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5,11,17,23-Tetra-*tert*-butyl-25,26,-27,28-tetrakis(2-cyanobenzyloxy)-2,8,14,20-tetrathiacalix[4]arene–dichloromethane (1/2)

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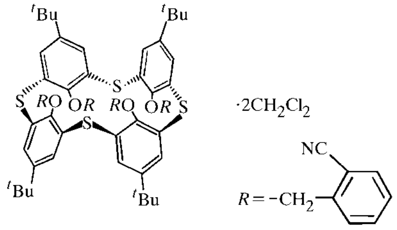
A new *p-tert*-butylthiacalix[4]arene derivative, $C_{72}H_{68}N_4O_4S_4 \cdot 2CH_2Cl_2$, has been synthesized and is comprised of one tetra-*p-tert*-butyltetrakis(2-cyanobenzyloxy)tetrathiacalix[4]arene and two dichloromethane molecules. The calix[4]arene molecule is centrosymmetric and adopts an unusual 1,2-alternate conformation *via* π–π interactions between adjacent cyanophenyl rings on the lower rim of the parent thiacalix[4]arene system.

Comment

Thiacalix[4]arenes (TCAs) have emerged very recently as new members of the well known calixarene family (Kumagai *et al.*, 1997). It has been demonstrated that one of the remarkable results of the replacement of CH_2 by S is that TCAs can quantitatively extract transition metal ions, such as Co^{2+}, Cu^{2+} and Zn^{2+}, from an aqueous phase into chloroform (Morohashi *et al.*, 2001) and, furthermore, oxidation of the sulfur bridges to sulfoxide or sulfone moieties leads to new types of ligands with potentially interesting complexation abilities (Lhotak *et al.*, 2000).



(I)

For the parent calix[4]arene, four limit conformers (cone, partial cone, 1,2-alternate and 1,3-alternate) are found; to the best of our knowledge, however, for most tetrasubstituted calix[4]arene derivatives, the 1,2-alternate conformation is unknown (Cambridge Structural Database, Version of April 2001; Allen & Kennard, 1993). We report herein the structure of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-cyanobenzyloxy)-2,8,14,20-tetrathiacalix[4]arene–dichloromethane (1/2), (I), which adopts an unique 1,2-alternate conformation *via* π–π interactions between adjacent cyanophenyl rings on the lower rim of the parent thiacalix[4]arene system.

Single-crystal analysis reveals that the molecule is centrosymmetric. Two pairs of opposite aromatic rings, C1–C6/C1*A*–C6*A* and C11–C16/C11*A*–C16*A*, are parallel to each other. The dihedral angles between adjacent aromatic rings, *i.e.* C1–C6 and C11–C16, and C1*A*–C6*A* and C11*A*–C16*A*, are all 102.7 (1)°. Furthermore, adjacent cyanophenyl rings on the lower rim are nearly parallel, with a dihedral angle of 7.3 (2)°, and the two carbonitrile groups are oriented in roughly the same direction. The four bridging S atoms are coplanar and the average distances between two adjacent S atoms, S1···S2, and two opposite S atoms, S2···S2*A*, are 5.581 (1) and 8.409 (1) Å, respectively. The angles C5—S1—C11 and C1—S2—C15*A* are 101.54 (4) and 108.36 (4)°, respectively. The two dichloromethane solvent molecules do not enter the cavity, but are located on opposite sides of the thiacalix[4]arene molecule.

In conclusion, as the precursor of a new thiacalix[4]arene derivative, the title compound adopts an unusual 1,2-alternate conformation with two pairs of distal aromatic rings and two pairs of distal cyanophenyl rings being centrosymmetric. Hydrolysis of the cyanobenzyl groups on the lower rim to the benzoxy groups and the binding ability toward metal ions of the latter derivative are currently under investigation.

