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# Crystallographic and Inclusion Properties of Some Diacetylated Calix[4]arenes

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**Abstract**

Three 5,17-diacetylcalix[4]arene derivatives **3**–**5** have been prepared, evaluated for inclusion properties, and their single crystal X-ray structures determined. The diacetyl calixarenes **3** and **4** were obtained by acetylation of their parent dimethoxy **1** or dipropoxy **2** compounds, respectively, whereas 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene **5** was prepared by alkylation of **4**. Crystallisation of **3** resulted in no inclusion from chloroform, but yielded lattice inclusion compounds from acetonitrile or acetone. The calixarene **3** maintains its cone conformation in these crystals, but displays degrees of distortion depending upon the included solvent. Crystal structures of solvent-free **4** and **5** are also described. A new preparation of the monomethoxy derivative **6** is described, and its X-ray structure with chloroform guest is analysed.

## Introduction

Calixarenes are basket-shaped compounds of potential interest for host-guest complexation [1]. The ease of chemical modification at the lower rim (reaction of the -OH groups) and the upper rim (reactions at the *para*-positions of the aromatic rings) is an important feature of calix[4]arenes [2–4], and leads to a diverse range of molecules with unique properties. Although calix[4]arenes are conformationally flexible, they frequently exist in the cone conformation due to a network of intramolecular hydrogen bonding. The cone conformation in a calix[4]arene molecule can also be maintained by choosing appropriate functional groups. The selectivity of the recognition properties can be varied through modification at the phenolic oxygen atoms [5–16].

Acetylated calix[4]arenes are important precursors for the synthesis of functionalized calix[4]arenes. As a part of an ongoing research project aimed at developing deep cavity calix[4]arenes, we were interested in exploring the host-guest chemistry of diacetylcalix[4]arenes. In this paper, we describe the syntheses and inclusion properties of the 5,17-diacetyl-25,27-dialkoxycalix[4]arenes **3**–**4**, the 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene **5** and the 25-methoxycalix[4]arene **6**. X-ray crystallographic studies have been used to analyse the solvent-free or inclusion crystals obtained for **3**–**6**.

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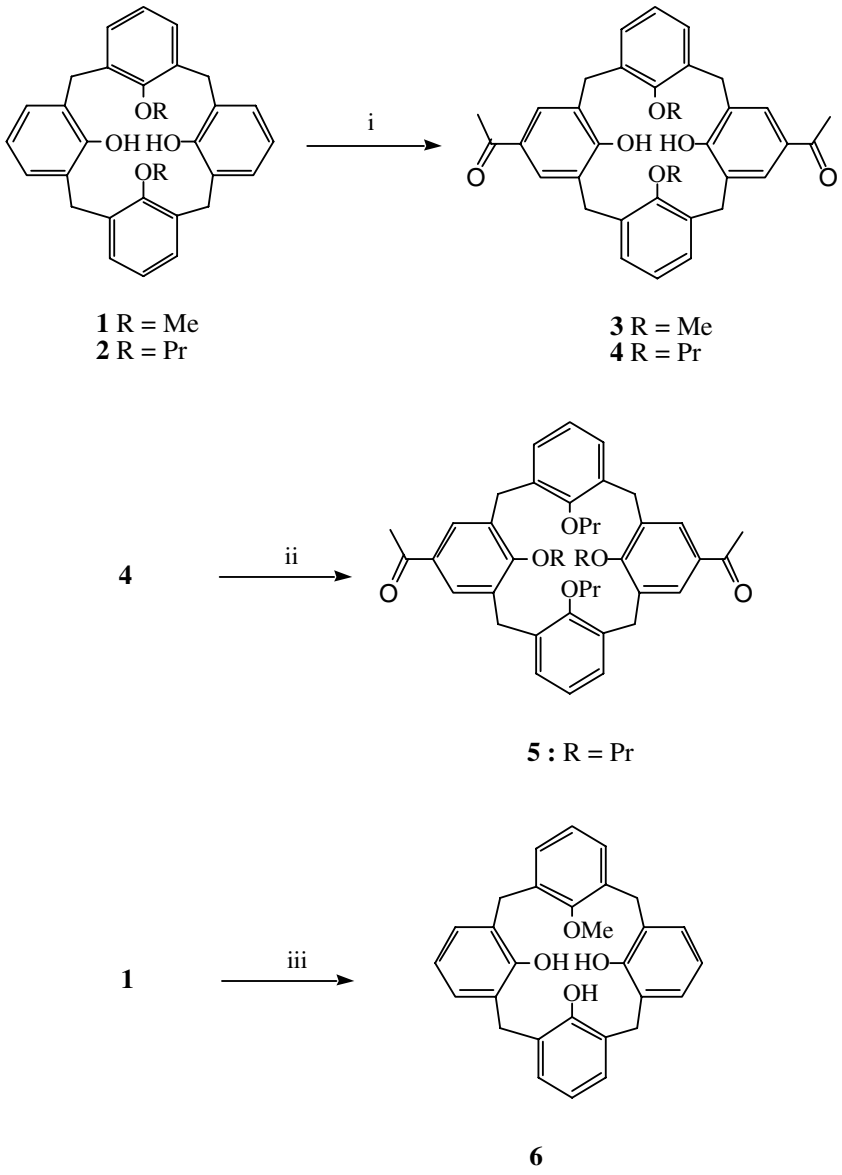
## Experimental

### *Preparation of the calix[4]arene derivatives*

All chemicals for the synthesis of the acetylated calix[4]arenes, acetyl chloride, propyl iodide, methyl-*p*-toluenesulfonate, diphenyl ether, *p*-tert-butyl phenol etc. were purchased from Aldrich Chemical Company. Melting points are uncorrected and were determined using a Kofler hot stage micromelting apparatus. $^{1}$H (300 MHz) and $^{13}$C NMR (75.6 MHz) spectra were obtained in $CDCl_3$ on a Bruker AMX300 spectrometer and are reported as chemical shifts ($\delta$) relative to TMS. Infrared spectra were recorded as paraffin mulls on a Thermo Nicolet Avatar 320 FT-IR spectrometer. The high resolution ESI mass spectra were recorded using a 7 Tesla Bruker BioApex II FTICR mass spectrometer with an electrospray ionisation source. Compounds **1** [1, 17, 18], **2** [19] and **3** [20, 21] were synthesised following literature procedures.

