

Experimental

The *N*-acetyl derivative (2b) was prepared from the parent O-bridged pyrimidine (2a) (Kettmann & Svetlík, 1996) by acetylation with acetic anhydride, as described by Kettmann, Dřimal & Svetlík (1996).

Crystal data

C₁₅H₁₆N₂O₄S

M_r = 320.36

Triclinic

P $\bar{1}$

a = 8.962 (3) Å

b = 9.651 (4) Å

c = 10.009 (4) Å

α = 68.45 (3)°

β = 71.46 (3)°

γ = 81.52 (3)°

V = 762.9 (5) Å³

Z = 2

D_x = 1.395 Mg m⁻³

D_m = 1.40 (1) Mg m⁻³

D_m measured by flotation in bromoform-hexane

Data collection

Syntex *P2*₁ diffractometer

$\theta/2\theta$ scans

Absorption correction: none

2893 measured reflections

2715 independent reflections

2008 reflections with

I > 2 σ (*I*)

*R*_{int} = 0.031

Refinement

Refinement on *F*²

R [*F*² > 2 σ (*F*²)] = 0.051

wR(*F*²) = 0.113

S = 1.132

2715 reflections

200 parameters

H atoms not refined

w = 1/[$\sigma^2(F_o^2) + (0.0905P)^2 + 0.4132P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.028

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 15 reflections

θ = 8–18°

μ = 0.232 mm⁻¹

T = 293 (2) K

Prism

0.35 × 0.25 × 0.20 mm

Colourless

θ_{max} = 25.06°

h = 0 → 10

k = -11 → 11

l = -10 → 11

2 standard reflections

frequency: 100 min

intensity decay: none

$\Delta\rho_{\text{max}}$ = 0.623 e Å⁻³

$\Delta\rho_{\text{min}}$ = -0.472 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.002 (5)

Scattering factors from

International Tables for Crystallography (Vol. C)

N1—C2—N3—C13 -156.5 (3) C4—C5—C6—N1 -45.8 (3)

N1—C2—N3—C4 16.1 (3) C2—N3—C13—O2 -161.9 (3)

C2—N3—C4—C5 -54.4 (3)

All H atoms were located in difference maps and were not refined, with *U*_{iso} set to 1.2*U*_{eq} of the parent atom.

Data collection: Syntex *P2*₁ diffractometer software. Cell refinement: Syntex *P2*₁ diffractometer software. Data reduction: *XP21* (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1098). Services for accessing these data are described at the back of the journal.

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The Cone Conformer of a Tetrakis(methylthio)tetrapropoxycalix[4]arene

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Abstract

5,11,17,23-Tetrakis(methylthio)-25,26,27,28-tetrapropoxycalix[4]arene, C₄₄H₅₆O₄S₄, adopts a 'distorted-cone' conformation in the solid state. This distortion

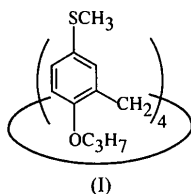
Table 1. Selected geometric parameters (Å, °)

S1—C2	1.666 (3)	C4—C7	1.492 (4)
N1—C2	1.322 (3)	C4—C5	1.514 (4)
N1—C6	1.456 (3)	C5—C6	1.518 (4)
C2—N3	1.366 (3)	C6—O1	1.426 (3)
N3—C13	1.411 (4)	C8—O1	1.365 (4)
N3—C4	1.472 (3)	C13—O2	1.199 (4)
C2—N1—C6	129.1 (2)	N3—C4—C5	107.8 (2)
N1—C2—N3	116.2 (2)	C4—C5—C6	105.0 (2)
N1—C2—S1	120.5 (2)	N1—C6—C5	109.1 (2)
N3—C2—S1	123.1 (2)	C8—O1—C6	115.5 (2)
C2—N3—C13	126.3 (2)	O2—C13—N3	117.6 (3)
C2—N3—C4	116.3 (2)	O2—C13—C14	121.5 (3)
C13—N3—C4	117.0 (2)	N3—C13—C14	120.7 (3)
C6—N1—C2—N3	6.8 (4)	N3—C4—C5—C6	67.8 (3)
C6—N1—C2—S1	-177.7 (2)	C2—N1—C6—C5	10.4 (4)

from a perfect cone shape is well known from other structural studies of calix[4]arene derivatives. Two opposite benzene rings lean towards one another forming a dihedral angle of $-15(1)^\circ$, while the other two lean away from one another and form an angle of $108(1)^\circ$.

