24-h intervals. The reaction was quenched after 112 h with the careful addition of methanol. Water was then added to precipitate the calixarene, which was then collected and washed with further proportions of water to yield the crude material. The crude calixarene was purified by flash chromatography (19:1 petroleum spirit:ethyl acetate) to yield a white powder (2.12 g, 34%), m.p. 269.5°C. Found: C 82.5; H 9.8%, $C_{56}H_{80}O_4$, required: C 82.3; H 9.9%.

IR: 2964% cm^{-1} (ν_{as} CH_3); 1602 and 1479 cm^{-1} (aromatic C═C); 1460 cm^{-1} (CH_2 scissor); 1364 cm^{-1} (δ_s CH_3); 1202 cm^{-1} (Ar—O—C antisymmetric stretch); 1115 cm^{-1} (Ar—O—C symmetric stretch). ^{1}H NMR: δ 1.09 [s, 36H, C(CH_3)$_3$]; 1.40 [d, $J = 6.2$ Hz, 24H, (CH_3)$_2$CH]; 3.06 [d, $J = 12.1$ Hz, 4H, Ar—CH_2—Ar (equatorial)]; 3.99 [m, 4H, —CH(CH_3)$_2$]; 4.51 [d, $J = 12.1$ Hz, 4H, Ar—CH_2—Ar (axial)]; 6.81 [s, 8H, ArH]. ^{13}C NMR: δ 23.56 (CH(*C*H_3)$_2$); 31.78, 32.23 (C(CH_3)$_3$); 34.47 (Ar—CH_2—Ar); 77.85 (O—*C*H); 125.32, 135.26, 144.32, 152.14 (aromatic).

Structure determinations

Full spheres of CCD area detector diffractometer data were measured (ω scans, monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 150 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $I > 2\sigma(I)$ being considered 'observed'. Anisotropic displacement parameter forms were refined in the large block least-squares refinements, hydrogen atom treatment following a 'riding' model; reflection weights were $(\sigma^2(F^2) + (aP)^2(+bP))^{-1}$. Neutral atom complex scattering factors were employed within the SHELXL 97 program (*10*). Pertinent results are given in the table and figures; full.*cif* depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC 683867–683870.

Crystal/refinement data

1. $C_{40}H_{48}O_4$, $M_r = 592.8$. Tetragonal, space group $I4_1/a$ (C^6_{4h}, No. 88), $a = 19.627(3)$, $c = 17.867(3)$ Å, $V = 6883$ Å^3. D_c ($Z = 8$) $= 1.14_4$ g cm^{-3}. $\mu_{Mo} = 0.072$ mm^{-1}; specimen = 0.17 × 0.13 × 0.07 mm; 'T'$_{min/max} = 0.94$. $2\theta_{max} = 58°$; $N_t = 31{,}581$, $N = 4352$ ($R_{int} = 0.061$), $N_o = 2139$; $R1 = 0.065$, $wR2 = 0.147$ ($a = 0.021$, $b = 5.50$); $S = 1.03$. $|\Delta\rho_{max}| = 0.13$ e Å^{-3}.

Variata. Both isopropyl groups were modelled as disordered over pairs of sets of sites, seemingly concerted, site occupies refining to 0.698(9) (major components) and complement.

1·½$CHCl_3$. $C_{40.5}H_{48.5}Cl_{1.5}O_4$, $M_r = 652.5$. Tetragonal, space group $P4/ncc$ (D^8_{4h}, No. 130), $a = 19.266(3)$, $c = 19.225(3)$ Å, $V = 7136$ Å^3. D_c ($Z = 8$) $= 1.21_5$ g cm^{-3}. $\mu_{Mo} = 0.184$ mm^{-1}; specimen = 0.75 × 0.18 ×0.09 mm; 'T'$_{min/max} = 0.79$. $2\theta_{max} = 58°$; $N_t = 68{,}517$, $N = 4612$ ($R_{int} = 0.040$), $N_o = 3282$; $R1 = 0.056$, $wR2 = 0.18$ ($a = 0.126$, $b = 2.321$); $S = 0.90$. $|\Delta\rho_{max}| = 1.25$ e Å^{-3}.

Variata. Isopropyl group disorder was modelled similarly to that in **1**, site occupancies refining to 0.816(3) and complement. The carbon atom of the chloroform molecule lies on a crystallographic four-fold axis with the chlorine component concomitantly disordered.

