geometry at the chloroform C atom. All hydroxy H atoms were clearly resolved in difference maps; they were included in the refinement as riding atoms using *AFIX* 147 instructions as allowed for in *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD-4/PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93. Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF* (Ferguson, 1996).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1430). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Calix[4]arene with Diethylthiocarbamoylmethyloxy Substituents in the 1,3 Positions

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Abstract

The title compound 5,11,17,23-tetra-*tert*-butyl-*N*,*N*,-*N'*,*N'*-tetraethyl-26,28-dihydroxypentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,-19(28),21,23-dodecaene-25,27-diylbis(oxythioacetamide), $C_{56}H_{78}N_2O_4S_2$, was synthesized from the reaction of the known 1,3-bis(diethylamide)-substituted calix[4]-arene with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent). The calixarene is found to have a pinched-cone conformation, with no solvent molecule in the cavity.

Comment

The complexation of metal cations by calixarenes has been studied intensively in recent years. The focus of much of this work has been the binding of hard cations, from group I, group II and the lanthanides (for reviews see Bünzli & Harrowfield, 1991; Arnaud-Neu, 1994; Böhmer, 1995; Roundhill, 1995; McKervey, Schwing & Arnaud-Neu, 1996). More recently, examples of calixarene complexes of soft-metal cations have been reported; these include complexes of ligands involving metal–aryl ring interactions (Harrowfield, Ogden, Richmond, Skelton & White, 1993; Casnati *et al.*, 1995) and complexes of calixarenes functionalized with soft donor groups (Delaigue, Hosseini, Kyritsakas, De Cian & Fischer, 1995; Roundhill, 1995; Loeber, Matt, Briard & Grandjean, 1996; Xu, Vittal & Puddephatt, 1996). A relatively unexploited route to introducing soft donor

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Acta Crystallographica Section C
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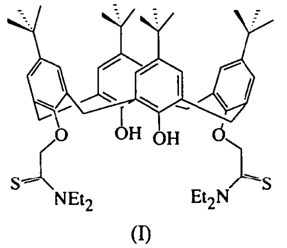
atoms into a calixarene framework is the conversion of amide functional groups to thioamides, by reaction with, for example, Lawesson's reagent (Scheibye, Pedersen & Lawesson, 1978). As part of our investigation of the cation-binding properties of amide-functionalized calix[4]arenes (Beer, Drew, Gale, Leeson & Ogden, 1994; Beer, Drew, Leeson & Ogden, 1995, 1996; Beer, Drew, Kan, Leeson, Ogden & Williams, 1996), we have structurally characterized a 1,3-bis(diethylthioamide)-substituted calix[4]arene, (I).



(I)

The asymmetric unit is comprised of a single calix[4]arene unit in the cone conformation. Remarkably, no solvent molecules are found in the cone cavity nor indeed anywhere in the structure. This conformation is often described with reference to the plane of the four methylene C atoms, C17, C27, C37 and C47. The angles of intersection with the planes of the four phenyl rings are: ring 1 87.7 (1), ring 2 40.8 (1), ring 3 82.4 (1) and ring 4 41.6 (1)°. Rings 1 and 3, which carry the thioamide substituents, are close to being perpendicular to the average plane of the methylene C atoms and the cone conformation has quasi C_2 symmetry rather than the C_4 symmetry usually found for an unsubstituted calix[4]arene. A similar conformation is found for the bis-substituted calix[4]arene bearing CH_2CN moieties (McKervey *et al.*, 1991); the analogous angles of intersection for the phenyl rings are 84.5, 38.6, 82.2 and 39.1°. It is possible that this 'pinching' of the cone prevents inclusion of solvent molecules within the cavity. The two thioamide groups in the title compound are oriented in a divergent fashion, though clearly it is possible that the conformation could easily change to convergent to form metal complexes similar to those found with the analogous amide compounds (Beer, Drew, Leeson & Ogden, 1996).

The H atoms presumed to reside on the unsubstituted phenol O atoms (O250 and O450) were not located. It is notable, however, that the interatomic distances to the neighbouring ether O atoms are not symmetrical (analogous distances for the dinitrile calix[4]arene mentioned above are given in square brackets): O250···O150 2.856 (5) [2.903 (3)], O250···O350 3.146 (4) [3.055 (4)], O450···O150 3.199 (4) [3.076 (4)], O450···O350 2.767 (5) Å [2.941 (3) Å]. The H atoms were located in the dinitrile structure and found to be associated with the shorter phenolic O···O distances. It is likely, therefore, that a phenolic H atom is positioned between O150 and O250, and between O350 and O450.