Comment

Calixarenes are a class of macrocyclic compounds comprising four, five, six or more phenolic moieties joined in a cyclic array at the *meta* positions by methylene groups. They are prepared from *p*-alkylphenols and formaldehyde in the presence of a catalytic amount of base. The size of the ring can be controlled by the nature and amount of the base. The special feature of 5,11,17,23-tetrakis(methylthio)-25,26,27,28-tetrapropoxy-calix[4]arene, (I), discussed here, is the four methylthio



groups which have been introduced in order to make a calixarene suitable for self assembly on gold surfaces. It has been demonstrated through extensive research activities in the past ten years using FT-IR, ESCA, STM, MS, contact-angle measurements, surface plasmon resonance and grazing-angle X-ray diffraction that alkanethiols, CH₃(CH₂)_nSH, with $n = 8, 9, \dots, 16$, form highly textured monolayers on gold (Fenter, Eberhardt & Eisenberger, 1994). These stable organic monolayers are ideal model systems for the study of physical and chemical properties of organic surfaces and are easily prepared using simple chemisorption methods. Likewise, modified calixarenes with thiol groups anchored to the rim of the bowl-shaped assembly of aromatic rings, have been shown to produce ordered monolayers on clean flat gold surfaces (Huisman, Velzen, Veggel, Engbersen & Reinhoudt, 1995) but have not yet been characterized. The calixarenes have an outstanding capacity as molecular receptors, due to their variable chemical modification potential and their conformational pliability which enables them to adapt to the shape of suitable guest molecules. The possibility of making well defined monolayers of calixarenes opens up a whole new range of experimental characterization techniques, among those being grazing-angle X-ray diffraction using synchrotron radiation. The present calixarene, (I), is believed to form a monolayer on gold (111) surfaces. In order to interpret grazing-angle X-ray diffraction data recorded on this system at the BW2 beamline, Hasylab, Hamburg, Germany, we needed to determine the three-dimensional crystallographic structure which is reported here.

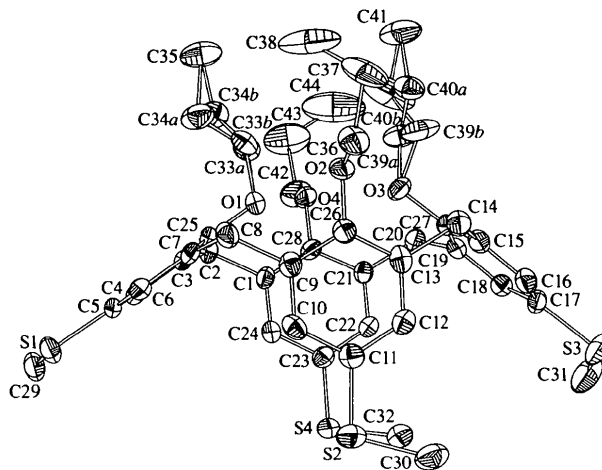


Fig. 1. ORTEP III (Burnett & Johnson, 1996) drawing of one calixarene molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms have been omitted for clarity.

In the crystal structure of (I), the calixarene is found to adopt a distorted cone configuration similar to that of many calixarenes with *p*-*tert*-butyl substituents (Grootenhuys *et al.*, 1990). Following the approach of Uguzzoli & Andreotti (1992), the present structure is unequivocally described by four pairs of conformational parameters (torsion angles): $(\varphi, \chi)_1 = 51.2(5), -112.2(4)$; $(\varphi, \chi)_2 = 111.7(4), -61.0(5)$; $(\varphi, \chi)_3 = 57.6(5), -99.0(4)$; $(\varphi, \chi)_4 = 100.6(4), -51.3(5)^\circ$. This conformation is often described as the (+-+-+-) conformation.

Experimental

Compound (I) was prepared from the corresponding tetrabromocalix[4]arene cone in a lithium bromine exchange reaction followed by quenching with CH₃SSCH₃. The final product was recrystallized from acetonitrile.