2. $C_{56}H_{80}O_4$, $M_r = 817.2$. Monoclinic, space group $P2_1/c$ (C^5_{2h}, No. 14), $a = 10.901(5)$, $b = 22.919(10)$, $c = 41.74(2)$ Å, $\beta = 97.068(8)°$, $V = 10{,}349$ Å^3. D_c ($Z = 8$) $= 1.04_9$ g cm^{-3}. $\mu_{Mo} = 0.064$ mm^{-1}; specimen = 0.15 × 0.06 × 0.06 mm; 'T'$_{min/max} = 0.81$. $2\theta_{max} = 50°$; $N_t = 78{,}765$, $N = 18{,}426$ ($R_{int} = 0.24$), $N_o = 4348$; $R1 = 0.11$, $wR2 = 0.30$ ($a = 0.123$); $S = 0.75$. $|\Delta\rho_{max}| = 0.51$ e Å^{-3}.

2·$CHCl_3$. $C_{57}H_{81}Cl_3O_4$, $M_r = 936.6$. Monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), $a = 17.425(1)$, $b = 21.365(2)$, $c = 15.461(1)$ Å, $\beta = 102.620(2)°$, $V = 5617$ Å^3. D_c ($Z = 4$) $= 1.10_8$ g cm^{-3}. $\mu_{Mo} = 0.204$ mm^{-1}; specimen = 0.20 × 0.18 × 0.14 mm; 'T'$_{min/max} = 0.89$. $2\theta_{max} = 65°$; $N_t = 53{,}761$, $N = 10{,}176$ ($R_{int} = 0.047$), $N_o = 6444$; $R1 = 0.056$, $wR2 = 0.17$ ($a = 0.107$); $S = 1.00$. $|\Delta\rho_{max}| = 66$ e Å^{-3}.

