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5,11,17,23-Tetra-*tert*-butyl-25,27-bis(carboxymethoxy)-26,28-bis(2-methoxyethoxy)calix[4]arene–methanol (1/1)

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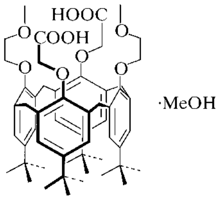
In the methanol solvate crystal form of the title diacid diglycol calixarene, $C_{54}H_{72}O_{10}\cdot CH_4O$, two calixarene molecules (in the cone conformation) are dimerized *via* two methanol molecules hydrogen bonded to the carboxyl groups. An intramolecular bond is also formed between a carboxylic proton and an ether O atom. This result is relevant to the interpretation of the acidic and complexation properties of calixarene carboxylic acids.

Comment

Calixarenes are macrocyclic molecules made up of *p*-substituted phenolic units linked by methylene bridges *ortho* to the OH functions (Gutsche, 1989; Vicens & Böhmer, 1991; Böhmer, 1995). The ability of parent phenolic calixarenes, as well as of their chemically modified derivatives obtained by the substitution of the phenolic H atoms with various types of ligating groups, to bind metal ions is well established (Böhmer, 1995).

With calix[4]arenes, the substituents frequently immobilize the molecule in a single conformation: cone, partial cone, 1,2- or 1,3-alternate. Calixarene carboxylic acids, in which the carboxylic groups are attached to the phenolic O atoms, display interesting complexation properties towards alkali and alkali earth metal cations (McKervey *et al.*, 1996), as well as towards the lanthanides and Th (Arnaud-Neu *et al.*, 1997). The tetra(carboxymethoxy) derivative of *p*-*tert*-butylcalix[4]arene has been shown recently to display a high selectivity for Ac^{III} cations (Chen *et al.*, 1998). The systematic study of the acid–base and complexation properties towards alkali metal cations of a series of calixarene carboxylic acids has been reported by McKervey *et al.* (1996). The determination of pK_a values in methanol showed that, whatever the number of carboxylic acid functions (except for one mono-acid compound), the *p*-*tert*-butylcalix[4]arene carboxylic acid derivatives in the cone conformation are less acidic than phenoxyacetic acid. This observation was interpreted in terms of stabilization of the protonated form by intramolecular hydrogen bonding. The structure of the title methanol solvate, (I), reported herein, indicates that, in solution in methanol, intermolecular hydrogen bonds leading to dimerization are also to be taken into account.



(I)

The asymmetric unit of (I) comprises one calixarene and one methanol molecule. The calixarene is in a distorted cone conformation, in which the dihedral angles between the four aromatic rings and the mean plane defined by the four methylenic bridges are 49.62 (7), 84.69 (5), 48.42 (6) and 88.05 (5)°. The two rings bonded to the glycolic chains are more vertical than the other two rings. Such a pseudo-$C2$ geometry is rather frequent in calix[4]arenes bearing different bulky substituents and the resulting pinching of the cone has been thought to prevent solvent inclusion in the calixarene cavity (Drew *et al.*, 1997), which is confirmed in the present case. This geometry enables one of the carboxylic O atoms (O7) to be directed towards the inside of the molecule and to

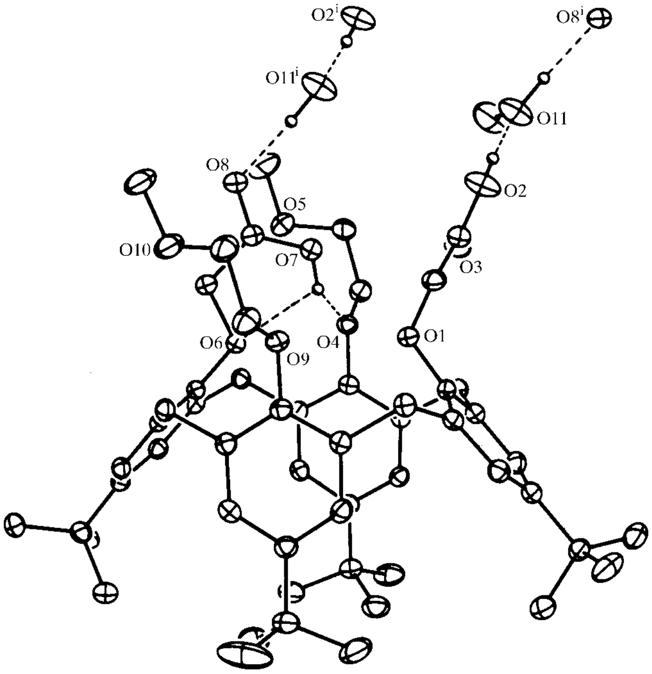


Figure 1
A view of the molecule of (I) with the atom-numbering scheme. H atoms are omitted for clarity, apart from those involved in hydrogen bonds, which are drawn as small spheres of an arbitrary radius. Hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 40% probability level [symmetry code: (i) $-x, -y, -z$].

form hydrogen bonds with the ether atoms O4 and O6 (see Table 1).

The methanol molecule forms two hydrogen bonds, one with the carboxylic atom O2, pertaining to the acid group directed outwards, and the other with the atom O8($-x$, $-y$, $-z$) from another calixarene molecule, related to the first one by the symmetry centre (see Fig. 1). This leads to the formation of dimers, including two head-to-head calixarene molecules, with their main axis parallel to each other, interconnected by two methanol molecules. Obviously, such a dimerization would not be possible if both carboxylic groups were involved in intramolecular hydrogen bonds. On the other hand, a dimerization by direct bonding of the carboxylic groups of the two molecules would probably be hampered by the steric hindrance of the glycolic chains. The present bonding pattern must be taken into consideration when complexation equilibria in methanol, during cation transportation, are considered.

Experimental

Compound (I) was synthesized according to the literature method of Barakat *et al.* (1998) and was recrystallized from methanol.

Crystal data

$C_{54}H_{72}O_{10}{\cdot}CH_4O$
$M_r = 913.16$
Monoclinic, $P2_1/c$
$a = 17.7426\ (9)$ Å
$b = 15.5402\ (6)$ Å
$c = 19.8147\ (10)$ Å
$\beta = 104.279\ (2)^\circ$
$V = 5294.6\ (4)$ Å^3
$Z = 4$

$D_x = 1.146$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18 139 reflections
$\theta = 2.62$–25.68°
$\mu = 0.078$ mm^{-1}
$T = 127\ (2)$ K
Platelet, colourless
0.45 × 0.28 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
18 139 measured reflections
9972 independent reflections
6410 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$

$\theta_{\max} = 25.68^\circ$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 18$
$l = -24 \rightarrow 24$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.138$
$S = 1.009$
9972 reflections
614 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 1.7978P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.274$ Å^{-3}
$\Delta\rho_{\min} = -0.233$ Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0049 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$\cdots$O4	0.947	2.042	2.820 (2)	138
O7—H7$\cdots$O6	0.947	2.144	2.630 (2)	111
O2—H2$\cdots$O11	0.939	1.698	2.634 (3)	176
O11—H11$\cdots$O8$^{\rm i}$	0.95	1.77	2.719 (3)	175

Symmetry code: (i) $-x, -y, -z$.

The carboxyl and hydroxyl (methanol) protons were found on the difference Fourier map and introduced as riding atoms with a displacement factor equal to 1.2 times that of the attached O atom. All other H atoms were introduced at calculated positions as riding atoms with a displacement factor equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the attached C atom.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97; molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1335). Services for accessing these data are described at the back of the journal.

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