

C2—O1—C6	108.4 (3)	O1—C6—C5	109.5 (3)
O1—C2—O3	112.7 (2)	O8—P7—C15	112.97 (13)
O1—C2—P7	107.3 (2)	O8—P7—C9	113.20 (12)
O3—C2—P7	107.3 (2)	C15—P7—C9	106.81 (11)
C2—O3—C4	109.2 (3)	O8—P7—C2	114.42 (11)
O3—C4—C5	109.0 (3)	C15—P7—C2	104.10 (11)
C6—C5—C4	108.8 (3)	C9—P7—C2	104.49 (11)
C6—O1—C2—O3	64.5 (3)	C15—P7—C9—C14	69.0 (2)
C6—O1—C2—P7	−177.6 (3)	C2—P7—C9—C14	−40.9 (2)
O1—C2—O3—C4	−64.7 (4)	O8—P7—C9—C10	16.1 (3)
P7—C2—O3—C4	177.5 (3)	C15—P7—C9—C10	−108.8 (2)
C2—O3—C4—C5	58.5 (5)	C2—P7—C9—C10	141.2 (2)
O3—C4—C5—C6	−55.2 (5)	O8—P7—C15—C16	−6.7 (3)
C2—O1—C6—C5	−59.1 (4)	C9—P7—C15—C16	118.3 (2)
C4—C5—C6—O1	55.7 (5)	C2—P7—C15—C16	−131.5 (2)
O1—C2—P7—O8	−62.6 (2)	O8—P7—C15—C20	174.6 (2)
O3—C2—P7—O8	58.6 (2)	C9—P7—C15—C20	−60.3 (2)
O1—C2—P7—C15	61.1 (2)	C2—P7—C15—C20	49.9 (2)
O3—C2—P7—C15	−177.6 (2)	H2—C2—P7—O8	−176.7 (13)
O1—C2—P7—C9	173.0 (2)	H2—C2—P7—C9	59.0 (13)
O3—C2—P7—C9	−65.7 (2)	H2—C2—P7—C15	−52.9 (13)
O8—P7—C9—C14	−166.0 (2)		

Table 2. Asymmetry parameters (°) (Duax & Norton, 1975) of the 1,3-dioxane ring of (1)

$\Delta C_1(O1) = \Delta C_1(C4)$	6.4 (8)	$\Delta C_2(O1-C2) = \Delta C_2(C4-C5)$	4.4 (8)
$\Delta C_2(C2) = \Delta C_2(C5)$	0.5 (8)	$\Delta C_2(C2-O3) = \Delta C_2(C5-C6)$	5.1 (9)
$\Delta C_1(O3) = \Delta C_1(C6)$	6.7 (8)	$\Delta C_2(O3-C4) = \Delta C_2(C6-O1)$	9.2 (9)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...O8 ⁱ	1.02 (2)	2.22 (2)	3.242 (3)	172 (2)
C6—H61...O8 ⁱ	1.00 (5)	2.79 (5)	3.609 (5)	139 (3)
C10—H10...O8	0.89 (3)	2.68 (3)	3.069 (4)	108 (3)
C14—H14...O8 ⁱ	0.99 (3)	2.79 (3)	3.762 (3)	168 (2)
C16—H16...O8	0.97 (4)	2.53 (4)	3.050 (4)	114 (3)
C18—H18...O3 ⁱⁱ	0.99 (4)	2.52 (4)	3.363 (4)	142 (3)
C20—H20...O8 ⁱ	1.02 (3)	2.75 (3)	3.705 (4)	155 (2)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$.

Anisotropic displacement parameters were applied for all non-H atoms. H atoms were found in a difference Fourier map and refined isotropically.

Data collection: *CAD-4 Manual* (Schagen, Straver, van Meurs & Williams, 1989). Cell refinement: *CAD-4 Manual*. Data reduction: *SDP* (Frenz, 1986). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP in SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXTL-Plus* and *CSU* (Vicković, 1988).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Duax, W. L. & Norton, D. A. (1975). In *Atlas of Steroid Structures*. New York: Plenum.
- Frenz, B. A. (1986). *Enraf-Nonius Structure Determination Package; SDP Users Guide*. Version of 17 December 1986. Enraf-Nonius, Delft, The Netherlands.
- Mikołajczyk, M., Graczyk, P., Potrzebowski, M., Wieczorek, M. W. & Błaszczyk, J. (1995). *Phosphorus Sulfur Silicon*, **103**, 111–124.
- Mikołajczyk, M., Graczyk, P. & Wieczorek, M. W. (1994). *J. Org. Chem.* **59**, 1672–1693.