### *5,17-Diacetyl-25,27-dimethoxy-26, 28-dihydroxycalix[4]arene* **3**

A solution of acetyl chloride (1.04 g, 13.26 mmol) and aluminium (III) chloride (0.98 g, 7.40 mmol) in chloroform (100 ml) was added dropwise to an ice-cooled solution of 25,27-dimethoxy-26,28-dihydroxycalix[4]arene **1** (1.01 g, 2.21 mmol) in dichloromethane (15 ml). The




*Scheme 1.* (i) $AlCl_3$, $CH_3COCl$ in $CH_2Cl_2$ at 0 °C; (ii) NaH, PrI in DMF at r.t.; (iii) $SnCl_4$, $Cl_2CH{-}O{-}CH_3$.

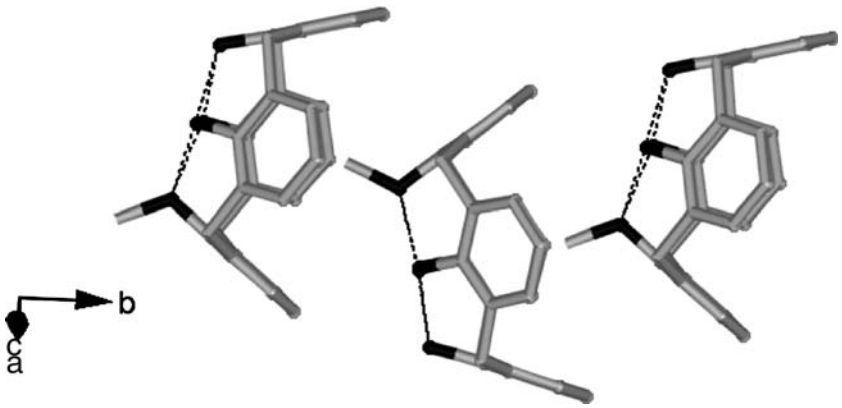



*Figure 1.* The methoxy group of one molecule of **6** is located within the calixarene bowl of its neighbour. Repetition of this construction mode creates chains along *b*. Hydroxy group hydrogen bonding is indicated by dashed lines. One set of superimposed hydrogen bonds is removed in Figures 1 and 2 to make these dashed symbols clearer. For clarity hydrogen atoms are omitted in this, and subsequent, figures.

mixture was allowed to warm to room temperature and stirred for a further 24 h. The mixture was poured into cold water (100 ml), and after stirring for 1 h at room temperature the organic phase was collected. It was washed with sodium hydrogen carbonate solution, dried over anhydrous sodium sulfate and solvent evaporated from the

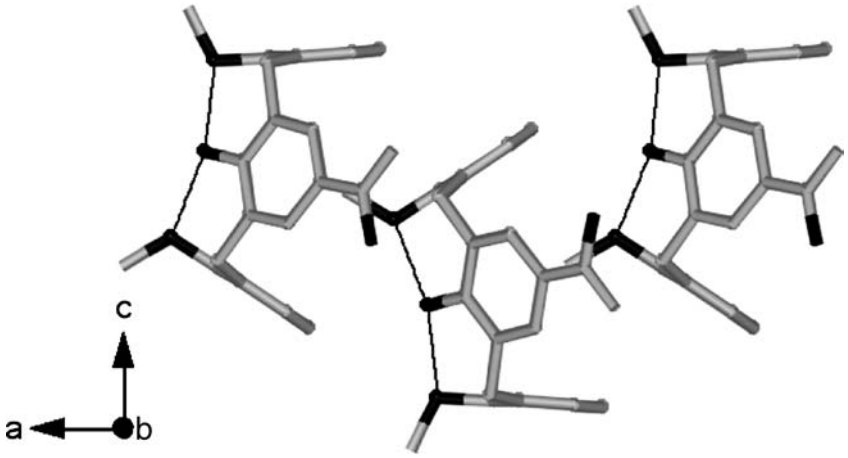



*Figure 2*. Only one of the two methoxy groups of the calixarene derivative **3** is positioned within the bowl of its neighbour. The second methoxy group is located along the outer edges of the calixarene chain.

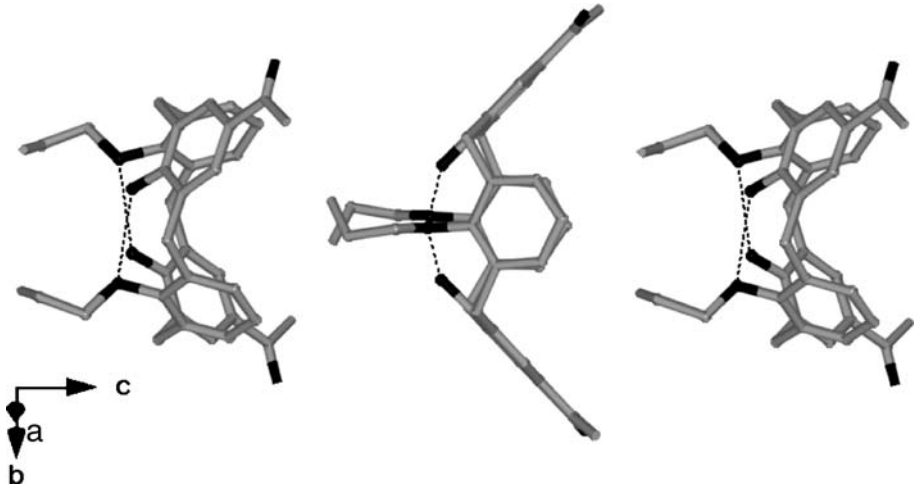



*Figure 3*. The straight-chain calixarene packing present in the crystal structure of the dipropoxy derivative **4**. Note that there is mutual rotation of the molecules along the assembly.