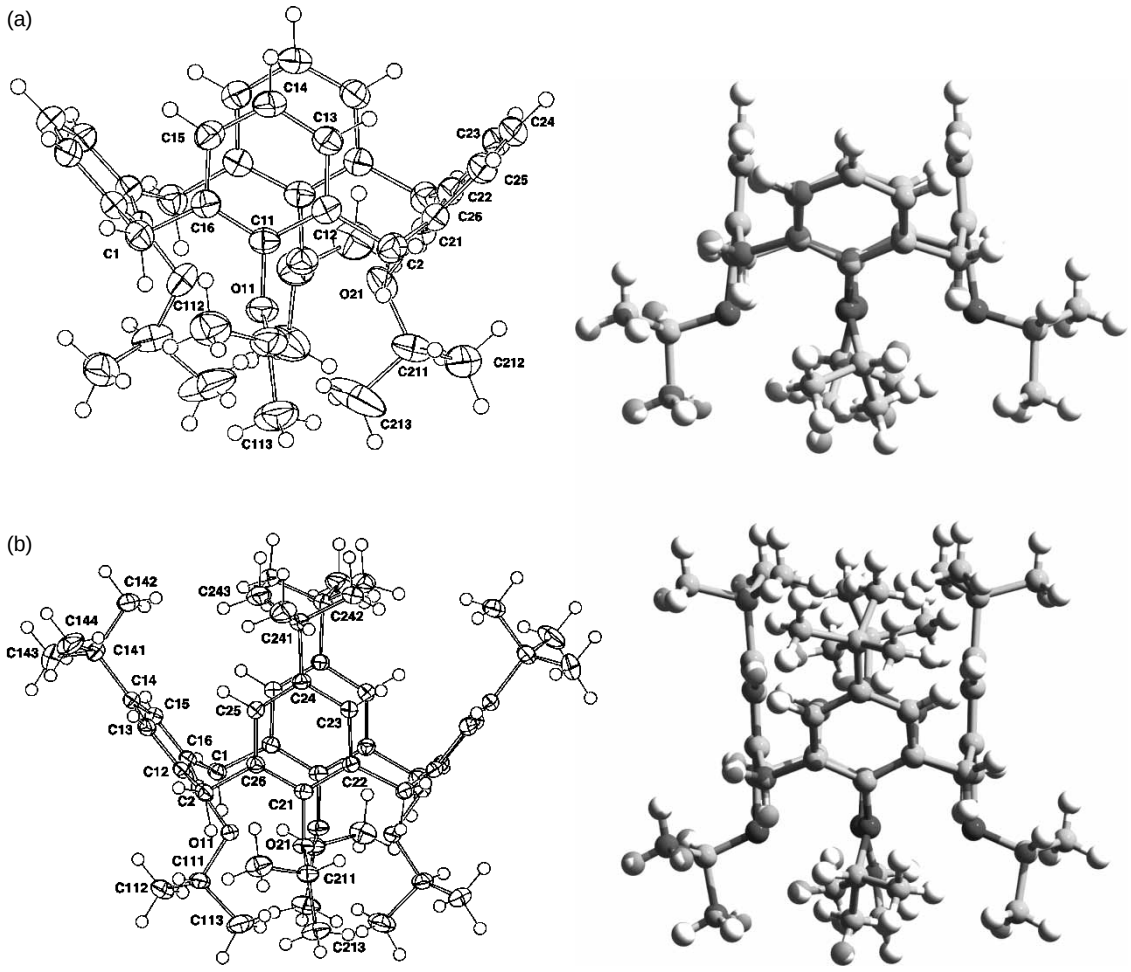

Figure 1. Representations of the molecular structures of (a) **1** (major component) and (b) **2** (mol. 1), illustrating the 'pinched cone' conformation of the calixarene.

Results and discussion

Synthesis

The syntheses of **1** and **2** were achieved following well-established procedures for the alkylation of calixarenes, using sodium hydride as the base to favour the formation of the cone conformer. While a previous report indicates that alkylation with the isopropyl group can be achieved as readily as with the *n*-propyl reagent (*9*), in our hands a large excess, and repeated addition of the alkylating agent was required, presumably because of the tendency of 2-bromopropane to eliminate HBr. The reaction was carried out at room temperature over an extended time period, in an effort to minimise the impact of the elimination reaction. With these precautions, the products could be isolated at acceptable (30–35%) yields after purification by column chromatography. The NMR spectra were consistent with the calixarenes being locked into the cone conformation.

Structural characterisation

Crystals appropriate for structure determination of **1** and **2** were grown by the diffusion of methanol into chloroform solutions of the calixarenes. The results of the structure determinations were consistent with the formulations **1**·$\frac{1}{2}$$CHCl_3$ and **2**·$CHCl_3$. The molecular structures of the unsolvated calixarenes are shown in Figure 1. In **1**, the molecules are disposed about crystallographic two-fold

Table 1. Interplanar dihedral angles (°).

Compound	C_6/C_6	C_6/C_6 (opposed)	C_6/O_4
1	81.6(1)	87.98(6), 19.48(6)	44.34(7), 80.06(6)
1·$\frac{1}{2}$$CHCl_3$	85.87(6)	7.65(6), 83.12(6)	85.93(4), 48.59(5)
2·$CHCl_3$	87.97(5)	75.41(4), 3.21(4)	52.29(4), 88.40(3)

In **2**, the C_6/C_6 angles are (mols 1,2): 86.0(4), 85.4(4) (1/2); 8.3(4), 7.5(4) (1/3); 89.9(4), 87.9(4) (2/3); 88.1(4), 89.1(4) (1/4); 74.1(4), 71.6(4) (2/4); 86.1(4), 84.9(4) (3/4). The C_6/O_4 angles are (mols 1;2): 77.8(1), 73.0(1), 77.0(1), 65.9(1); 78.7(1), 77.7(1), 76.5(1), 64.8(1)°.