- Mikołajczyk, M., Graczyk, P., Wieczorek, M. W. & Bujacz, G. (1988). *Tetrahedron Lett.* **29**, 6801–6804.
- Mikołajczyk, M., Graczyk, P., Wieczorek, M. W. & Bujacz, G. (1992). *Tetrahedron*, **48**, 4209–4230.
- Mikołajczyk, M., Graczyk, P., Wieczorek, M. W., Bujacz, G., Struchkov, Y. T. & Antipin, M. Y. (1988). *J. Org. Chem.* **53**, 3609–3612.
- Mikołajczyk, M., Mikina, M., Graczyk, P., Wieczorek, M. W. & Bujacz, G. (1991). *Tetrahedron Lett.* **32**, 4189–4192.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Schagen, J. D., Straver, L., van Meurs, F. & Williams, G. (1989). *CAD-4 Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.
- Wieczorek, M. W., Bujacz, G., Majzner, W. R., Graczyk, P. & Mikołajczyk, M. (1995). *Heteroatom Chem.* **6**, 377–386.

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Intra- and Intermolecular Hydrogen Bonding in a Tetrahydroxycalix[4]arene

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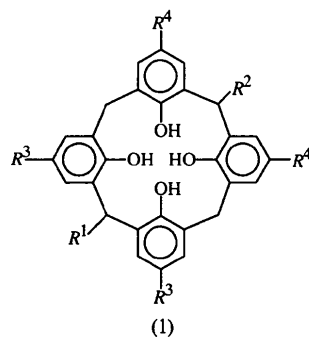
Abstract

The title calix[4]arene, *cis*-11,17-di-*tert*-butyl-2,5,23-trimethyl-14-(4-nitrophenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene-25,26,27,28-tetraol-chloroform (1/0.5), C₄₅H₄₉NO₆·0.5CHCl₃, substituted at two opposite methylene bridges by methyl and *p*-nitrophenyl groups, forms centrosymmetric hydrogen-bonded dimers in the solid state. This results in an eight-membered (O—H...O)₈ ring, with O...O distances in the range 2.637(4)–2.828(4) Å. Pairs of calix[4]arene molecules (related by another inversion centre) each have a *p*-methyl group of one molecule fitting snugly into the cavity of the other, with shortest intermolecular C...C

contacts corresponding to normal C··· π -arene interactions. The half-occupancy chloroform molecule lies disordered about another independent inversion centre filling what would otherwise have been a void in the crystal lattice.

Comment

Due to their closed circle of intramolecular hydrogen bonds, calix[4]arenes are rather apolar molecules, forming molecular lattices in the crystalline state where usually no intermolecular OH···O contacts are found. In calix[4]arenes with two opposite *para* positions bridged by an aliphatic chain, a gradual distortion of the cone conformation is possible by reduction of the chain length (Goldmann, Vogt, Paulus & Böhmer, 1989). This leads to weaker intramolecular hydrogen bonds, shown in solution by changes in the IR and NMR spectra. For the shortest bridging chain with five C atoms, an arrangement was found where two molecules form pairs with intermolecular O···O distances (2.83 and 2.86 Å) being in the range associated with hydrogen bonds (Böhmer *et al.*, 1990). However, since the H atoms could not be clearly located in that case, a clear distinction between intra- and intermolecular hydrogen bonds was not made. We have recently synthesized calix[4]arenes of general formula (1) with one or two opposite methylene bridges replaced by alkanediyl bridges (Grüttner *et al.*, 1994; Biali *et al.*, 1996). Interpretation of the ¹H NMR spectra for these compounds suggested that they assume the usual open-cone conformation in solution, with aliphatic residues R¹ (or R²) preferring an equatorial orientation; no pronounced preferences were found for aromatic residues. We report here on the structure of the *cis* isomer of compound (2) (R¹ and R³ = Me, R² = 4-NO₂-Ph and R⁴ = ^tBu), where there is clear evidence for the first time of intermolecular O—H···O hydrogen bonding.



Molecule (2) crystallizes in the triclinic system with one molecule of the calixarene (Fig. 1) and half a molecule of CHCl₃ per asymmetric unit. The calixarene molecule is in the familiar open-cone conformation. The shape of the calix cavity is defined by the interplanar

angles which the various aromatic rings make with the plane of the four methylene C atoms (C17, C27, C37 and C47) which link them; these angles are 124.6(1), 121.9(1), 108.3(1) and 132.7(2)° for rings C11–C16 (*i* = 1–4), respectively. In (1) (R¹, R² = H and R³, R⁴ = ^tBu, and which has crystallographic fourfold symmetry), the corresponding value is 123° (Andreetti, Ungaro & Pochini, 1979), but dihedral angles in the range 115–137° have been reported in other calix[4]arenes (Ungaro, Pochini, Andreetti & Sangermano, 1984).

