The host–guest complex between cone-25,26:27,28-bis(methylene-dioxy)calix[4]arene and dichloro-methane

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The title compound, 25,26:27,28-bis(methylenedioxy)penta-cyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25)3,5,7(28),9,11,13(27),-15,17,19(26),21,23-dodecaene dichloromethane solvate, C$_{30}$-H$_{24}$O$_4$·CH$_2$Cl$_2$, possesses crystallographic twofold symmetry in both components. The calixarene shows a pinched cone conformation with an elliptical cavity, in which the guest dichloromethane solvent molecule is accommodated. The contact distance between guest and host (H···ring centroid = 2.44 Å) is extremely short.

Comment

An important property of calix[4]arenes is that they possess cavities that can accommodate neutral guest molecules (see, for example, Vicens & Böhmer, 1991; Mandolini & Ungaro, 2000). This behaviour requires the calixarene to be maintained in the cone conformation, although some inclusion complexes have been reported with partial cone conformers (Arduini *et al.*, 2001). The most frequently employed method for locking the cone conformation is to tether large substituents to the narrow rim, thus hindering the transannular rotation of the individual phenol rings. Another method, employed in the present study, consists in linking two pairs of proximal O atoms with short bridging units. The latter method offers the advantage of making the whole calixarene molecule more rigid, a property that is expected to enhance the efficiency of guest complexation. We describe here the synthesis (see *Experimental* and *Scheme*) and structure of the title compound, (I), a calix[4]arene locked in the cone conformation, which crystallizes with a well ordered guest molecule of dichloromethane.

The structure of the closely related 5,11,17,23-tetra-*tert*-butyl-substituted analogue, which crystallized without any guest molecule, has been published by Neri *et al.* (1992), but

no coordinates were deposited; we redetermined the structure and deposited it in the Cambridge Structural Database (Allen, 2002) under refcode YAHVOS01. It consists of two independent molecules of similar conformation (the r.m.s. deviation of all atoms except the *tert*-butyl groups is 0.20 Å). The additional bridging reduces the approximate *mm*2 symmetry of a standard calixarene (having a cone conformation) to approximate twofold symmetry (having a distorted or 'pinched' cone conformation and an elliptical cavity).
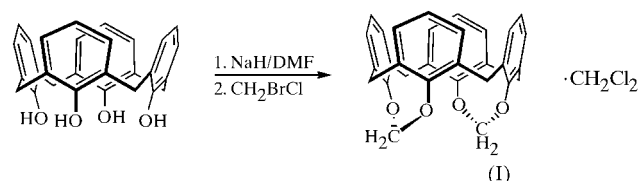
The title calixarene, lacking *tert*-butyl substituents, displays exact twofold symmetry [symmetry code: (i) $-x, y, -z + \frac{1}{2}$], but the conformation is similar to that reported by Neri *et al.* (1992), with an r.m.s. deviation of 0.24 Å from molecule 1 of that structure. The methylene bridges cause the O···O distances across the cavity to differ appreciably; O1···O1^i = 2.854 (2) Å and O2···O2^i = 4.590 (2) Å. The interplanar angles to the calixarene reference plane composed of atoms C17, C27 and their symmetry equivalents (exactly planar by symmetry) are 148.16 (3) and 109.44 (4)° for rings C11–C16 and C21–C26, respectively. The centroids of the symmetry-equivalent rings lie 7.54 Å apart for ring C11–C16 and 6.03 Å apart for ring C21–C26. The latter ring is not eclipsed with its symmetry-generated counterpart (as shown, for example, by the torsion angle C24—*Cg*1···*Cg*1^i—C24^i of 19°, where *Cg*1 is the centroid of ring C21–C26).