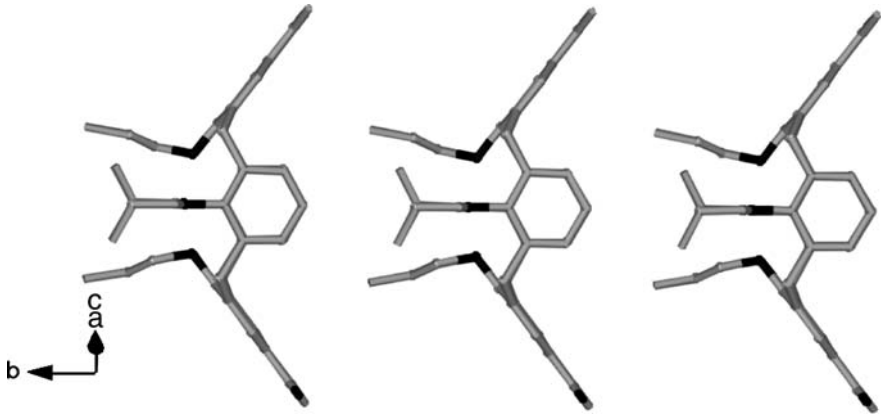



*Figure 4*. The straight-chain calixarene packing present in the crystal structure of the tetrapropoxy derivative **5**. Once again there is no insertion of a substituent into the calixarene bowl of its neighbour.

filtrate to yield 5,17-diacetyl-25,27-dimethoxy-26,28-dihydroxycalix[4]arene as a white powder. The crude product was recrystallised from chloroform/methanol to give **3** (0.50 g, 42%) as colourless needles, m.p. 277–279 °C (dec.) (lit. [20, 21] 65%, > 300 °C); MS $m/z$ ($M + Na^+$) 559; IR ($\nu_{max}$, paraffin mull) 3333 (s), 3233 (s), 2924 (s), 1666 (s), 1597 (s), 1465 (s), 1430 (s), 1360 (m), 1315 (m), 1281 (m), 1246 (w), 1191 (w), 1152 (w), 1095 (w), 1070 (w), 998 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 8.44 (s, 2, ArOH), 7.75 (s, 4, ArH), 6.90 (d, 4, ArH), 6.75 (t, 2, ArH), 4.29 and 3.49

*Table 1.* Numerical details of the solution and refinement of the crystal structures

| Compound | **3a** | **3b** | **3b** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Formula | $C_{34}H_{32}O_6$ | $C_{34}H_{32}O_6{\cdot}(C_2H_3N)$ | $(C_{34}H_{32}O_6)_2{\cdot}(C_3H_6O)$ | $C_{38}H_{40}O_6$ | $C_{44}H_{52}O_6$ | $(C_{29}H_{26}O_4){\cdot}(CHCl_3)$ |
| Formula mass | 536.6 | 577.7 | 1131.3 | 592.7 | 676.9 | 557.9 |
| Space group | Pnma | $P2_1/c$ | $Pna2_1$ | Pccn | C2/c | $P2_1/c$ |
| $a$/Å | 11.116(5) | 15.423(8) | 23.191(6) | 10.174(3) | 22.459(4) | 14.205(3) |
| $b$/Å | 15.666(7) | 17.490(4) | 11.462(4) | 17.855(5) | 9.755(1) | 11.302(1) |
| $c$/Å | 15.809(7) | 11.348(7) | 22.317(6) | 18.056(5) | 18.589(3) | 21.311(5) |
| $\beta$/° | 90 | 101.38(2) | 90 | 90 | 106.569(6) | 127.326(8) |
| $V$/Å$^3$ | 2753(2) | 3001(2) | 5932(3) | 3280(2) | 3903.5(9) | 2720.7(9) |
| $T$/K | 294(1) | 294(1) | 294(1) | 294(1) | 294(1) | 294(1) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_{calc.}$ /g cm$^{-3}$ | 1.29 | 1.28 | 1.27 | 1.20 | 1.15 | 1.36 |
| Radiation, $\lambda$/Å | $MoK_\alpha$, 0.7107 | $MoK_\alpha$, 0.7107 | $MoK_\alpha$, 0.7107 | $MoK_\alpha$, 0.7107 | $MoK_\alpha$, 0.7107 | $MoK_\alpha$, 0.7107 |
| $\mu$/mm$^{-1}$ | 0.086 | 0.085 | 0.085 | 0.079 | 0.074 | 0.373 |
| Scan mode | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ |
| $2\theta_{max.}$/° | 46 | 46 | 50 | 50 | 50 | 46 |
| No. of intensity meas. | 1996 | 4152 | 5361 | 2877 | 3432 | 3780 |
| Criterion for obs. ref. | $I/\sigma(I) > 2$ | $I/\sigma(I) > 2$ | $I/\sigma(I) > 2$ | $I/\sigma(I) > 2$ | $I/\sigma(I) > 2$ | $I/\sigma(I) > 2$ |
| No. of indep. obsd. ref. | 833 | 1948 | 2882 | 1078 | 2088 | 2663 |
| No. of reflections ($m$) | 833 | 1948 | 2882 | 1078 | 2088 | 2663 |
| Variables ($n$) in final ref. | 157 | 189 | 337 | 128 | 227 | 183 |
| $R = \Sigma^m\|\Delta F\|/\Sigma^m\|F_o\|$ | 0.072 | 0.061 | 0.057 | 0.058 | 0.048 | 0.079 |
| $R_w = [\Sigma^{m_w}\|\Delta F\|^2/\Sigma^{m_w}\|F_o\|^2]^{1/2}$ | 0.081 | 0.067 | 0.059 | 0.059 | 0.058 | 0.126 |
| $s = [\Sigma^{m_w}\|\Delta F\|^2/(m-n)]^{1/2}$ | 1.83 | 1.73 | 1.59 | 1.55 | 1.78 | 1.89 |
| Crystal decay | None | 8% | None | None | None | 16% |
| $R$ for mult. meas. | – | 0.031 | – | – | 0.009 | 0.045 |
| Largest peak in final diff. map/$e$ Å$^{-3}$ | 0.48 | 0.70 | 0.78 | 0.35 | 0.36 | 0.99 |
| CCDC Number | 283449 | 283450 | 283451 | 283452 | 283453 | 283454 |

(AB q, 8, $J$ 13.2 Hz, $ArCH_2Ar$), 4.01 (s, 6, $ArOCH_3$), 2.55 (s, 6, $ArCOCH_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 192.2, 158.3, 153.4, 132.4, 129.9, 129.7, 129.3, 128.2, 125.9, 64.1, 31.4, 26.5. Crystallisation from chloroform gave crystals **3a** of the apohost; crystals **3b** from acetonitrile, the inclusion compound (**3**)·(acetonitrile); and crystals **3c** from acetone, the inclusion compound $(\mathbf{3})_2$·(acetone).