Crystal data

C₄₄H₅₆O₄S₄
M_r = 777.20
 Monoclinic
*P*2₁/*n*
a = 12.479 (3) Å
b = 27.145 (8) Å
c = 12.591 (4) Å
 β = 97.40 (1)°
V = 4230 (2) Å³
Z = 4
D_x = 1.22 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 54 reflections
 θ = 9–12°
 μ = 0.265 mm⁻¹
T = 120 K
 Thick plate
 0.3 × 0.3 × 0.1 mm
 Colourless

Data collection

Huber four-circle diffractometer
 R_{int} = 0.026
 θ_{max} = 25.0°

$\theta/2\theta$ scans $h = -14 \rightarrow 14$
 Absorption correction: none $k = 0 \rightarrow 29$
 6324 measured reflections $l = 0 \rightarrow 14$
 5999 independent reflections 2 standard reflections
 4431 reflections with every 50 reflections
 $I > 2\sigma(I)$ intensity decay: 8%

Refinement

Refinement on F $\Delta\rho_{\max} = 0.67 (6) \text{ e } \text{\AA}^{-3}$
 $R = 0.057$ $\Delta\rho_{\min} = -0.39 (6) \text{ e } \text{\AA}^{-3}$
 $wR = 0.067$ Extinction correction: type 1,
 $S = 1.466$ Lorentzian isotropic
 4431 reflections (Becker & Coppens,
 508 parameters 1975); mean path length
 H-atom parameters put to 1
 constrained Extinction coefficient:
 $w = 1/[\{\sigma(F^2) + 1.03F^2\}^{1/2}$ $4 (4) \times 10$
 $- |F|^2]$ Scattering factors from *Inter-*
 $(\Delta/\sigma)_{\max} = 0.004$ *national Tables for X-ray*
Crystallography (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

S1—C5	1.780 (4)	O2—C26	1.390 (5)
S1—C29	1.790 (5)	O2—C36	1.434 (5)
S2—C11	1.772 (4)	C1—C2	1.532 (5)
S2—C30	1.790 (5)	C2—C3	1.500 (6)
O1—C25	1.369 (5)	C7—C8	1.513 (6)
O1—C33a	1.453 (14)	C8—C9	1.531 (5)
O1—C33b	1.481 (10)		
C24—C1—C2—C3	51.2 (5)	C12—C13—C14—C15	57.6 (5)
C1—C2—C3—C4	-112.2 (4)	C13—C14—C15—C16	-99.0 (4)
C6—C7—C8—C9	111.7 (4)	C18—C19—C20—C21	100.6 (4)
C7—C8—C9—C10	-61.0 (5)	C19—C20—C21—C22	-51.3 (5)

Data collection was performed at 120 K by means of a Huber four-circle diffractometer equipped with an Oxford Cryosystems Cryostream unit (Cosier & Glazer, 1986). The unit-cell dimensions were determined from reflections measured at $\pm 2\theta$. Data were corrected for background, Lorentz and polarization effects. The positions of H atoms were calculated. Non-H atoms were refined anisotropically. The propoxy groups attached to the two phenyl groups inclined to the axis of the molecule exhibit a twofold disorder. The disorder influences only the two middle atoms of the propoxy groups and the occupation factors were refined to 0.50 (2):0.50 (2) for one propoxy group and 0.42 (2):0.58 (2) for the other (sites labelled *a* and *b* in Fig. 1). The large displacement parameters of the C atoms in the propoxy groups clearly indicate that additional disorder is present but this was not modelled since the data available did not warrant the introduction of more parameters.

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *KRYSTAL*. Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*. Software used to prepare material for publication: *KRYSTAL*.

We are indebted to the Carlsberg Foundation and to the Danish Science Research Council for financing the Huber diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1468). Services for accessing these data are described at the back of the journal.

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A Benzannulated [5.3.1] Propellanone Related to the ABC Ring System of TaxolTM

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Abstract

The title compound, (3 α ,10 α)-11,11-dibromo-6-methoxy-2,3,3a,10a-tetrahydro-1*H*,4*H*-3a,10a-methanobenz[*f*]azulen-9(10*H*)-one, C₁₆H₁₆Br₂O₂, is shown to contain a C6-methoxylated aromatic ring and bears some resemblance to the ABC ring system of paclitaxel (TaxolTM).

Comment

In connection with efforts to use certain cyclohexannulated [5.3.1]propellanes for construction of the ABC ring system associated with the anticancer agent TaxolTM (Banwell, Gable, Peters & Phyland, 1995),