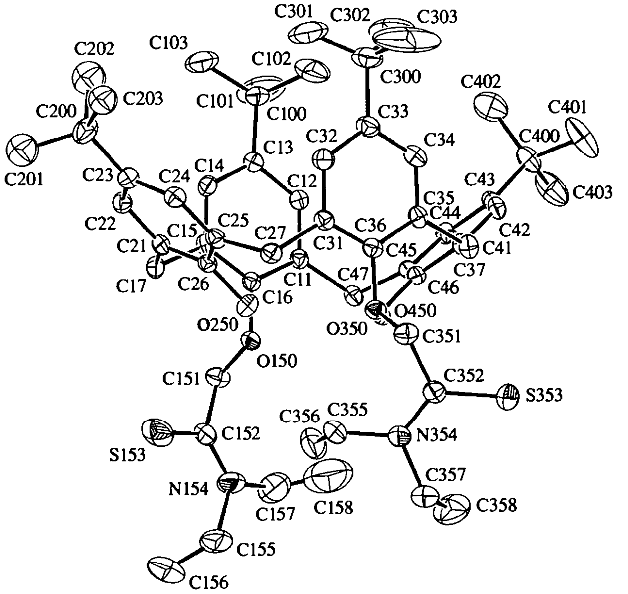


Fig. 1 The structure of the title compound. Displacement ellipsoids are plotted at the 25% probability level. H atoms are included with small arbitrary radii.

Experimental

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(diethylcarbamoyl)methoxy]-26,28-dihydroxycalix[4]arene (McKervey *et al.*, 1991) (1.0 g, 1.1 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent; Scheibye, Pedersen & Lawesson, 1978) (0.5 g, 1.2 mmol) were dissolved in dry toluene (50 ml). The mixture was heated at 333 K for 4 h and then filtered to give a yellow solution. The solvent was removed at reduced pressure and the resulting yellow solid was purified by column chromatography [alumina, dichloromethane/methanol (199/1)] to give the product (0.45 g). Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of the product in chloroform/ethanol. Analysis found: C 74.1, H 8.92, N 3.11, S 6.62%; calculated for $C_{56}H_{78}N_2O_4S_2$: C 74.1, H 8.67, N 3.09, S 7.07%.

Crystal data

$C_{56}H_{78}N_2O_4S_2$
$M_r = 907.32$
Triclinic
$P\overline{1}$
$a = 12.815\,(9)$ Å
$b = 14.798\,(12)$ Å
$c = 15.584\,(14)$ Å
$\alpha = 82.648\,(10)°$
$\beta = 77.869\,(10)°$
$\gamma = 67.661\,(10)°$
$V = 2669\,(4)$ Å^3
$Z = 2$
$D_x = 1.129$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1250 reflections
$\theta = 3.34$–$26.15°$
$\mu = 0.144$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
0.25 × 0.25 × 0.18 mm
Colourless

Data collection

Marresearch Image Plate
95 frames at 2° intervals, counting time 2 min
Absorption correction: none
16 265 measured reflections
9432 independent reflections
6739 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\rm max} = 26.15°$
$h = 0 \rightarrow 15$
$k = -16 \rightarrow 18$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.0831$
$wR(F^2) = 0.2928$
$S = 0.615$
9432 reflections
595 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.2778P)^2 + 11.3102P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.438$
$\Delta\rho_{\rm max} = 0.562$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.446$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection used rotation about a single axis, giving 85.6% data completeness. Interframe scaling indicated no significant intensity decay. H atoms were constrained to ideal positions with a riding model including torsional freedom for methyl groups and with isotropic displacement parameters [$U(\rm H) = 1.2U_{\rm eq}(\rm C)$]. One *tert*-butyl group was disordered. The *tert*-butyl groups in general had high displacement parameters with significant anisotropy; this could indicate further disorder, but it could not be resolved. The highest Δ/σ ratio is for atoms in the disordered groups and these are probably responsible for the high final residuals.

Data collection: *XDS* (Kabsch, 1988). Cell refinement: *XDS*. Data reduction: *XDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*94 (Spek, 1994).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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meta-Nitroacetophenone at 173 K

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Abstract

The title compound, methyl 2-nitrophenyl ketone, $C_8H_7NO_3$, crystallizes as a nearly planar molecule. Layers parallel to the $(\bar{2}02)$ plane are stabilized by intermolecular C—H···O contacts. The molecular geometry is very similar to that of *para*-nitroacetophenone, but some bond lengths of the aromatic ring are significantly different. The molecular geometry agrees well with a recent room-temperature structure determination.

Comment

The crystal structure of *m*-nitroacetophenone, (I), has been determined. The structure agrees well with the recent room-temperature structure determination of *m*-nitroacetophenone (Feeder, Jones, Chorlton & Docherty, 1996); a least-squares fit of all non-H atoms shows an r.m.s. deviation of 0.018 Å. Bond lengths and angles are as expected.