

# 1,3-Bridged *p*-methyloctahomotetra-oxacalix[4]arene–bis-crown-3

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Received 11 March 2002

Accepted 16 April 2002

Online 21 May 2002

The title compound, 13,21,35,43-tetramethyl-3,6,9,17,25,28,-31,39,46,49-decaoxaheptacyclo[21.21.3.3<sup>11,33</sup>.0<sup>2,41</sup>.0<sup>10,15</sup>.0<sup>19,24</sup>.0<sup>32,37</sup>]pentaconta-1,10,12,14,19,21,23,32,34,36,41,43-dodecaene, C<sub>44</sub>H<sub>52</sub>O<sub>10</sub>, differs from previously reported 1,3-bridged calix[4]arene–bis-crown compounds in having an enlarged calixarene ring and shorter polyoxyethylene bridges. The cavity is partly filled by the bridges.

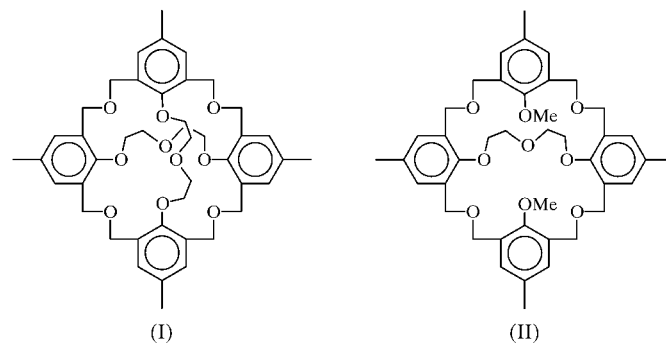
## Comment

In octahomotetraoxacalix[4]arenes, the CH<sub>2</sub> groups linking the aromatic rings in the typical calix[4]arene series are replaced by CH<sub>2</sub>OCH<sub>2</sub> units (Masci, 2001). Although the same main conformations as in calix[4]arene can be considered, the size and flexibility of the macrocyclic ring are much increased (Masci *et al.*, 1998) and lower rim substituents can be partly included in the cavity (Masci *et al.*, 2001).

In the present study, the tricyclic derivative (I) has distal aromatic rings bridged at the lower rim by dioxyethylene chains, thus forcing the compound to adopt a highly distorted 1,3-alternate conformation. Some bis-crown[*n*]ether (*n* = 5–7) compounds with the 1,3–2,4 bridging pattern have been investigated in the calix[4]arene series, and in all reported cases, moderate deviations from a regular 1,3-alternate arrangement have been observed, the opposed aromatic units being almost parallel and the molecule having an elongated globular shape (Casnati *et al.*, 2001; Thuéry *et al.*, 2000).

The enlarged calixarene ring and the shorter polyoxyethylene bridges account for the different shape of (I). The least-squares planes *P*1, *P*2, *P*3 and *P*4, defined by the four aromatic rings 1, 2, 3 and 4 containing atoms C11, C21, C31 and C41, respectively (Fig. 1), form dihedral angles between vicinal aromatic rings which are small in the case of rings *P*2 and *P*3 [24.6 (1)°] and large in the case of rings *P*1 and *P*2, *P*3 and *P*4, and *P*1 and *P*4 [74.4 (1), 74.9 (1) and 68.9 (1)°, respectively]. A reference least-squares plane defined by atoms O1, O2, O3 and O4 is intersected by planes *P*1, *P*2, *P*3 and *P*4 at angles of 68.0 (1), 21.8 (1), 14.3 (1) and 72.1 (1)°,

respectively. On extending to homooxalixarenes the notation of Kanamathareddy & Gutsche (1993), the conformation can be indicated as *u*, *do*, *uo*, *d*.



Apart from the orientation of the aromatic rings, the conformation of homooxalixarenes relies on the arrangement of the ArCH<sub>2</sub>OCH<sub>2</sub>Ar, which are usually found to be in an *anti-anti* or *anti-gauche* conformation. In the case of (I), opposite ArCH<sub>2</sub>OCH<sub>2</sub>Ar units are in the same gross conformation, namely almost *anti-gauche* around atoms O2 and O4, and *gauche-gauche* around atoms O1 and O3 [torsion angles 73.0 (5) and –63.4 (5)° around O1, 159.4 (4) and –73.6 (5)° around O2, 72.4 (4) and –73.3 (4)° around O3, and 158.0 (4) and –66.9 (5)° around O4].

