

## A 1:1:1 chloroform/tetrahydrofuran solvate of *p*-*tert*-butyltetrahomodioxacalix[4]arene

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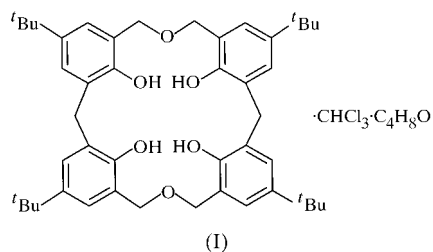
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The title compound, 7,13,21,27-tetra-*tert*-butyl-3,17-dioxapentacyclo[23.3.1.1<sup>5,9</sup>.1<sup>11,15</sup>.1<sup>9,23</sup>]ditriaconta-1(29),5,7,9(30),-11(31),12,14,19(32),20,22,25,27-dodecaene-29,30,31,32-tetraol, crystallizes as a solvate with one molecule of chloroform and one molecule of tetrahydrofuran, C<sub>46</sub>H<sub>60</sub>O<sub>6</sub>·CHCl<sub>3</sub>·C<sub>4</sub>H<sub>8</sub>O. The calixarene assumes a cone-like conformation stabilized by intramolecular hydrogen bonds involving both phenolic and ether O atoms. The two solvent molecules are located in each of the two half-cone cavities of the calixarene.

### Comment

We have recently reported the first crystal structures of *p*-*tert*-butyltetrahomodioxacalix[4]arene and its uranyl ion complex (Thuéry *et al.*, 2001). Two forms presenting slightly different conformations have been found for the uncomplexed ligand, associated with some differences in the ether bridge conformations and intramolecular hydrogen-bond pattern. In each case, two solvent molecules (acetonitrile or pyridine) are included in the calixarene cavity.



The main features of these structures are present in the case of the new solvate, (I), but the conformation is slightly different from the previous ones. The asymmetric unit in (I) is

composed of one calixarene and two different solvent molecules. The calixarene symmetry was higher in one of the cases reported previously, (II), in which the molecule was located around a binary axis. If the plane defined by the four phenolic O atoms is taken as a reference [greatest deviation from mean plane 0.459 (4) Å], the dihedral angles made with it by the four phenyl rings are 132.4 (1), 125.7 (1), 148.2 (2) and 156.2 (1)° in (I), *i.e.* they span a wider range than those in the more symmetrical and regular form, (II), described previously [132.8 (2)–141.2 (2)°]. However, this range was even larger in the second form described previously, (III) [109.4 (1)–157.3 (2)°]. The intramolecular hydrogen-bond pattern is different in the two previous forms; in (II), two phenolic units give bifurcated hydrogen bonds with the other phenolic units and the ether groups, whereas in (III), one of those bifurcated

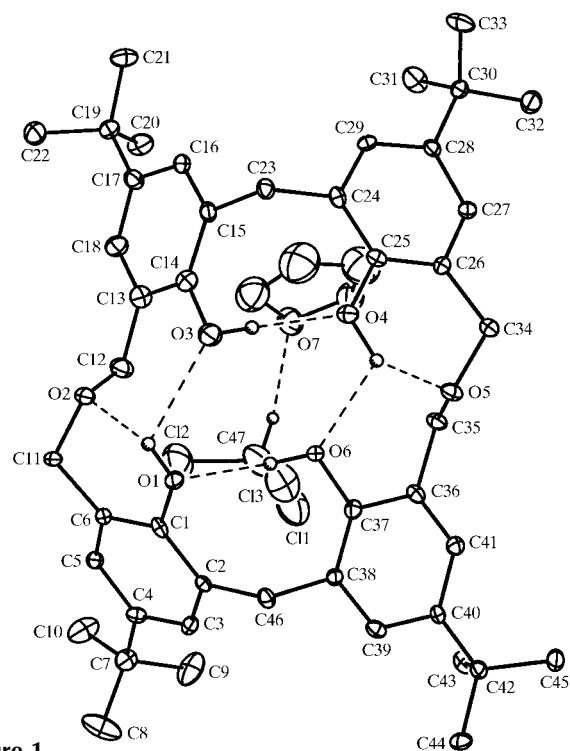


Figure 1

The title molecule with the atomic numbering scheme. H atoms have been omitted for clarity, except for those involved in hydrogen bonds, which are drawn as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

