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p-Methyltetrahomodioxacalix[4]arene

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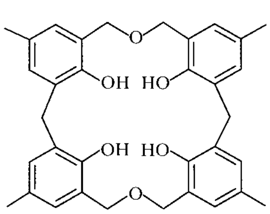
The title compound, 7,13,21,27-tetramethyl-3,17-dioxapentacyclo[23.3.1.1^{5,9}.1^{11,15}.1^{9,23}]ditriaconta-1(29),5,7,9(30),11(31),12,14,19(32),20,22,25,27-dodecaene-29,30,31,32-tetraol, $C_{34}H_{36}O_6$, assumes in the solid state a very distorted cone-like conformation stabilized by intramolecular simple and bifurcated hydrogen bonds involving both phenolic and ether O atoms. One part of the molecule, comprising an ether link, is included in the cavity of an adjacent calixarene related by a screw axis, giving rise to a one-dimensional self-inclusion polymer.

Comment

We have recently reported the first crystal structures of *p-tert*-butyltetrahomodioxacalix[4]arene and its uranyl ion complex (Thuéry, Nierlich, Vicens, Masci & Takemura, 2001; Thuéry, Nierlich, Vicens & Masci, 2001). Three forms of the uncomplexed ligand have been described, all of them with included solvent molecules (acetonitrile, pyridine and chloroform/tetrahydrofuran) and presenting slightly different conformations and intramolecular hydrogen-bonding patterns. We report herein a closely related new compound, (I), with a methyl substituent in the *para* position, which crystallizes without any included solvent molecule.



(I)

The asymmetric unit in (I) (Fig. 1) is composed of one calixarene molecule. The conformation of the macrocycle is that of a very distorted cone. It can be characterized by the dihedral angles between the planes of the four phenolic rings and the reference plane defined by the four phenolic O atoms [greatest deviation from mean plane 0.026 (3) Å], which are 158.3 (1), 169.6 (1), 109.8 (1) and 118.6 (1)°. These dihedral angles span a wider range than that observed in the three previous compounds, the presence of the ether links allowing for some flexibility while not disrupting the hydrogen-bonding pattern. In terms of conformation, two kinds of ether links can be distinguished in this family of compounds, which can be characterized by their torsion angles. In the present case, both torsion angles for each bridge correspond to *anti* geometries: C3—C8—O2—C9 177.0 (3), C8—O2—C9—C10 −162.9 (3), C20—C25—O5—C26 179.4 (3) and C25—O5—C26—C27 165.9 (3)°. In the previous cases, both ether bridges or at least one of them had one *anti* and one approximately *gauche* (values in the range 58.4–86.0°) angle. The first case (two *anti* angles) gives rise to a quasi-planar '*w*' shape for the three bridge atoms and the two aromatic C atoms to which they are linked, and the second (one *anti* and one *gauche* angle) to a succession of four planar atoms only. In (I), the plane defined by atoms C3, C8, O2, C9 and C10 [greatest deviation 0.164 (4) Å] makes a dihedral angle of 52.2 (2)° with the reference O_4 plane, whereas the plane defined by C20, C25, O5, C26 and C27 [greatest deviation 0.112 (4) Å] is nearly parallel to it, with a dihedral angle of 8.4 (2)°. O2 is displaced by 0.089 (3) Å on one side of the reference O_4 plane, while O5 is displaced by 2.241 (3) Å on the opposite side. The conformation of the macrocycle can be described as a distorted cone in the sense that all four O atoms are roughly pointing in the same direction with respect to the mean plane of the molecule. However, it is strongly distorted towards a 1,2-alternate conformation (Masci *et al.*, 1998; Masci, 2001). If one considers the units comprising two aromatic rings and a central ether link, *i.e.* the units separated by the methylenic C atoms C17 and C34, one of them has its concave side directed downwards, and the other one upwards. This confirms that the confor-