The title calixarene crystallizes with a guest molecule of dichloromethane, which also shows exact twofold symmetry. Host–guest geometry involving calixarenes as hosts has been
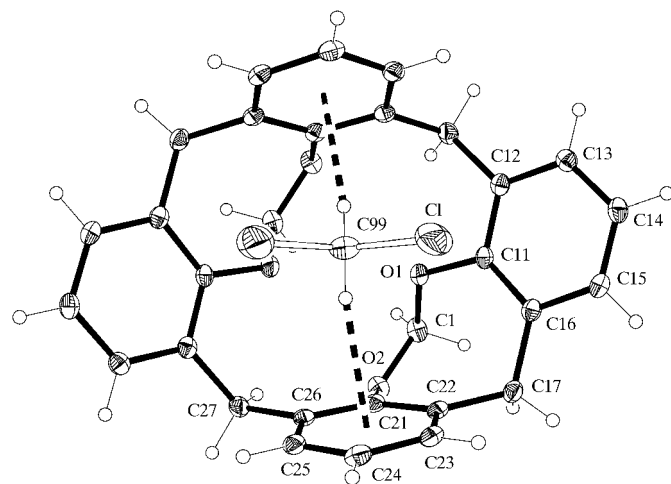

Figure 1
The formula unit of the title compound in the crystal. Ellipsoids represent 30% probability levels and H-atom radii are arbitrary. Only the asymmetric unit is numbered. The C—H···π interactions are indicated by dashed bonds.
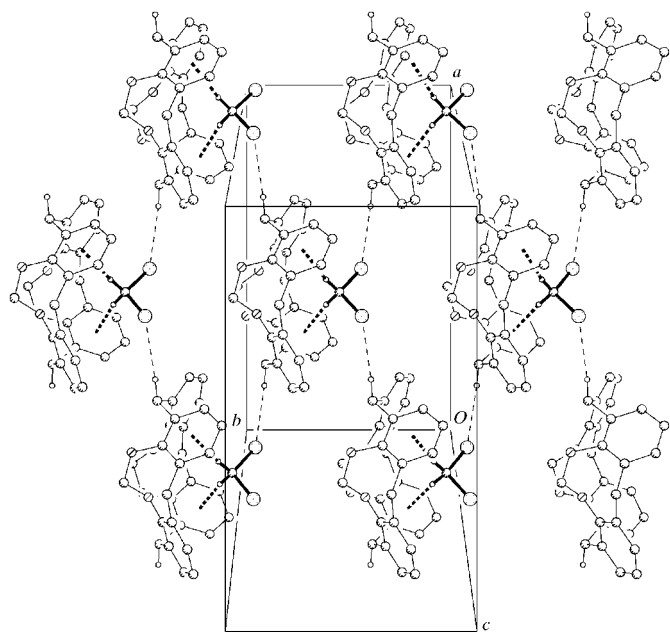
organic compounds

Figure 2
Packing diagram of the title compound, viewed perpendicular to the *ab* plane. Hydrogen bonds are indicated by dashed lines and H atoms not involved in hydrogen bonding have been omitted.

discussed extensively by Arduini *et al.* (2001), and the same nomenclature for angles and distances is used here. The dichloromethane molecule forms extremely short C99—H99···π contacts to ring C21–C26 (Fig. 1), with an H···π distance of 2.44 Å. If the C99—H99 bond length is normalized to 1.08 Å, then the 'true' value for the contact is even shorter, at 2.35 Å. The favourable directionality of the interaction is shown by the angles α (8.5°; between the vector C99—*Cg*1 and the normal to the ring plane) and σ (166°; between the vectors C99—H99 and H99—*Cg*1). A search of the Cambridge Structural Database (CSD; Allen, 2002; version of 2003) for short contacts from dichloromethane hydrogen to a calixarene ring centroid revealed 43 hits for a contact distance less than 3.1 Å; the five shortest (2.42–2.46 Å) were seen for the CSD refcodes KOCQEY (Parlevliet *et al.*, 2000), NOVNOB (Giannini *et al.*, 1997), PAYHOM (Giusti *et al.*, 1997), TARXOZ (Beer, Drew, Grieve *et al.*, 1996) and ZUVNAF (Beer, Drew, Kan *et al.*, 1996). It is noteworthy that all these structures are calixarenes modified either by internal bridging or, equivalently, by metal complex formation.