*5,17-Diacetyl-25,27-dipropoxy-26, 28-dihydroxycalix[4]arene* **4**

A solution of acetyl chloride (11.12 g, 0.14 mol) and aluminium chloride (10.7 g, 80.3 mmol) in chloroform (100 ml) was added dropwise to an ice-cooled solution of 25,27-dipropoxy-26,28-dihydroxycalix[4]arene **2** (12.0 g, 23.6 mmol) in dichloromethane (100 ml). The mixture was allowed to warm to room temperature and stirred for further 24 h. The mixture was poured into cold water (150 ml) and stirred for 1 h. The organic phase was separated, washed with saturated sodium hydrogen carbonate solution and dried over sodium sulfate. The filtrate was concentrated and the product precipitated with methanol to give **4** (6.03 g, 43%) as a white solid m.p. 176–179 °C; HRMS $m/z$: Found ($M + Na^+$): 615.709514; Calcd for $C_{38}H_{40}O_6Na$: 615.7104; IR ($\nu_{max}$, paraffin mull) 3750 (s), 2924 (s), 2854 (s), 1674 (s), 1572 (s), 1463 (s), 1418 (s), 1357 (m), 1306 (m), 1184 (m), 1006 (w), 956 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$): $\delta$ 8.99 (s, 2, ArOH), 7.73 (s, 4, ArH), 6.95 (d, 4, $J$ 7.53 Hz, ArH), 6.75 (t, 2, $J$ 7.53 Hz, ArH), 4.29 and 3.44 (AB q, 8, $J$ 13.2 Hz, $ArCH_2Ar$), 4.00 (t, 6, $J$ 6.21 Hz, $ArOCH_2CH_2CH_3$), 2.53 (s, 6, $ArCOCH_3$), 2.07 (m, 4, $ArOCH_2CH_2CH_3$), 1.31 (m, 6, $J$ 7.53 Hz, $ArOCH_2CH_2CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta$ 196.8, 158.3, 151.7, 132.6, 129.5, 129.2, 128.8, 127.9, 125.5, 78.4, 31.3, 26.1, 23.4, 10.8. Crystallisation from acetonitrile gave crystals of solvent-free **4**.

*5,17-Diacetyl-25,26,27,28-tetrapropoxycalix[4]arene* **5**

Sodium hydride (0.51 g, 21.3 mmol; 60% dispersion in oil) was added to a solution of 5,17-diacetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene **4** (3.16 g, 5.3 mmol) in dry dimethylformamide (5 ml) followed by the addition of propyl iodide (2.08 g, 12.24 mmol). The mixture was stirred at room temperature for 5 days. The reaction mixture was diluted with methanol (50 ml) and evaporated to dryness. The residue was suspended in methanol (50 ml) containing water (2 ml) and potassium hydroxide (1 g), and refluxed for 2 h. After evaporation of methanol, the residue was extracted with chloroform (2 × 40 ml), washed with water (50 ml), dried over sodium sulfate and the filtrate evaporated to yield a pale yellow oil. Recrystallisation

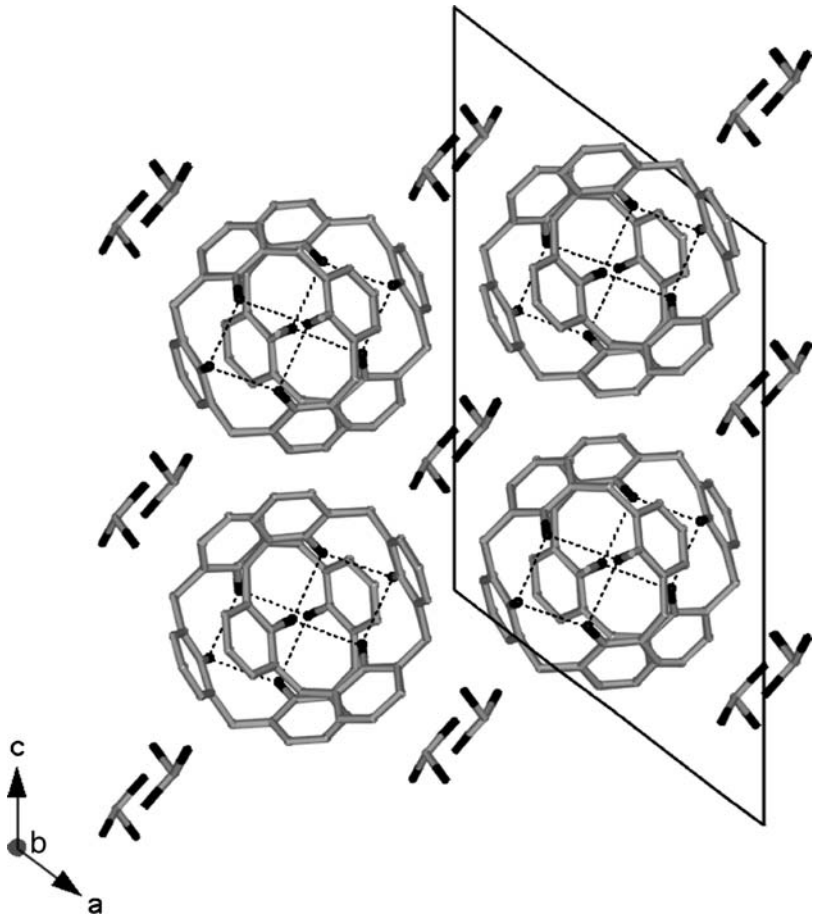



*Figure 5*. Crystal structure of (**6**)·(chloroform) projected onto the *ac* plane, and showing the chloroform guest molecules positioned between the zig-zag calixarene chains.