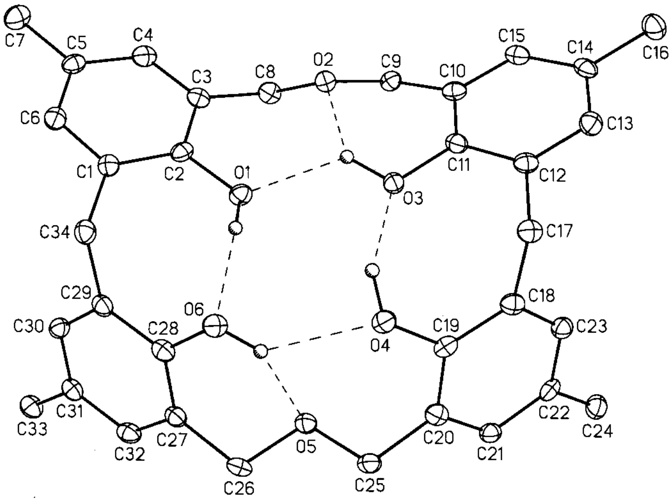


Figure 1
The title molecule with the atomic numbering scheme. H atoms have been omitted for clarity, except for those involved in hydrogen bonds, which are drawn as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

mation analysis of homooxacalix[4]arenes is much more complicated than that of calix[4]arenes (Masci *et al.*, 1998), both in solution and in the solid state. The hydrogen-bonding pattern is composed of two simple and two bifurcated hydrogen bonds, the latter involving the ether O atoms, as previously observed in *tert*-butyl derivatives.

The most original feature of the present structure with respect to those of the *tert*-butyl derivative lies in the crystal packing (Fig. 2). The molecules related by the screw axis parallel to **b** are positioned so that one of the units defined above, comprising the ether link corresponding to O5 and the two adjacent aromatic rings, points towards the cavity of the neighbouring macrocycle, with intermolecular contacts as short as 3.339 (4) Å [between O5 and C25^{i}; symmetry code: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$]. Such an arrangement, described as giving a self-inclusion polymer, has also been described in *p-tert*-butylcalix[5]arene (Gallagher *et al.*, 1994), in which the molecules are related by a glide plane. In this case, one *tert*-butyl group is the included moiety. The resulting one-dimensional columnar arrangement has been compared to a molecular 'zipper'. It may be assumed that the replacement of *tert*-butyl by methyl groups in (I) reduces the affinity of the macrocycle for solvent molecules, the cavity then being available for self-inclusion.

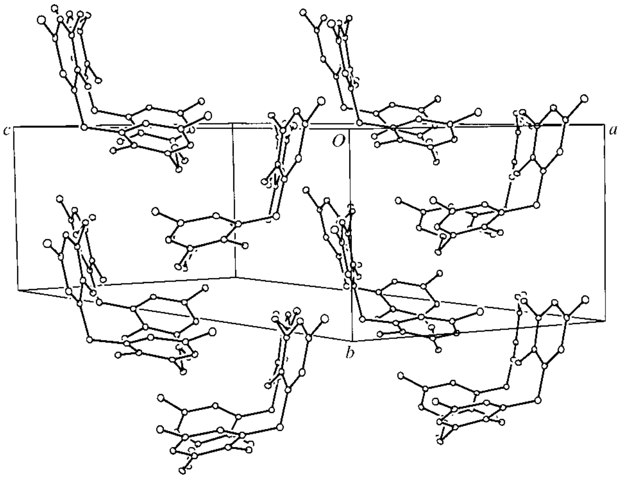


Figure 2
The packing arrangement of the title molecules. H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 10% probability level.

Experimental

p-Methyltetrahomodioxacalix[4]arene was synthesized (Masci, B., in preparation) and recrystallized from chloroform.

Crystal data

$C_{34}H_{36}O_6$
$M_r = 540.63$
Monoclinic, $P2_1/n$
$a = 12.4311$ (14) Å
$b = 8.4379$ (5) Å
$c = 26.5719$ (18) Å
$\beta = 100.115$ (4)°
$V = 2743.9$ (4) Å^3
$Z = 4$

$D_x = 1.309$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20349 reflections
$\theta = 2.9$–25.7°
$\mu = 0.09$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
0.50 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
20349 measured reflections
5116 independent reflections
2825 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$

$\theta_{\rm max} = 25.7°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -32 \rightarrow 31$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.188$
$S = 0.97$
5116 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 5.7020P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6	0.89	1.90	2.747 (4)	157
O3—H3···O1	1.03	2.06	2.813 (4)	128
O3—H3···O2	1.03	1.82	2.689 (4)	139
O4—H4···O3	0.94	1.94	2.803 (4)	152
O6—H6···O4	0.90	2.23	2.939 (4)	135
O6—H6···O5	0.90	2.03	2.710 (4)	131

Hydroxyl H atoms were found in 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 and CH_2) or 1.5 (CH_3) times that of the parent atom.

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL* and *PARST*97 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1514). Services for accessing these data are described at the back of the journal.

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