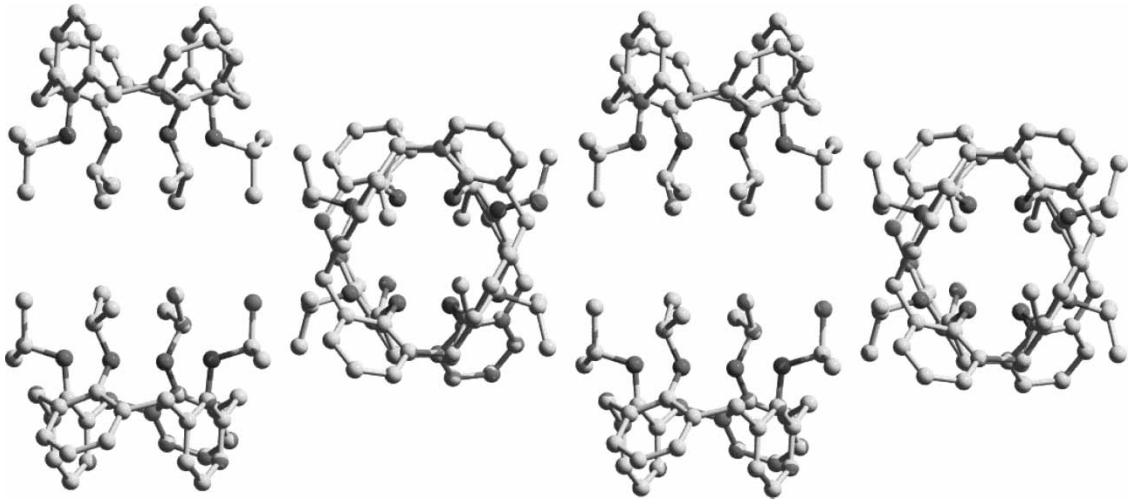

Figure 2. The columnar structure of lower rim to lower rim stacked solvated **1** generated by the screw axis in the *c*-direction.

axis, one-half of the molecule comprising the asymmetric unit of the structure; in **2**, two independent molecules, devoid of crystallographic symmetry, make up the asymmetric unit of the structure. Both calixarenes, **1**, **2**, assume a 'pinched' cone conformation, as is often found in these macrocycles, where hydrogen bonds at the phenolic rim are eliminated (*11*). The calixarene cavities are empty, with the upright aromatic rings close to parallel (Table 1), and the presence of the *p*-*t*-butyl groups in **2** presumably limiting the inward tilt of the phenyl rings in comparison to **1**.

Calixarene **1** crystallised with a 1:2 chloroform:calixarene ratio, also disposed about a crystallographic two-fold axis, with one-half of the substrate molecule comprising the asymmetric unit of the structure, but this time in space group $P4/ncc$ rather than $I4_1/a$; the chloroform molecule is disordered about a crystallographic four-fold axis, the carbon atom lying on that axis. The structure (of the solvate) can be viewed as comprising inversion-related pairs of calixarene molecules stacked lower rim to lower rim. The crystal structure is produced by columnar arrangement of these pairs, generated by a two-fold screw axis in the *ab*-direction (Figure 2).

The resulting columns are interleaved, as shown in Figure 3, where each column has been designated by a single colour. The chloroform molecules, rather than being included, reside in cavities between the stacked columns. The view down the *c*-axis shows the layered nature of the resulting structure and the disposition of the solvent molecules relative to the layers.

Calixarene **2** crystallises from chloroform as a 1:1 solvate. Once again the calixarene cavity is unoccupied, as expected with the pinched cone conformation; the chloroform molecules reside within the layers, normal to *b*, defined by the calixarene molecules (Figure 4).

In the course of determining the melting point of **1**, it was found that the calixarene sublimed rather than melted at atmospheric pressure. Sublimation at reduced pressure produced crystals appropriate for structure determination, the results of which showed that the crystals were free

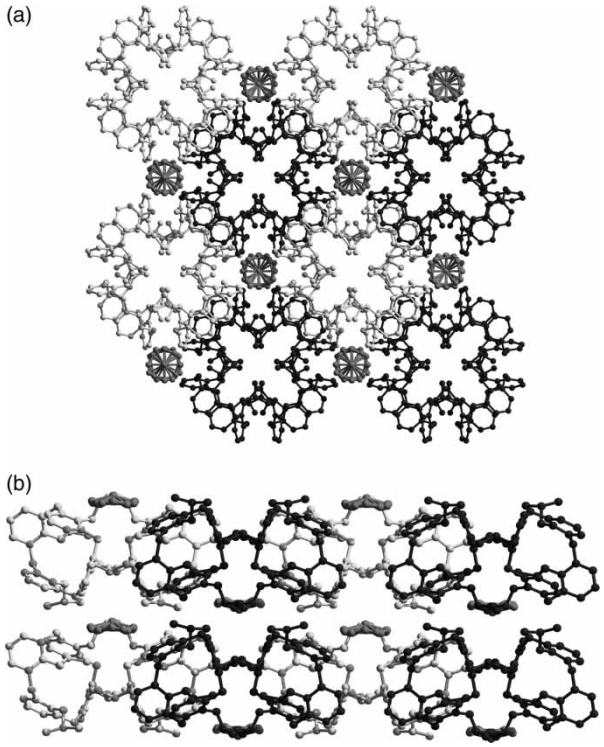

Figure 3. Crystal lattice packing of the chloroform solvate of calixarene **1**, showing (a) the interleaved columns (projection down *c*) and (b) the view along the *ab* diagonal showing the layered nature of the structure.

