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Self-inclusion in 5,11,17,23-tetra-*tert*-butyl-26,27,28-trihydroxy-25-(methoxycarbonylmethoxy)calix[4]arene chloroform trisolvate

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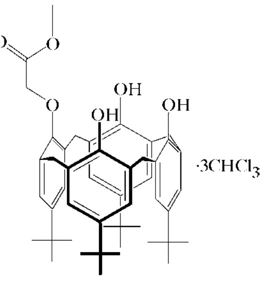
The title compound, $C_{47}H_{60}O_6\cdot 3CHCl_3$, is the first example of a lower-rim mono-ester calixarene derivative to be crystallographically characterized. The cone conformation adopted by the macrocycle is stabilized by three intramolecular hydrogen bonds. Self-inclusion of the methyl ester chain in the cavity of an adjacent molecule gives rise to infinite chains parallel to the *c* axis. C—H$\cdots\pi$ interactions involving the methyl group most imbedded in the cavity contribute to the stabilization of the system.

Comment

Lower-rim ester derivatives of calixarenes (Thondorf *et al.*, 2001) have been the subject of much attention, in particular for their ionophoric properties (Arnaud-Neu *et al.*, 2001). Numerous di- and tetra-ester derivatives of *R*-calix[4]arene have been synthesized and characterized, but to the best of our knowledge, no crystal structure of a mono-ester derivative has been reported. The title mono-ester, (I), was prepared to be used in the synthesis of new dendrimers (Cheriaa *et al.*, 2004). We have reported previously the syntheses and crystal structures of the related compound 5,11,17,23-tetra-*tert*-butyl-25,27-di(methoxycarbonylmethoxy)-26,28-dimethoxycalix[4]arene, (II), and its complexes with Na^+ and K^+ (Oueslati *et al.*, 2000); while calix[4]arene derivatives usually adopt a cone conformation stabilized by intramolecular hydrogen bonding (Gutsche, 1998), the absence of hydroxy groups in (II) results in it crystallizing in a partial cone conformation. In contrast, the dimethyl ester derivative of calix[4]arene 1,3-di(methoxycarbonylmethoxy)-2,4-dihydroxycalix[4]arene, which is unsubstituted at the *para* positions, is in a cone conformation (Coles *et al.*, 2002), as is 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(methoxycarbonylmethoxy)calix[4]arene and the corresponding tetraethyl ester derivative (Arnaud-Neu *et al.*, 1989). A search of the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002) identified several crystal structures of diethyl ester derivatives with *tert*-butyl or H substituents in the *para* positions (Creaven *et al.*, 2001; Genorio *et al.*, 2003; Bolte *et al.*, 2003; Dudič *et al.*, 2003), but only two triethyl ester compounds have been described (Cooper *et al.*, 2000).



(I)

Compound (I) crystallizes as a chloroform trisolvate, with one complete molecule in the asymmetric unit (Fig. 1). The macrocycle adopts a cone conformation, as expected from the presence of intramolecular homodromic hydrogen bonds (Steiner, 2002) involving the three phenol hydroxide groups and the substituted phenol O atom (Table 1). The mean plane defined by the four methylene C-atom bridges (r.m.s. deviation = 0.042 Å) was chosen as a reference plane. The plane defined by the four phenol O atoms (O1, O4, O5 and O6; r.m.s. deviation = 0.007 Å) makes a dihedral angle of 2.82 (8)° with this reference plane, whereas the four aromatic rings make dihedral angles of 66.43 (8), 54.24 (10), 56.30 (10) and 62.23 (9)°. The cone conformation thus appears to be regular, but the aromatic ring that bears the ester substituent is more