The distance from C99 to the ring centroids is 4.373 Å to C11–C16 (*Cg*2) and 3.411 Å to C21–C26 (*Cg*1), leading to a Σ_4 value (sum of the C···π distances) of 15.568 Å; the distance of C99 to the reference plane (see above) is 2.909 (3) Å. There is no tilting of the guest molecule relative to the reference plane, with the interplanar angles γ (between the CCl$_2$ plane and the reference plane) and η (between CH$_2$ and the reference plane) both being 90° by symmetry.

The crystal packing is further characterized by a C—H···Cl hydrogen bond (Table 2). The overall effect is to form layers of calixarene and solvent molecules parallel to the *ab* plane (Fig. 2). Within the layers, only translation symmetry is involved. There are two such layers per cell at $c \simeq 0.25, 0.75$.

Experimental

To a suspension of NaH (0.565 g, 11.78 mmol) in dimethylformamide (30 ml), cooled to 273 K, was added calix[4]arene (1.000 g, 2.36 mmol) in small portions. After stirring for 2 h, CH$_2$BrCl (6.097 g, 47.12 mmol) was added dropwise over a period of 15 min. After 3 h, cooling was stopped and the solution was stirred for a further 12 h at room temperature. Excess NaH was decomposed with MeOH (10 ml) and the solvent was removed *in vacuo*. The residue was taken up in CH$_2$Cl$_2$ (100 ml), and washed successively with 1 *M* HCl (50 ml) and water (2 × 50 ml). The organic layer was dried with MgSO$_4$ and filtered. Evaporation of the solvent afforded a solid that was purified by flash chromatography using CH$_2$Cl$_2$/hexane (1:1 *v/v*) as eluant. After evaporation of the solvent and recrystallization from CH$_2$Cl$_2$– MeOH (1:5 *v/v*), colourless crystals were obtained (SiO$_2$, R_F = 0.54, CH$_2$Cl$_2$/hexane, 1:1 *v/v*). Yield: 0.600 g (57%); m.p. > 523 K; FAB mass spectrum: *m/z* 448 (M^+, 100%). Analysis found: C 70.02, H 5.09%; calculated for C$_{30}$H$_{24}$O$_4$·CH$_2$Cl$_2$ (448.52 + 84.93): C 69.80, H 4.91%.

Crystal data

C$_{30}$H$_{24}$O$_4$·CH$_2$Cl$_2$	Mo $K\alpha$ radiation
M_r = 533.42	Cell parameters from 64
Monoclinic, $C2/c$	reflections
a = 16.042 (2) Å	θ = 8–27°
b = 9.4781 (10) Å	μ = 0.30 mm^{-1}
c = 17.599 (2) Å	T = 173 (2) K
β = 111.490 (10)°	Block, colourless
V = 2489.9 (5) Å^3	0.7 × 0.6 × 0.5 mm
Z = 4	
D_x = 1.423 Mg m^{-3}	

Data collection

Siemens *P*4 diffractometer	h = −18 → 7
ω scans	k = 0 → 11
3350 measured reflections	l = −20 → 19
2173 independent reflections	3 standard reflections
1894 reflections with $I > 2\sigma(I)$	every 247 reflections
R_{int} = 0.014	intensity decay: none
θ_{max} = 25.0°	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$+ 1.8139P]$
$wR(F^2)$ = 0.093	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
2173 reflections	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
168 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

C11—O1—C1—O2	111.24 (14)	C1—O2—C21—C26	132.11 (14)
C21—O2—C1—O1	−29.61 (18)	O2—C21—C26—C27	−7.00 (19)
C1—O1—C11—C12	136.93 (13)	C21—C26—C27—C12^i	−115.70 (15)
C16—C11—C12—C27^i	−178.65 (13)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C27—H27A···Cl^i	0.99	2.83	3.8128 (17)	170

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} + y, z$.

H atoms were included using a riding model with fixed C—H bond lengths of 0.95 (Csp^2) or 0.99 Å (methylene). U_{iso}(H) values were fixed at $1.2U_{eq}$ of the parent atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1530). Services for accessing these data are described at the back of the journal.

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