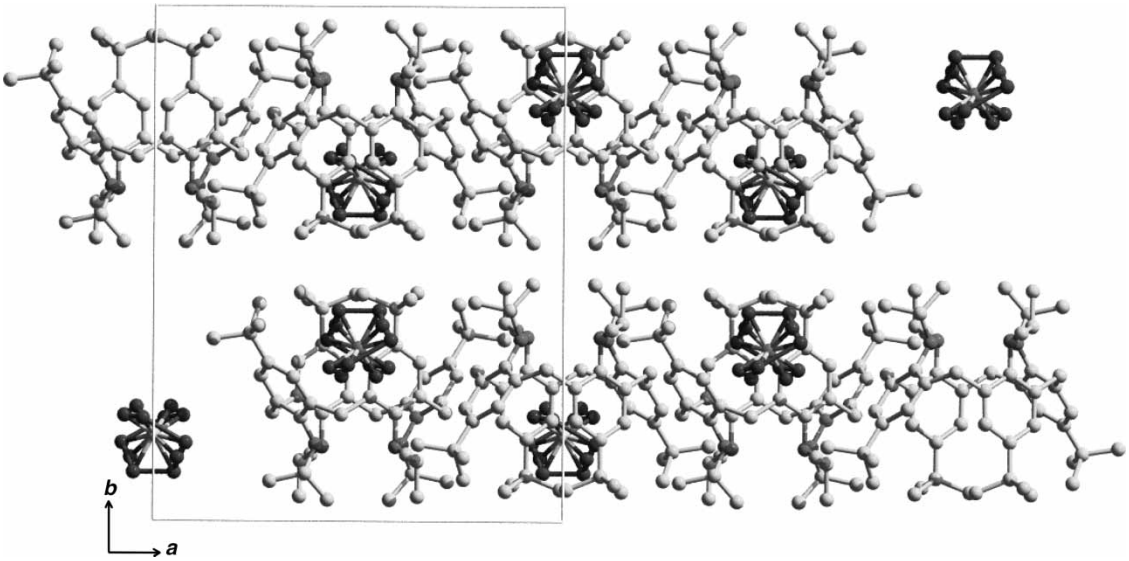

Figure 4. The crystal packing of **2**·$CHCl_3$, projected down *c*.

of solvent. The molecular conformation of the calixarene is comparable to that observed in the chloroform solvate, although the pinching of the cone is even more extreme (Table 1). In this case, the calixarenes are packed in a columnar fashion, aligned along the axis of the calixarene cone. The orientation of the calixarene alternates up:down within the columns that are aligned with the *c*-axis (Figure 5). This structure is similar to that reported for the *n*-butyl-substituted calix[4]arene, and it is interesting to note that the *n*-butyl derivative was crystallised from chloroform to give the solvent-free structure (*11*).