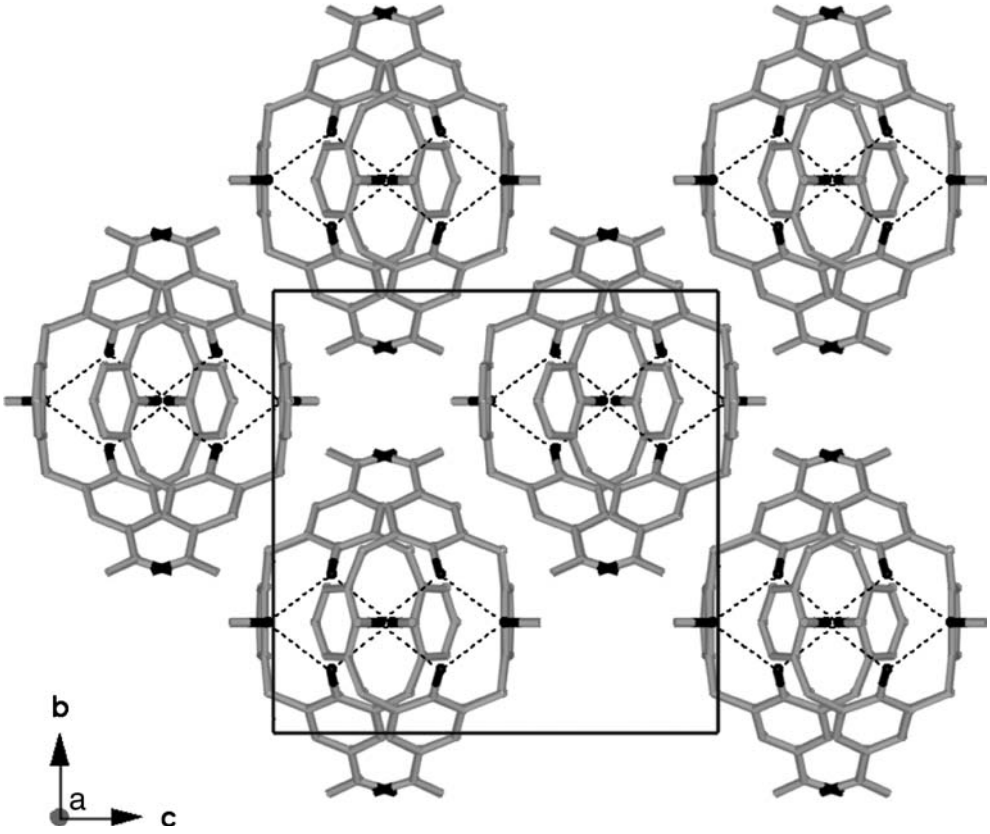



*Figure 6*. Crystal structure of the apohost structure **3a** viewed down *a* and showing projections of the zig-zag calixarene chains.

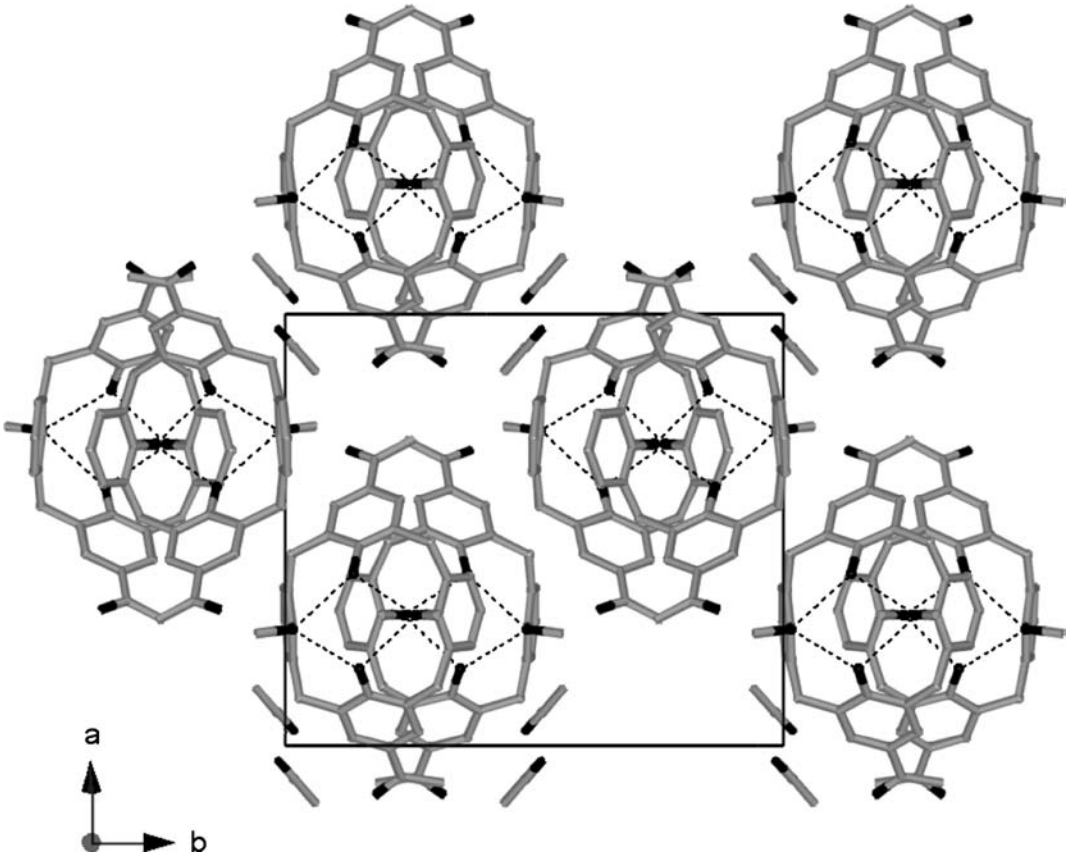



*Figure 7.* Crystal structure **3b**, namely (**3**)·(acetonitrile), projected onto the *ab* plane, and showing the acetonitrile guest molecules positioned between the zig-zag calixarene chains.

of the crude product from chloroform/methanol mixture gave 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene **5** (1.83 g, 51%) as a white solid m.p. 50–53 °C; HRMS: Found MS *m*/*e* ($M + Na^+$) 699.364754; Calcd for $C_{44}H_{52}O_6Na$: 699.3656; IR ($\nu_{max}$, paraffin mull) 3333 (s), 3233 (s), 2924 (s), 1666 (s), 1597 (s), 1465 (s), 1430 (s), 1360 (m), 1315 (m), 1281 (m), 1246 (w), 1191 (w), 1152 (w), 1095 (w), 1070 (w), 998 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 7.17 (s, 4, ArH), 6.68 (m, 6, ArH), 4.47 and 3.20 (AB q, 8, *J* 13.5 Hz, $ArCH_2Ar$), 3.89 (t, 8, $ArOCH_2CH_2CH_3$), 2.26 (s, 6, $ArCOCH_3$), 1.91 (m, 8, $ArOCH_2CH_2CH_3$), 1.01 (m, 12, $ArOCH_2CH_2CH_3$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 197.3, 160.8, 156.4, 135.1, 134.7, 131.1, 128.6, 128.5, 122.3, 76.7, 30.9, 26.0, 23.3, 23.1, 10.3, 10.1. Crystallisation from propionitrile gave crystals of solvent-free **5**.

