Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Redetermination of 5,11,17,23-tetra-*tert*-butyl-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene chloroform disolvate at low temperature

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The title compound, $C_{52}H_{68}O_8{\cdot}2CHCl_3$, previously reported by Ferguson *et al.* [*Supramol. Chem.* (1996), **7**, 223–228], has been rerefined against new intensity data. The geometric parameters are comparable, as far as they are available. However, the results of the present structure determination are of significantly higher precision.

Received 10 March 2003
Accepted 17 March 2003
Online 31 March 2003

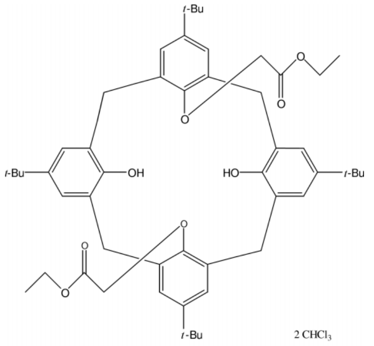
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.094
wR factor = 0.297
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

1,3-Diethers of calix[4]arenes with a *syn* orientation of the ether groups are easily available precursors for various derivatives (Collins *et al.*, 1989). The title compound, (I), was first described by Arnaud-Neu *et al.* (1989) and its structure has been reported some years ago (Ferguson *et al.*, 1996) [(II) hereafter]; however, their crystal diffracted very weakly and the data were of quite low resolution [only 16% of the measured data could be labelled observed in the 2 to 20° θ range, with $I > 2\sigma(I)$]. Thus, the aromatic rings had to be treated as rigid groups and restraints were necessary for C—C and C—O bonds. In addition, the solvent could not be identified, but had to be treated with the SQUEEZE option in *PLATON* (Spek, 1990). Furthermore, no coordinates of (II) are available in the Cambridge Structural Database (Version 5.24 of November 2002; Allen, 2002).



(I)

We present here the structure of (I), determined from low-temperature data with significantly higher precision. Since the coordinates of the published structure are not available, we had to restrict the comparison of both structure determinations to the values printed explicitly in the paper. We have labelled the atoms in the same way and Fig. 1 shows nearly the same view as for (II). The O···O distances, the interplanar angles between the aromatic rings and the shortest distance of the clathrated ester residue to the guest molecule are comparable (Table 2). The molecule adopts the cone conformation which is stabilized by two intramolecular hydrogen bonds. One of the ester residues is located in the molecular cavity of a symmetry-related molecule. The shortest C···C distance from the terminal methyl group is C16A···C1$B^{\rm i}$

DOI: 10.1107/S1600536803006032

3.685 (6) Å [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$]. The reference plane of the calixarene, defined as the mean plane of the bridging C atoms (here C7*A*, C7*B*, C7*C* and C7*D*), is almost planar (r.m.s. deviation = 0.136 Å); the rings C1*A*–C6*A*, C1*B*–C6*B*, C1*C*–C6*C*, and C1*D*–C6*D* subtend angles of 64.91 (7), 57.81 (11), 67.10 (10) and 53.42 (12)°, respectively, with this plane.

Experimental

The title diester was prepared, according to the literature method of Jakobi *et al.* (1996), by refluxing *tert*-butylcalix[4]arene with ethyl bromoacetate in dry acetonitrile in the presence of potassium carbonate. Single crystals formed during recrystallization from chloroform/methanol.

Crystal data

$C_{52}H_{68}O_8 \cdot 2CHCl_3$
$M_r = 1059.80$
Orthorhombic, *Pbca*
$a = 17.7766$ (2) Å
$b = 20.4108$ (1) Å
$c = 32.0452$ (2) Å
$V = 11627.11$ (16) Å^3
$Z = 8$
$D_x = 1.211$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.5$–24.8°
$\mu = 0.34$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.43 × 0.32 × 0.28 mm

Data collection

Siemens SMART CCD three-circle diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.866$, $T_{\max} = 0.910$
52500 measured reflections

10229 independent reflections
6797 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 25.0°$
$h = -21 \rightarrow 13$
$k = -24 \rightarrow 24$
$l = -37 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.095$
$wR(F^2) = 0.297$
$S = 1.01$
10229 reflections
643 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1605P)^2 + 26.7478P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1*D*—H1*D*···O1*A*	0.84	1.89	2.722 (4)	168
O1*B*—H1*B*···O1*C*	0.84	1.94	2.777 (4)	171

Table 2
Comparative table of the geometric parameters (Å, °) of (I) and (II).

	(I)	(II)
Angle *A*/*C*	48.08 (14)	49
Angle *B*/*D*	68.77 (11)	72
O1*A*···O1*B*	3.037 (4)	3.2
O1*B*···O1*C*	2.777 (4)	2.9
O1*C*···O1*D*	3.094 (4)	3.1
O1*D*···O1*A*	2.723 (4)	2.7
C16*A*···C1*B*$^{\rm i}$	3.685 (6)	3.60

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$.

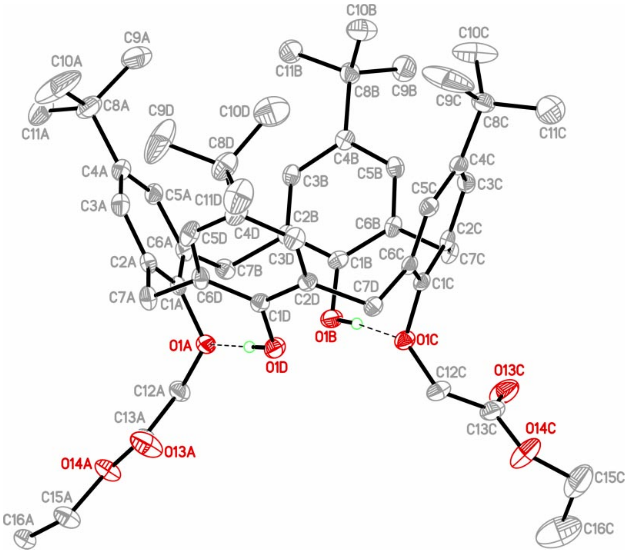


Figure 1
Perspective view of the title compound with the atom numbering; displacement ellipsoids are drawn at the 30% probability level. H atoms bonded to C atoms and the solvent molecules have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

One of the two chloroform molecules is disordered over two sites. The site-occupation factors of the H atom and the three Cl atoms refined to 0.597 (7)/0.403 (7). All C—Cl distances were restrained to 1.78 (1) Å. H atoms bonded to C atoms were refined with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C$_{\rm methyl}$)], using a riding model with tertiary C—H = 1.00 Å, secondary C—H = 0.99 Å, methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å. The hydroxyl H atoms were located in a difference map and were refined with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O)], using a riding model with O—H = 0.84 Å. In addition, the O—C torsion angle was allowed to refine. The highest peak in the final difference map is located 2.00 Å from H16*D*, 2.09 Å from Cl11, 2.09 Å from H1*L* and 2.34 Å from C1*L*.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

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