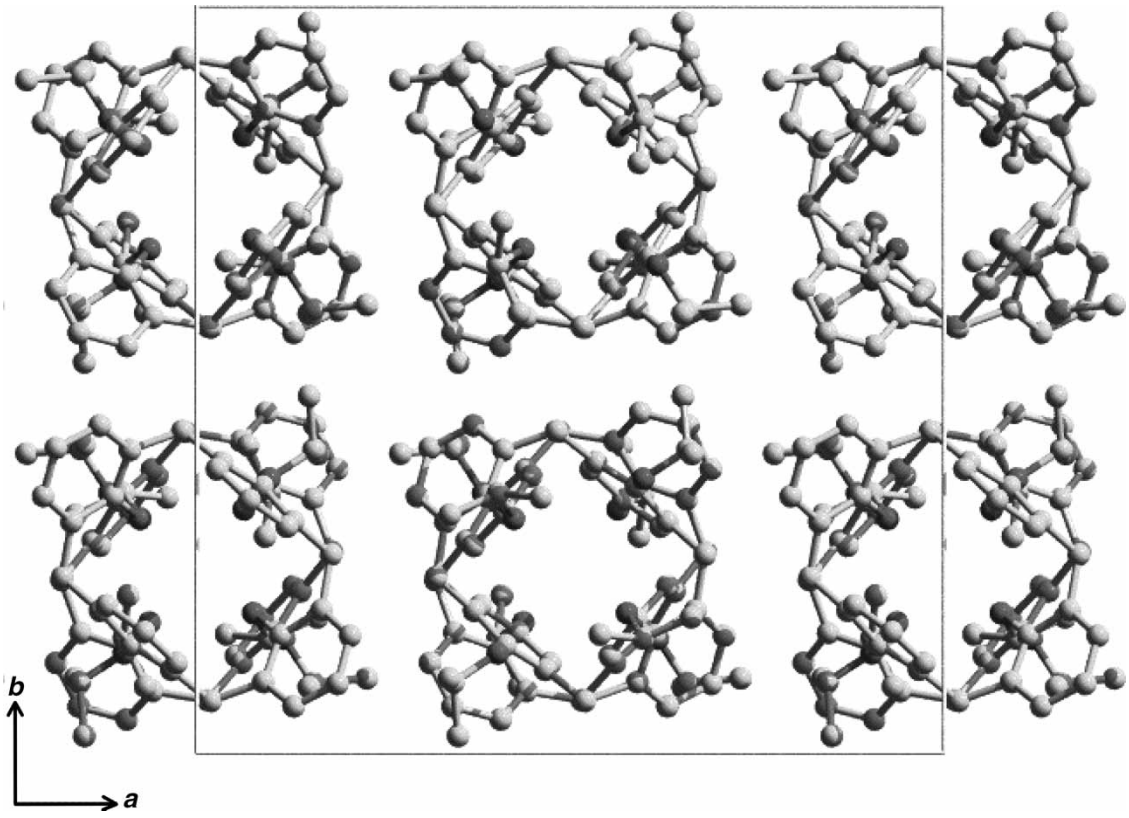

Figure 5. The crystal packing of sublimed **1**, projected down *c*.

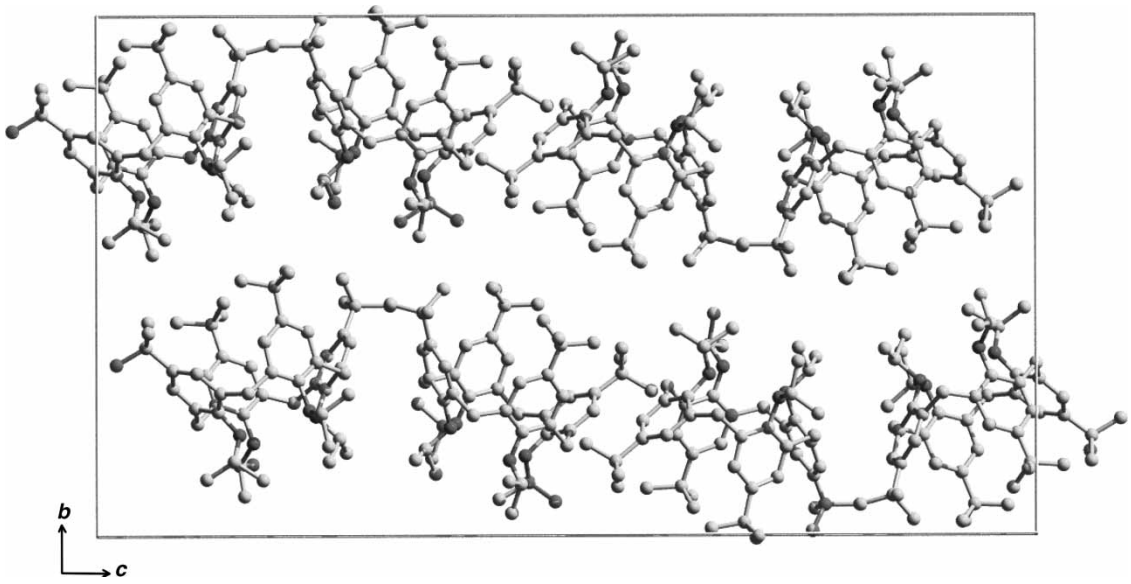

Figure 6. The crystal packing of **2** (crystallised from acetone) projected down *a*.