bonds is replaced by a simple one (with the ether group). In (I), both hydrogen bonds are bifurcated, the phenol–phenol ones being seemingly somewhat less strong than in (II). The conformation around the ether bridges is identical to that in (II), the slight geometrical differences between those two compounds being possibly connected with the difference in the solvents included. In contrast with the parent calixarenes, in which the hydrogen-bond pattern is rather well defined and contributes to the rigidity of the molecule, the presence of the ether groups in oxacalixarenes makes this pattern more variable and the molecule more flexible.

The inclusion of two chemically different solvent molecules in a calixarene cavity is a somewhat uncommon feature, at least for small calixarenes [in both compounds (II) and (III), two identical molecules were included, acetonitrile in (II), pyridine in (III)]. It has been suggested that the ability of calixarenes to hold two different species relatively close one to the other was indicative of their potential as 'enzyme mimics' (Asfari *et al.*, 1991). The location of the chloroform H atom is indicative of a possible hydrogen bond with the O atom of tetrahydrofuran. Feeble interactions are thus present between the three species in this complex.

## Experimental

*p*-*tert*-Butyltetrahomodioxacalix[4]arene was synthesized as reported previously (Dhawan & Gutsche, 1983) and recrystallized from chloroform/tetrahydrofuran (1:1).

### Crystal data

$C_{46}H_{60}O_6 \cdot CHCl_3 \cdot C_4H_8O$	Mo $K\alpha$ radiation
$M_r = 900.41$	Cell parameters from 35687 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 2.69\text{--}25.68^\circ$
$a = 9.2248$ (5) Å	$\mu = 0.235$ mm $^{-1}$
$b = 17.6451$ (15) Å	$T = 100$ (2) K
$c = 30.282$ (3) Å	Parallelepiped, colourless
$V = 4929.1$ (7) Å $^3$	$0.28 \times 0.28 \times 0.25$ mm
$Z = 4$	
$D_x = 1.213$ Mg m $^{-3}$	

### Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.084$
$\varphi$ scans	$\theta_{\text{max}} = 25.68^\circ$
35687 measured reflections	$h = 0 \rightarrow 10$
9064 independent reflections	$k = -21 \rightarrow 21$
5464 reflections with $I > 2\sigma(I)$	$l = -36 \rightarrow 36$

**Table 1**  
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 $\cdots$ O2	0.84	2.00	2.699 (8)	140
O1—H1 $\cdots$ O3	0.84	2.41	2.870 (8)	116
O3—H3 $\cdots$ O4	0.94	1.83	2.712 (8)	154
O4—H4 $\cdots$ O5	1.05	1.75	2.662 (8)	143
O4—H4 $\cdots$ O6	1.05	2.32	2.939 (8)	117
O6—H6 $\cdots$ O1	0.93	1.91	2.833 (8)	177
C47—H47 $\cdots$ O7	0.98	2.15	3.113 (10)	168

### Refinement

Refinement on $F^2$	H atoms constrained
$R[F^2 > 2\sigma(F^2)] = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.1216P)^2]$
$wR(F^2) = 0.213$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.960$	$(\Delta/\sigma)_{\text{max}} = 0.001$
9064 reflections	$\Delta\rho_{\text{max}} = 0.71$ e Å $^{-3}$
562 parameters	$\Delta\rho_{\text{min}} = -0.39$ e Å $^{-3}$

4517 Friedel pairs have been measured. The structure was refined as a racemic twin with a Flack (1983) parameter of 0.37 (13). Hydroxyl and chloroform H atoms were found on the Fourier difference map and introduced as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. All other H atoms were introduced at calculated positions as riding atoms with a displacement parameter equal to 1.2 (CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. The tetrahydrofuran molecule behaves badly on refinement and some restraints had to be applied to the displacement parameters. One of the C—C distances in this molecule is shorter than usual [1.425 (14) Å].

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL* and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1482). Services for accessing these data are described at the back of the journal.

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