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5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene dichloromethane disolvate

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Key indicators

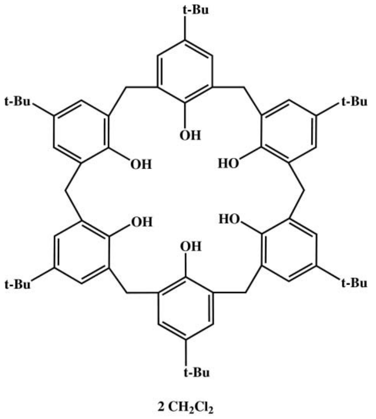
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.133
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Crystallization of the title compound, $C_{66}H_{84}O_6 \cdot 2CH_2Cl_2$, from a methanol–dichloromethane solution yields a 1:2 inclusion compound with dichloromethane. The host–guest compound crystallizes with one host and two guest molecules in the asymmetric unit. The molecular geometry is stabilized by intramolecular O—H⋯O hydrogen bonds, whereas the packing structure is dominated by van der Waals forces.

Comment

In contrast with the calix[4]arenes, which form a variety of well characterized host–guest and solvent-free structures, only a few structure analyses of inclusion compounds of calix[6]arenes are reported in the literature (Mandolini *et al.*, 2000). Apart from a poor characterization of the title compound, (I), in its solvent-free form (Andreetti *et al.*, 1987), inclusion compounds with benzene (Halit *et al.*, 1988), tetrachloroethylene (Andreetti *et al.*, 1989), carbon disulfide (Schatz *et al.*, 2000), dimethyl sulfoxide (DMSO; Wolfgong *et al.*, 1996), acetonitrile (Dale *et al.*, 2003; Thuery *et al.*, 1995) and toluene (Lu *et al.*, 1999) are known. With the exception of the DMSO clathrate, in which the calix[6]arene adopts a double partial cone conformation, in all other structures the calixarene is found in a pinched cone conformation, in which two of the methylene groups point to the centre of the bowl. This means that two aromatic units are in an out orientation and four are in an up orientation with respect to the mean plane of the six methylene C atoms of the macrocycle. As a result of the molecular conformation, a closed cyclic system of hydrogen bonds is formed between the phenol hydroxy groups at the lower rim of the calix framework, characterized by rather ideal bonding dimensions.



(I)

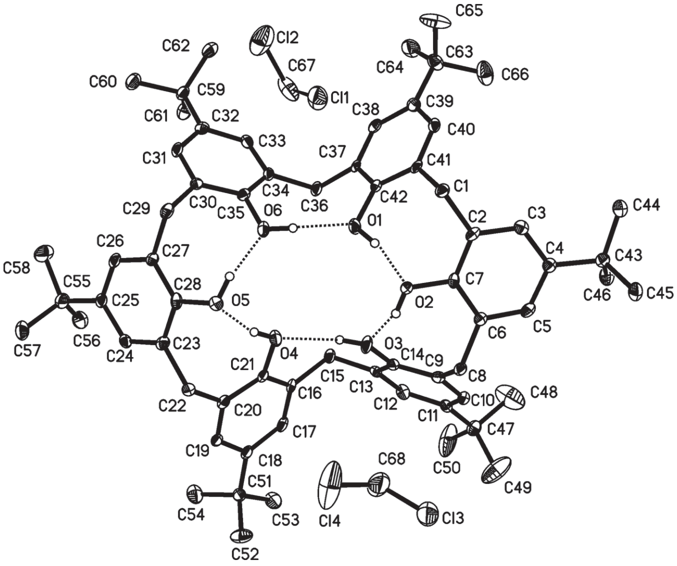


Figure 1
Perspective view of (I), showing 50% probability displacement ellipsoids for the non-H atoms. With the exception of hydrogen-bonding atoms H1–H6, all H atoms and minor disorder groups have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