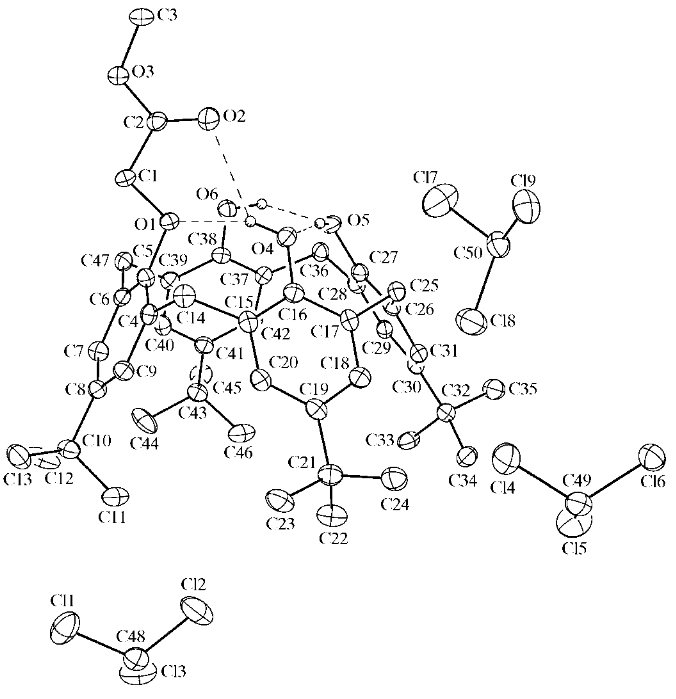


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted, except for those involved in hydrogen bonds, which are drawn as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

inclined with respect to the reference plane than the other three rings. Comparable conformations were found in diethyl ester derivatives (Creaven *et al.*, 2001; Bolte *et al.*, 2003), whereas the cone conformation is much more distorted in tetra-ester derivatives (Arnaud-Neu *et al.*, 1989) as a result of increased steric interactions. The conformation of the ester chain in (I) is extended and roughly perpendicular to the reference plane. Atom C1 points towards the exterior of the macrocycle [the torsion angles around the $C_{arom}—O1$ bond are −93.8 (4) and 87.7 (4)°], whereas the torsion angles around the O1—C1, C1—C2 and C2—O3 bonds do not deviate from ideal *syn* or *anti* values by more than 19°. An additional close interaction, possibly a weak hydrogen bond, between atoms O4 and O2 may stabilize this conformation of the chain, the H atom bound to atom O4 being thus involved in a dissymmetric bifurcated hydrogen bond.

The methyl ester chain is included in the cavity of the neighbouring calixarene along the *c* axis, thus giving rise to infinite chains of parallel calixarenes held together by weak interactions directed along this axis (Fig. 2). The chloroform solvent molecules are located in the voids between these chains. Such self-inclusion phenomena are not uncommon in calixarene structures, but very often they involve the *para* substituents and, as a consequence, the upper rims of adjacent molecules are facing one another and offset (Gallagher *et al.*, 1994; Böhmer *et al.*, 1996; Brouwer *et al.*, 2001). Self-inclusion of an ethyl ester residue in 5,11,17,23-tetra-*tert*-butyl-25,-27-di(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene has, however, also been reported recently (Bolte *et al.*, 2003). The C3 methyl group in (I) is located near the centre of the cavity of the neighbouring molecule. Atom C3 is located 4.002 (6)–4.178 (6) Å from the four aromatic *para* C atoms of the host molecule and 0.416 (4) Å (on the outer side) from the mean plane defined by these four aromatic C atoms (r.m.s. deviation = 0.042 Å). This methyl group is thus well imbedded in the cavity, as evidenced by the shortest $C3\cdots C_{arom}$ distance, 3.657 (6) Å, which involves atom C26 in an *ortho* position with respect to atom O5. This value is comparable to that found in the diethyl ester derivative [3.685 (6) Å; Bolte *et al.*, 2003], but the latter involves a C atom bearing a phenol O atom. Apart from van der Waals contacts, $C—H\cdots\pi$ interactions seem to play an important role in this self-inclusion phenomenon in (I). The three H atoms bound to atom C3 (not satisfactorily found, see *Experimental*) are possibly involved in $C—H\cdots\pi$ interactions with three aromatic rings [$H3A\cdots Cg1$ = 2.91 Å and $C3—H3A\cdots Cg1$ = 144°, $H3B\cdots Cg2$ = 2.93 Å and $C3—H3B\cdots Cg2$ = 149°, and $H3C\cdots Cg3$ = 2.77 Å and $C3—H3C\cdots Cg3$ = 144°, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the aromatic rings attached to atoms $O4^i$, $O1^i$ and $O5^i$, respectively; symmetry code: (i) *x*, *y*, 1 + *z*]. In the case of host–guest complexes of calixarenes, it has been suggested that the $C—H\cdots\pi$ interactions could be second to other interactions, such as packing forces (Brouwer, Enright & Ripmeester, 1996; Brouwer, Ripmeester & Enright, 1996). The relative contributions of such weak interactions cannot be separated on the basis of structural data alone (dipole–dipole interactions may also be present), but the arrangement observed in (I) supports the hypothesis that $C—H\cdots\pi$ interactions are important components in the stabilization of the system.