*25-Methoxy-26,27,28-trihydroxycalix[4]arene* **6**

To a solution of 25,27-dimethoxy-26,28-dihydroxycalix[4]arene **1** (0.21 g, 0.46 mmol) in dichloromethane (50 ml) at −12 °C was added rapidly a solution of $SnCl_4$ (1.24 g, 4.76 mmol) and dichloromethyl methyl ether (0.14 g, 1.21 mmol). The solution was warmed to room temperature and stirred for 24 h. The reaction mixture was poured into ice-cold water (100 ml) and stirred for 1 h. The organic phase was separated and washed with a saturated aq. solution of $NaHCO_3$ (3 × 100 ml). The organic phase was separated, dried over magnesium sulfate and the filtrate taken to dryness under reduced pressure. The brownish solid was recrystallised from dichloromethane/methanol mixture to give 25-methoxy-26,27,28-trihydroxycalix[4]arene **6** as a white powder (0.09 g, 44%); $^1H$ NMR ($CDCl_3$): $\delta$ 9.68 (s, 1, Ar–O*H*), 9.33 (s, 2, Ar–O*H*), 7.11 (d, 2, *J* 7.53 Hz, Ar–*H*), 7.08 (d, 2, *J* 7.53 Hz, Ar–*H*), 7.03 (d, 2, *J* 7.53 Hz, Ar–*H*), 6.90 (t, 1, *J* 7.53 Hz, *p*-Ar–*H*), 6.70 (t, 2, *J* 7.53 Hz, *p*-Ar–*H*), 4.39 (d, 2, *J* 13.2 Hz, Ar–C$H_2$–Ar), 4.30 (d, 2, *J* 13.9 Hz, Ar–C$H_2$–Ar), 4.13 (s, 3, Ar–OC$H_3$), 3.50 (d, 2, *J* 13.4 Hz, Ar–C$H_2$–Ar), 3.49 (d, 2, *J* 13.9 Hz, Ar–C$H_2$–Ar); $^{13}C$ NMR ($CDCl_3$): $\delta$ 152.2, 150.3, 148.9, 133.7, 129.0, 128.4, 128.3, 128.2, 128.04, 128.0, 125.8, 121.5, 120.6, 63.0, 31.5, 30.9. Crystallisation from chloroform gave crystals of the inclusion compound (**6**)·(chloroform).

*Crystal structure determinations*

Data for all six structures were recorded using a Nonius CAD-4 diffractometer at ambient temperature (Table 1). These data were not corrected for absorption as the coefficients were small. The positions of all atoms were determined by direct phasing (SIR92) [22]. Hydrogen atoms on C were included in calculated positions, while those on the hydroxy groups were included in positions indicated by a difference electron density map. In some instances, the hydroxy hydrogen atoms were disordered and they were then included with half occupancy in each

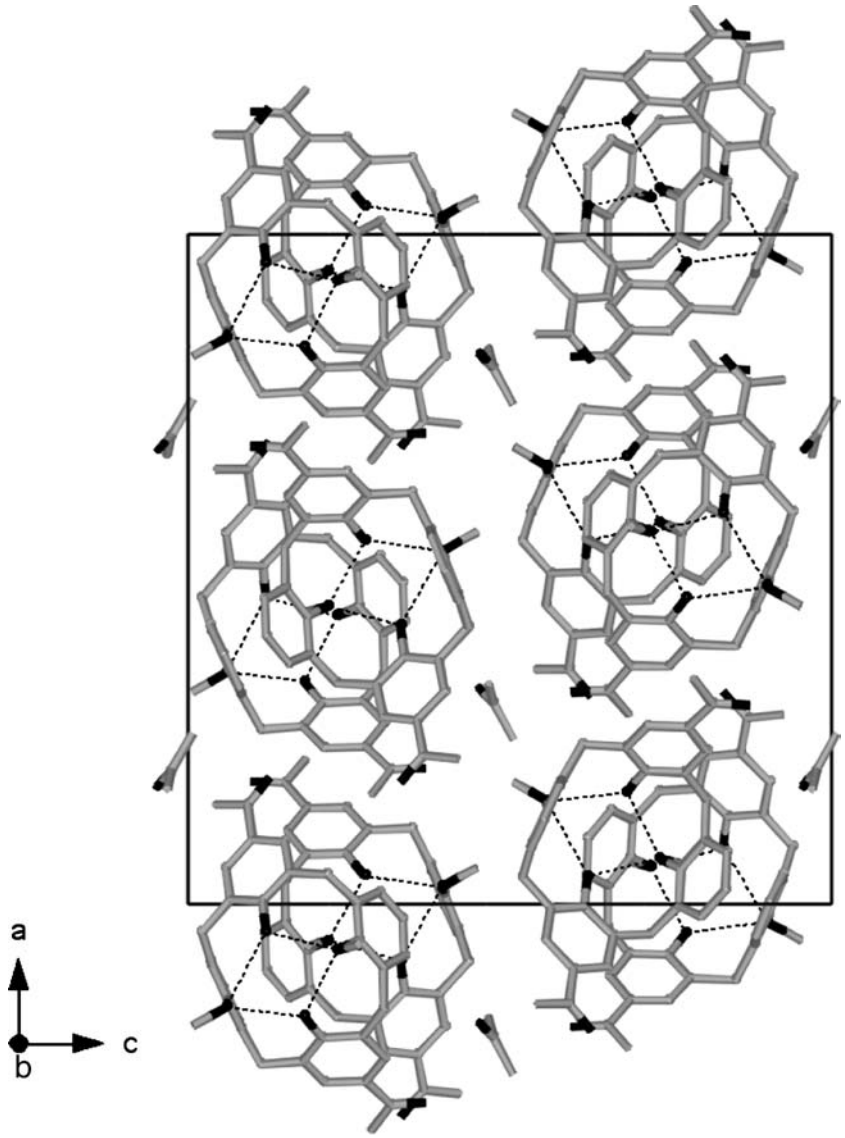



*Figure 8*. Crystal structure **3c**, namely $(\mathbf{3})_2$·(acetone), projected onto the *ac* plane. The larger guest has resulted in a change of the relative orientations of the zig-zag calixarene chains, but the chains themselves remain unchanged.