The relatively short bridges at the lower rim are apparently responsible for the latter unusual conformation, which has only previously been observed in the related bicyclic compound, (II) (Masci *et al.*, 2001). In (II), the methoxy-substituted aromatic rings are almost perpendicular to the plane defined by the ArCH<sub>2</sub>OCH<sub>2</sub>Ar O atoms [dihedral angles 79.7 (1) and 80.6 (1)°]. Another difference between the

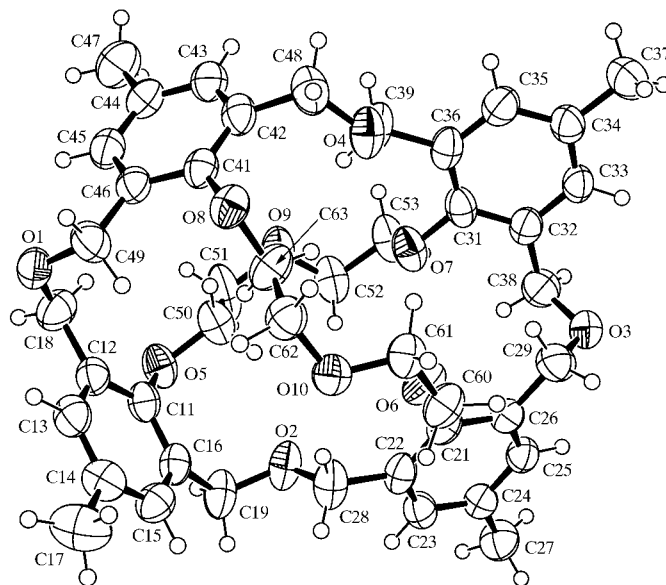


Figure 1

A view of the molecule of (I) in the crystal with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The methyl groups at C17, C27 and C37 are shown in the most populated conformation.

bicyclic and tricyclic compounds lies in the conformation of the dioxyethylene bridges, which are *anti*, *gauche*, *gauche*, *gauche*, *gauche* and *anti* in the bicycle, (II), and almost *anti*, *anti*, *gauche*, *anti*, *gauche* and *anti* for both bridges of the present macrotricyclic, (I). In fact, in (I), the torsion angles are 178.9 (4), 179.7 (4), -97.3 (5), -166.7 (4), 78.6 (5) and 173.9 (4)° from ring 1 to ring 3, and -166.2 (3), 175.1 (3), 84.4 (4), -162.2 (3), 74.6 (4) and 171.9 (3)° from ring 4 to ring 2.

The bridges in (I) partly fill the potential cavity formed by the two opposed aromatic rings and are not in close contact. The self-filled structure prevents the intermolecular inclusion noted in (II); the closest intermolecular contact detected in (I) [H33···O1<sup>i</sup> 2.37 Å, C33···O1<sup>i</sup> 3.317 (3) Å and C33—H33···O1<sup>i</sup> 168°; symmetry code: (i)  $x, 1 + y, z$ ] corresponds to a weak C—H···O hydrogen bond (Desiraju & Steiner, 1999).

## Experimental

Compound (I) was synthesized according to Masci & Saccheo (1993) and was recrystallized from benzene.

### Crystal data

C <sub>44</sub> H <sub>52</sub> O <sub>10</sub>	$D_x = 1.240 \text{ Mg m}^{-3}$
$M_r = 740.89$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 16 reflections
$a = 29.982 (5) \text{ \AA}$	$\theta = 14.0\text{--}18.0^\circ$
$b = 14.154 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 27.612 (2) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 137.36 (3)^\circ$	Prism, colourless
$V = 7937 (5) \text{ \AA}^3$	$0.3 \times 0.2 \times 0.2 \text{ mm}$
$Z = 8$	

### Data collection

Huber CS four-circle diffractometer	$h = 0 \rightarrow 39$
$\omega$ scans	$k = 0 \rightarrow 18$
11 136 measured reflections	$l = -35 \rightarrow 24$
9464 independent reflections	3 standard reflections
4754 reflections with $F > 3\sigma(F)$	every 97 reflections
$R_{\text{int}} = 0.022$	intensity decay: none
$\theta_{\text{max}} = 28^\circ$	

### Refinement

Refinement on $F$	H-atom parameters constrained
$R = 0.052$	$w = 1/(3.7038 + 0.0304F + 0.0009F^2)$
$wR = 0.067$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.85$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
4754 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
496 parameters	

The H atoms attached to atoms C17, C27 and C37 appeared as annular regions of electron density and were introduced in calculated positions (C—H = 0.95–0.97 Å) corresponding to two possible opposite conformations. One of these was such that one C—H bond was oriented normal to and the remaining C—H bonds were below the aromatic ring. Only the occupancy was refined for these methyl H atoms. All other H atoms showed up clearly in a difference synthesis, with the exception of the two H atoms on C51, which were introduced in calculated positions. For all H atoms, a riding model was used in the final refinement and their displacement parameters were kept equal to those of the parent atom.

Data collection: *XCS* (Colapietro *et al.*, 1992); cell refinement: *XCS*; data reduction: *XCS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CAOS* (Camalli & Spagna, 1994); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CAOS* and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1641). Services for accessing these data are described at the back of the journal.

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