While **2** could also be sublimed, it did not prove possible to produce crystals of sufficient quality for structure determination in this way. Further experimentation resulted in the production of good quality crystals from acetone solvent. The results of the structure determination showed that the crystals were free of included solvent. As was the case with calixarene **1**, the crystal packing of **2** without solvent is different to the solvated form. The structure is once again layered, this time in an undulating manner, along the *c*-axis (Figure 6). The calixarene molecules are paired along the layers with two up and two down. The asymmetric unit comprises two inequivalent molecules, which are similar in terms of the molecular conformation and again adopt a pinched cone conformation (Table 1).

It should be noted that the structure of the sublimed crystals may be different to the acetone crystallised system [indeed, this is the case for solvent-free *p-t*-butylcalix[4]-arene when sublimed (*2*) or crystallised from tetradecane solvent (*12*)], but determining this is beyond the scope of the present work.

Thermal analysis of the chloroform solvates

The remarkable stability of gas clathrates of calixarenes reported recently (*5*) prompted us to test the stability of the chloroform solvates reported here. The difference between the two products was considerable. Upon exposure to the atmosphere, **2**·$CHCl_3$ lost solvent rapidly such that thermogravimetric analysis (TGA) to monitor the solvent loss was not possible. By contrast, **1**·$\frac{1}{2}CHCl_3$ was found to retain solvent at elevated temperatures, with the onset of the release found to be 125°C (Figure 7), the percentage weight loss of 8.9% being consistent with the presence of a half equivalent of chloroform. The difference between the boiling point of the incorporated compound and the temperature of onset of loss ($T_{on} - T_b$) has been used as an indicator of the relative thermal stability of a host–guest system [although it is noted that this parameter is in fact a convolution of kinetic and thermodynamic processes and is only a qualitative indication of thermal stability (*13*)]. In this case, $T_{on} - T_b$ for **1**·$\frac{1}{2}CHCl_3$ is 64°C, compared with a value ≤ -36°C for **2**·$CHCl_3$.

After **1**·$\frac{1}{2}CHCl_3$ was thermally desolvated, it was possible to reverse the process by exposure to chloroform vapour. Subsequent TGA gave the same percentage weight loss as found initially, within experimental error. By contrast, upon exposure of sublimed **1** to chloroform vapour, the crystals were found to deliquesce. This suggests that the structure of the thermally desolvated **1** may not be the same as the sublimed material, but may

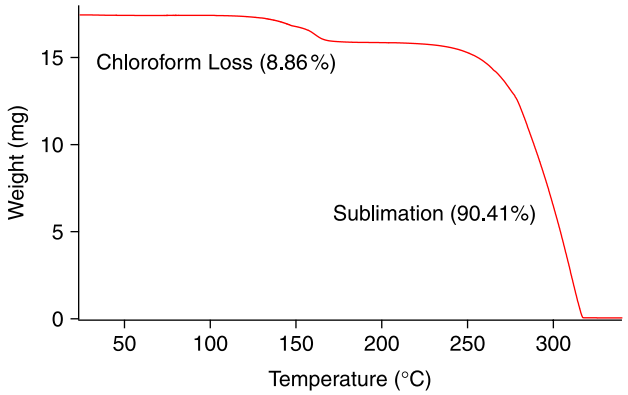

Figure 7. TGA–DTA trace of the chloroform solvate of calixarene **1** showing the loss of chloroform at elevated temperatures and subsequent sublimation.

retain the structure of the hemisolvate. It has been proposed that a lack of structural change upon desolvation may be associated with thermal stability (*5*). Attempts to confirm this hypothesis by single-crystal structure determination were not successful, as the crystals deteriorated during the desolvation process.

Conclusions

In conclusion, we have reported the solvated and solvent-free structures of two isopropyl functionalised calixarenes. The thermal stabilities of the two solvates were found to vary significantly, despite the fact that both form layered structures that do not appear to differ greatly in the nature of encapsulation of the guest. It is proposed that the variation in thermal stability may be associated with differences in the extent of structural change upon thermal desolvation.

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