location. In **3a**, the asymmetric unit is half of one calixarene molecule. Mirror symmetry relates the two halves. The acetyl group was disordered, with two possible orientations related by two fold rotation about the $C_{aromatic}$–$C_{acetyl}$ bond. A composite scattering curve was used for the C and O atoms with appropriate allowance included in the occupancies of the hydrogen atoms on the methyl group. In the inclusion compounds, **3b** and **3c**, there are one and two calixarene molecules in the asymmetric unit, respectively. Both structures were refined with rigid groups defining the aromatic rings. In all three structures, **3a**–**c**, the thermal motion of the atoms of the girdle of the calixarene was described by a 15 parameter TLX group (where T is the translation tensor, L is the libration tensor and X is the origin of libration). The remainder of the calixarene atoms were refined anisotropically. The acetonitrile guest in **3b** was refined as individual anisotropic atoms, while the acetone molecule of **3c** was refined as a rigid body with a TLX thermal group [23]. Structure 4 was refined as individual atoms, with the thermal motion treatment as for **3**, while for **5**, full anisotropic refinement was carried out. The inclusion compound of **6** was refined in a similar way to **3**. The chloroform guest was disordered over two positions of occupancies 0.85/0.15. Full details of the refinement are available in the cif.

Crystallographic data (cif) have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 283449–283454). 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

The dialkoxy calix[4]arene derivatives **1,2** were prepared by the reaction of the parent calix[4]arene with one equivalent of base, and either methyl *p*-toluenesulfonate or propyl iodide. These reactions gave only di-*O*-alkylation

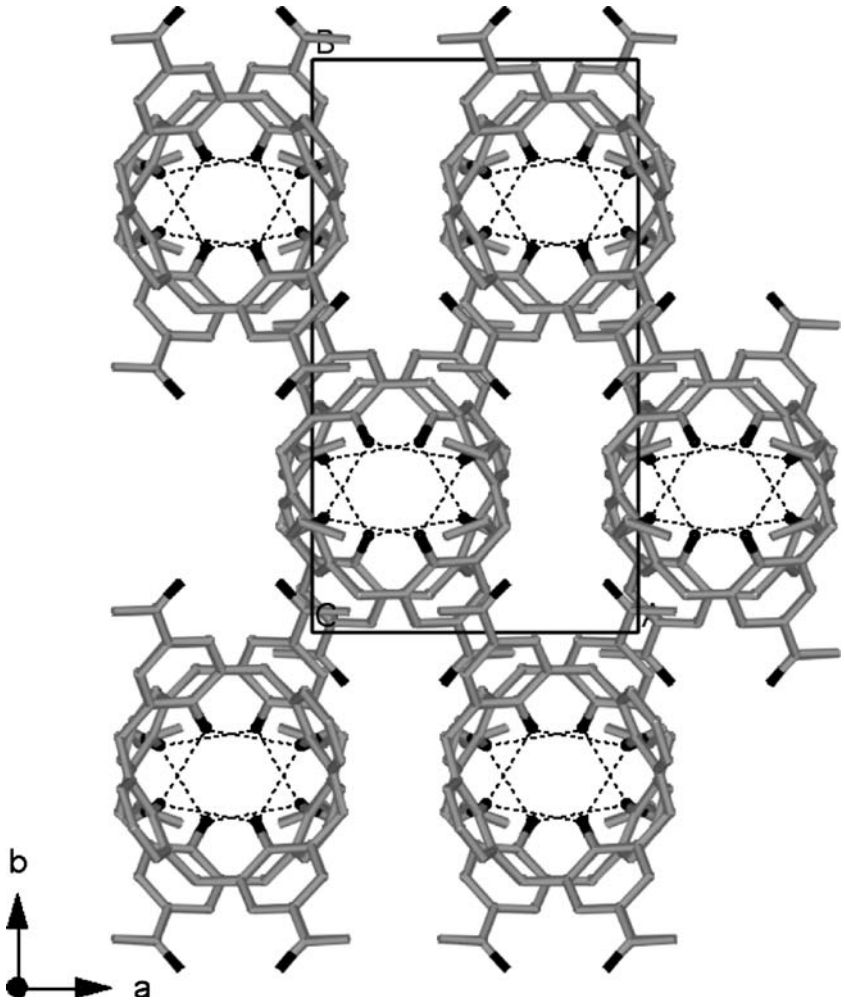



*Figure 9*. Crystal structure of the solvent-free dipropyl calixarene **4** crystal structure projected onto the *ab* plane.

products even when an excess of alkylating reagent was present. The synthesis of the diacetylated calix[4]arenes was accomplished as outlined in Scheme 1. The dimethoxy- and dipropoxy-compounds **1,2** were acetylated using $AlCl_3$ and acetyl chloride in dichloromethane to yield **3** and **4** in 43 and 42% yield, respectively. Although the calix[4]arenes **1,2** contain two alternative sites for electrophilic substitution reactions, only the products *para* to the phenolic–OH could be isolated in each case. This observation confirms the corrections made by Huang and Wang to the earlier literature [20, 21].

Compound **5** was prepared in 51% yield by further alkylation of **4**, using sodium hydride and propyl iodide in dry dimethylformamide. A much longer reaction time was required to form this tetra-alkylated product which is conformationally inflexible under the reaction conditions.

In some cases mono de-alkylation of the parent calixarenes was observed during the acetylation reaction. For example, 25-methoxy-26,27,28-trihydroxycalix[4]arene **6** was obtained during an attempted formylation of **1** with stannic chloride and dichloromethyl methyl ether. This compound has been synthesized on a number of prior occasions but using different reagents [24–26]. Crystal data for the inclusion compound (**6**)·(chloroform) have recently been published [27], but no description or illustrations of its structure have appeared previously in the literature.

*Description of the X-ray structures*

*Packing of the calixarene units*

The calix[4]arene derivatives pack together in their crystals in a reasonably predictable manner. In the solid state, as well as in solution, the individual calixarene molecules exist in the cone conformation. Where there are hydroxy groups located on the lower rim, these participate in hydrogen bonding (which may be disordered). The molecules then assemble into chains.

The presence of just one methoxy group on the lower rim (compound **6**) leads to an arrangement repeated along the chain where the methoxy group of one molecule is situated within the bowl of its neighbour (Figure 1).