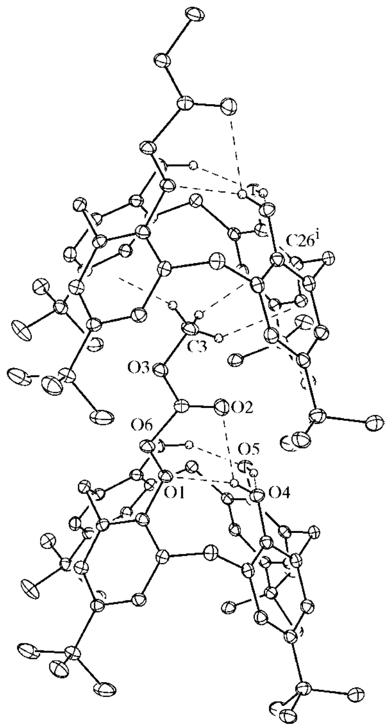


Figure 2
A view showing the self-inclusion in (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted, except for those involved in hydrogen bonds and $C—H\cdots\pi$ interactions, which are drawn as small spheres of arbitrary radii. Solvent molecules have been omitted. [Symmetry code: (i) *x*, *y*, 1 + *z*.]

Experimental

p-*tert*-Butylcalix[4]arene was refluxed in acetonitrile with three equivalents of bromomethyl acetate and 0.5 equivalents of potassium carbonate for a period of 18 h. After acidification, two-phase extraction with chloroform and evaporation of the solvents, the crude mixture was precipitated with methanol to give the title compound in 55% yield (m.p. > 421–422 K). Single crystals were obtained by diffusion of methanol into a chloroform solution of (I).

Crystal data

$C_{47}H_{60}O_6\cdot 3CHCl_3$
M_r = 1079.05
Orthorhombic, $Pna2_1$
a = 23.7595 (9) Å
b = 24.2234 (8) Å
c = 9.3546 (3) Å
V = 5383.9 (3) Å^3
Z = 4
D_x = 1.331 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 35 034 reflections
θ = 2.3–25.7°
μ = 0.51 mm^{-1}
T = 100 (2) K
Parallelepiped, colourless
0.26 × 0.14 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: refined from ΔF (*DELABS* in *PLATON*; Spek, 2000)
T_{min} = 0.891, T_{max} = 0.936
35 034 measured reflections
9864 independent reflections
7715 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 25.7°
$h = -28 \rightarrow 27$
$k = -29 \rightarrow 28$
$l = -11 \rightarrow 11$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.125$
$S = 1.05$
9864 reflections
600 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Absolute structure: Flack (1983), 4416 Friedel pairs
Flack parameter = 0.03 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O1	0.89	2.02	2.831 (4)	151
O4—H4$\cdots$O2	0.89	2.48	3.170 (4)	135
O5—H5$\cdots$O4	0.96	1.72	2.661 (4)	164
O6—H6$\cdots$O5	0.93	1.85	2.740 (4)	157

Hydroxy H atoms were found in a difference Fourier map and were introduced as riding atoms, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(O). All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (aromatic CH), 0.98 (aliphatic CH), 0.97 (CH_2) and 0.96 Å (CH_3), and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) for CH and CH_2 H atoms, and $1.5U_{\rm eq}$(C) for CH_3 H atoms. The H atoms bound to atom C3, which are probably involved in C—H$\cdots\pi$ interactions, could not be found, but this methyl group was treated as a rotating group and its position was calculated so as to maximize the sum of the electron density at the H-atom positions.

Data collection: *KappaCCD Server Software* (Nonius, 1997); 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* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1158). Services for accessing these data are described at the back of the journal.

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