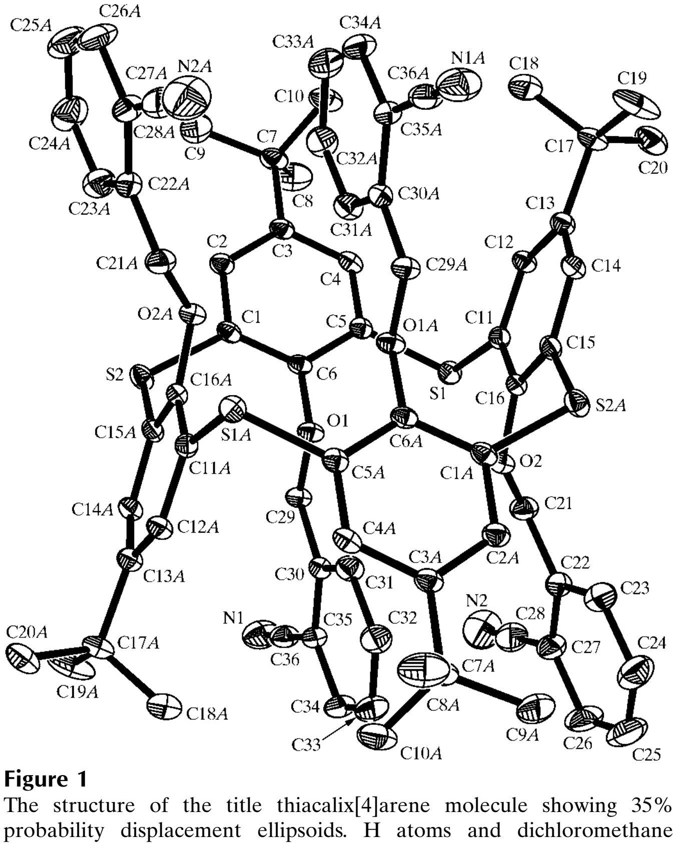


Figure 1
The structure of the title thiacalix[4]arene molecule showing 35% probability displacement ellipsoids. H atoms and dichloromethane solvent molecules have been omitted for clarity.

Experimental

The title compound was synthesized by reaction of thiacalix[4]arene with 2-(bromomethyl)benzonitrile in the presence of K_2CO_3 as catalyst. The solid product was collected by filtration and recrystallization from dichloromethane gave the title compound as flat colorless crystals.

Crystal data

$C_{72}H_{68}N_4O_4S_4\cdot 2CH_2Cl_2$
$M_r = 1351.40$
Monoclinic, $P2_1/n$
$a = 13.768$ (4) Å
$b = 17.021$ (5) Å
$c = 15.543$ (4) Å
$\beta = 105.424$ (5)°
$V = 3511.3$ (17) Å^3
$Z = 2$
$D_x = 1.278$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 80 reflections
$\theta = 2.4$–24.5°
$\mu = 0.34$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.40 × 0.30 × 0.20 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.877$, $T_{\max} = 0.935$
14 071 measured reflections
6105 independent reflections
3885 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 25.0°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 15$
$l = -18 \rightarrow 13$

Table 1
Selected geometric parameters (Å, °).

S1—C11	1.794 (3)	O2—C21	1.443 (4)
S1—C5	1.797 (3)	N1—C36	1.141 (5)
S2—C15$^{\rm i}$	1.775 (3)	N2—C28	1.134 (7)
S2—C1	1.785 (3)	C3—C7	1.538 (5)
O1—C6	1.386 (4)	C13—C17	1.545 (5)
O1—C29	1.438 (4)	C21—C22	1.504 (5)
O2—C16	1.365 (4)	C29—C30	1.501 (5)
C11—S1—C5	101.54 (14)	C14—C15—S2$^{\rm i}$	117.2 (2)
C15$^{\rm i}$—S2—C1	108.36 (14)	C16—C15—S2$^{\rm i}$	122.5 (2)
C6—O1—C29	114.2 (2)	O2—C16—C11	125.3 (3)
C16—O2—C21	118.0 (3)	O2—C16—C15	117.1 (3)
C6—C1—S2	124.5 (2)	O2—C21—C22	109.5 (3)
C2—C1—S2	115.3 (3)	N2—C28—C27	179.1 (6)
C12—C11—S1	118.1 (2)	O1—C29—C30	108.7 (3)
C16—C11—S1	122.1 (2)	N1—C36—C35	178.4 (5)

Symmetry code: (i) $-x, -y, 2-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.186$
$S = 1.06$
6105 reflections
406 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.9P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.052$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

H atoms were placed in calculated positions and refined as riding, with C—H distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene/dichloromethane H atoms, respectively.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1542). Services for accessing these data are described at the back of the journal.

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