Cecillon *et al*. have recently observed a similar phenomenon for a calix[4]arene functionalised with a pendant ethoxy acetate group at one of the phenolic sites, and which also forms one-dimensional head to tail chains [28]. They have commented that this motif is sufficiently robust to act as a general supramolecular

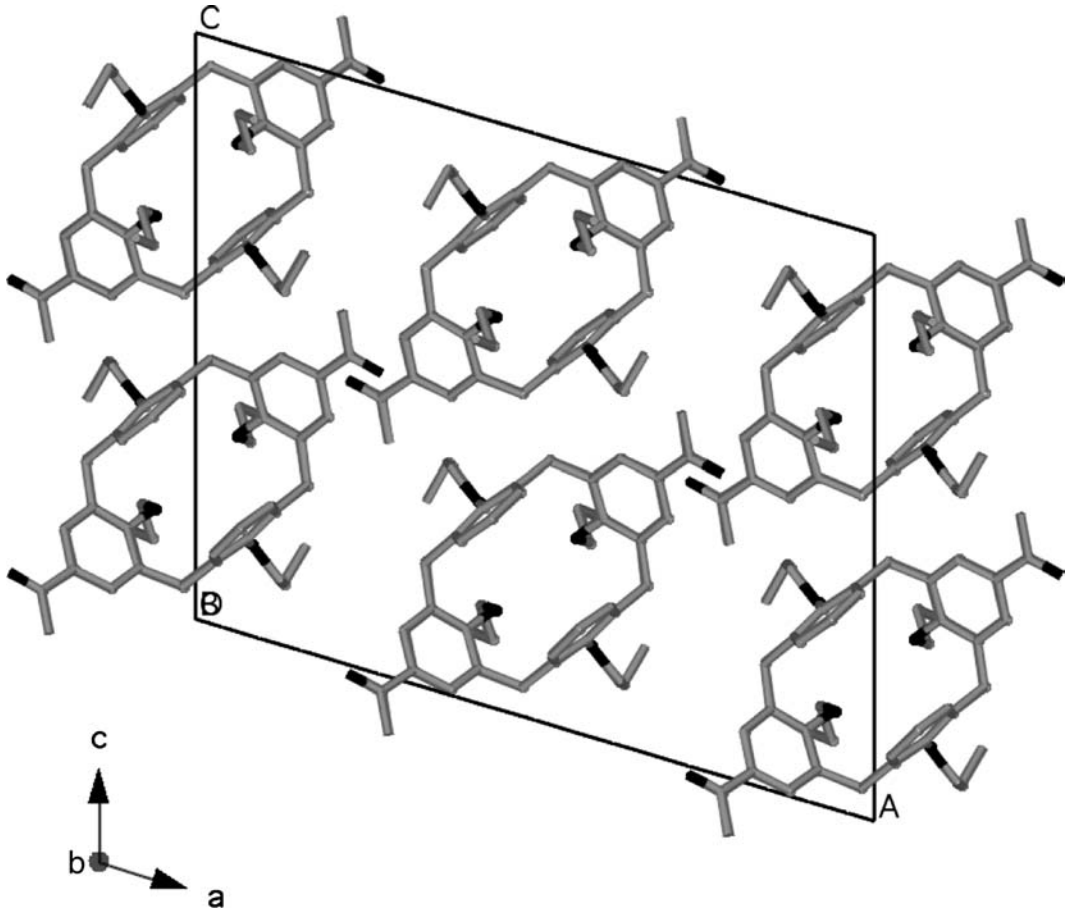



*Figure 10*. Crystal structure of the solvent-free tetrapropyl calixarene **5** crystal structure projected onto the *ac* plane. Note the quite different packing orientation of the parallel calixarene chains from the other cases.

synthon that can compete successfully with guest molecules seeking to position themselves within the calixarene bowl.

A similar outcome to that found for **6** is observed for compound **3** which has two methoxy groups. For both cases a zig-zag chain of calixarene molecules is produced. In the case of **3**, however, only one of the methoxy groups occupies the bowl site and the other is positioned on the edge of the chain (Figure 2). This arrangement is present in the structures of the apohost **3a** and also its two inclusion compounds **3b**,**3c**.

When the lower rim substituent is propoxy (compounds **4** and **5**), the group is no longer positioned within the bowl of its neighbour. The calixarene molecules simply align as a linear chain without a zig-zag being present (Figures 3 and 4). This observation reveals that there is a significant difference in supramolecular behaviour between the methyl groups of methoxy and propoxy groups. The electron-withdrawing nature of oxygen ensures that the hydrogen atoms of a methoxy group are more electron-deficient than those of a propoxy group. This provides an energetic incentive for the methyoxy group hydrogens of one molecule to interact with the electron-rich aryl rings of another. The packing observed in the crystal structures **3a**–**c** and **6** is therefore a direct result of weak O–C–H$\cdots\pi$ aryl attractions [29]. This is substantiated by the close approach of the O–*C*–H atoms (as short as 3.7 Å) to the aryl carbon atoms.

*Inter-chain and host-guest packing*

In all cases, the calixarene chains are packed within the cell in such a way as to optimize intermolecular contacts. The phenyl rings provide the possibility for offset face–face (OFF) interactions, which do occur in some of the structures. Where there is inclusion of a guest species, then these molecules are located between the calixarene chains to produce lattice inclusion compounds. In none of the present cases is there encapsulation of the guest with the bowl-like receptor of the calixarene to yield an inclusion complex, though this can occur in other circumstances.

The Figures 5–10 show molecular packing diagrams for the six crystal structures, viewed down the direction of the calixarene chain axis in each case. In all of these, the hydroxy group hydrogen bonding is represented by the dashed lines, and all hydrogen atoms have been omitted for clarity.

The tendency of the calixarene chains to pack in a columnar arrangement is a common feature amongst this group of calix[4]arenes. These columns are pushed apart when guest inclusion takes place, but the net crystal

density is hardly affected (1.27–1.29 g $cm^{-3}$) across the three structures involving compound **3**. Compared with **3a**–**c**, the densities of **4**,**5** are lower (1.20, 1.15 g $cm^{-3}$) due, in part, to the efficient intramolecular methoxy packing that occurs in structures **3a**–**c**. The compound **6** has a significantly increased density (1.36 g $cm^{-3}$) due to inclusion of chloroform. It is noteworthy that all three inclusion compounds reported here preferred to position their guest molecules between the calixarene chains, rather than within the calixarene bowls.

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