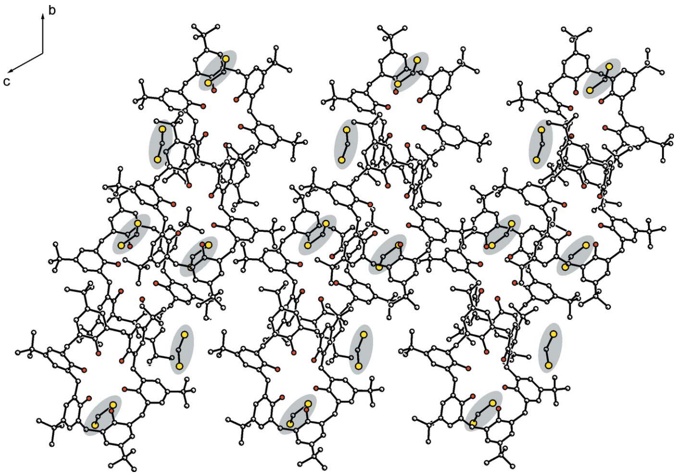


Figure 2
Packing diagram of (I), viewed along the crystallographic *a* axis. All H atoms and minor disorder groups have been omitted for clarity. Guest molecules are indicated by a shaded background.

A similar situation with pinched cone conformation (Fig. 1) and cyclic hydrogen bonding (Table 1) is found in the molecular structure of the present 1:2 inclusion compound of the calix[6]arene (I). The disordered solvent molecule is located in an interstitial cavity between two calixarene molecules. The positions of their Cl atoms and the resulting positions of the H atoms suggest weak C—H$\cdots\pi$ interactions (Nishio, 2004). However, due to the disorder, they are not structurally significant. On the other hand, the second ordered dichloromethane molecule is found on a non-centrosymmetric site in the bowl of the calixarene cavity, engaged in weak C—H$\cdots\pi$ contacts (Desiraju *et al.*, 1999) to the calixarene (Table 1). Thus, the mode of supramolecular host–guest relationship is both clathrate and cavitate type (Weber, 2004) for the two molecules of dichloromethane. The crystal packing (Fig. 2) is mainly stabilized by van der Waals forces. Hence, except for a potential π–π stacking, all possible interactions corresponding to the functional sites of the molecule of (I) are effective in the crystal structure.

Experimental

The calix[6]arene (I) was synthesized according to the procedure described by Percec *et al.* (2001) from formaldehyde, *p-tert*-butylphenol and potassium hydroxide. Recrystallization from methanol–dichloromethane (1:1) yielded the inclusion compound as colourless crystals.

Crystal data

$C_{66}H_{84}O_6\cdot 2CH_2Cl_2$
M_r = 1143.18
Triclinic, $P\bar{1}$
a = 12.2406 (10) Å
b = 17.2407 (6) Å
c = 17.4069 (6) Å
α = 118.615 (2)°
β = 92.644 (2)°
γ = 97.961 (2)°
V = 3166.9 (3) Å^3

Z = 2
D_x = 1.199 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9049 reflections
θ = 2.3–25.8°
μ = 0.24 mm^{-1}
T = 93 (2) K
Needle, colourless
0.39 × 0.11 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
35059 measured reflections
12156 independent reflections

6703 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.064
$\theta_{\rm max}$ = 25.8°
$h = -14 \rightarrow 14$
$k = -21 \rightarrow 21$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.133
S = 0.96
12156 reflections
731 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.013
$\Delta\rho_{\rm max}$ = 1.14 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.72 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0035 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6O$\cdots$O1	0.84	1.76	2.585 (2)	167
O5—H5O$\cdots$O6	0.84	1.87	2.638 (3)	151
O4—H4O$\cdots$O5	0.84	1.86	2.681 (2)	164
O3—H3O$\cdots$O4	0.84	1.85	2.666 (2)	163
O2—H2O$\cdots$O3	0.84	1.81	2.621 (3)	161
O1—H1O$\cdots$O2	0.84	1.74	2.561 (3)	167
C67—H67$B\cdots$C26$^{\rm i}$	0.99	2.62	3.606 (4)	179
C29—H29$A\cdots$C42$^{\rm ii}$	0.99	2.73	3.664 (3)	158

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

The H atoms were positioned geometrically and allowed to ride on their parent atoms, with O—H = 0.84 Å, C—H = 0.95–0.99 Å and $U_{\rm iso}$(H) = 1.2–1.5$U_{\rm eq}$(parent atom). One of the two dichloromethane guest molecules is disordered over two positions with occupancy factors of 0.7 (7) and 0.3 (7). In addition, one of the six *tert*-butyl groups of the calixarene reveals a twofold positional disorder with site occupancy factors 0.811 (3) and 0.189 (3). The highest density peak is located at atom Cl1.

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Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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