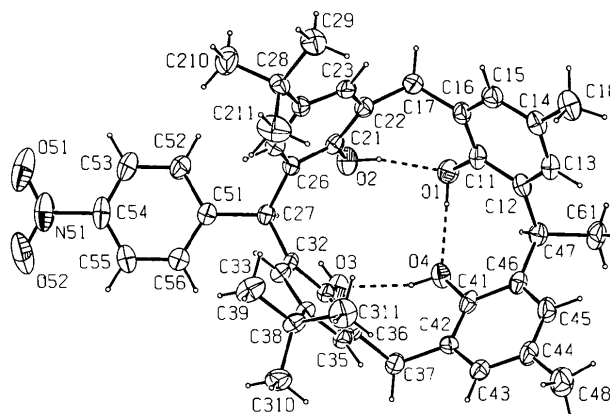


Fig. 1. The molecular conformation of (2) and the crystallographic numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

What is unusual about the present structure (2) is that instead of forming an intramolecular sequence of O—H···O hydrogen bonds at the base of the cone as has been seen in many previous calix[4]arenes and calix[5]arenes, the molecules are linked about an inversion centre at ($\frac{1}{2}, \frac{1}{2}, 0$) by pairs of intermolecular O—H···O hydrogen bonds to form centrosymmetric dimers with an eight-membered (O—H···)₈ ring having graph-set notation R₄⁴(16) (Bernstein, Davis, Shimoni & Chang, 1994). The intramolecular O—H···O hydrogen bonds [2.637(4)–2.703(4) Å; Table 2] are slightly shorter than the intermolecular one [2.828(4) Å]. The intramolecular O2···O3 distance of 3.250(5) Å corresponds to a normal non-bonded contact. It should be noted that the OH group of ring C31–C36, which is the closest to being perpendicular to the methylene plane, is the donor in the intermolecular hydrogen bonding. Consideration of intramolecular contacts and bond angles would indicate that this distortion of the calixarene skeleton appears not to be caused by the presence at C27 of the *p*-nitrophenyl group, which is symmetrically positioned and inclined at only 11.8(2)° to the plane of the methylene C atoms.

The further arrangement of these hydrogen-bonded dimers is not uncommon for calixarenes. There is mutual self-inclusion of one of the *p*-methyl groups

(C18) into the cavity of the adjacent molecule related by an inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2); the shortest intermolecular contact is $\text{C18} \cdots \text{C13}^{\text{ii}}$ [symmetry code: (ii) $1-x, 1-y, 1-z$] of 3.710 (6) Å and is typical of methyl $\cdots\pi$ -(arene) interactions (see *e.g.* Gallagher, Ferguson, Böhmer & Kraft, 1994). In this way, infinite chains of molecules are developed extending along the *c* direction.

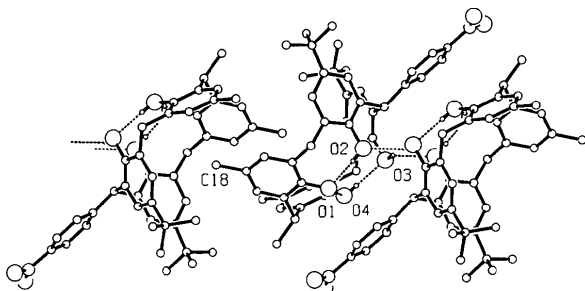


Fig. 2. Ensemble of three molecules of (2) showing the intermolecular hydrogen-bonded dimers and the mutual self-inclusion via the *p*-methyl groups. For clarity, all H atoms except hydroxy H atoms have been omitted.

The half-occupancy chloroform molecule lies disordered about another independent inversion centre (at 0,0,0), filling what would have been a void in the crystal lattice; it does not intrude into the calix cavity as has been observed in many cases, the cavity being already filled as noted above.

The reason for the unusual intermolecular hydrogen-bond formation in (2) is presumably a result of the fine interplay of hydrogen bonding and the myriad of intermolecular packing effects. The present example shows clearly that the cyclic array of intramolecular hydrogen bonds in calix[4]arenes is not so stable, that intermolecular hydrogen bonds cannot be formed if the molecules are suitably packed in the crystal lattice.

Experimental

Compound (2) was synthesized by fragment condensation from 4,4'-dimethyl-2,2'-(ethane-1,1-diyl)diphenol and 6,6'-dibromomethyl-4,4'-di-*tert*-butyl-2,2'-(4-nitrophenylmethanediyl)diphenol in dioxane with TiCl_4 (Böhmer, Merkel & Kunz, 1987). The alkanediyl diphenols were prepared by acid-catalysed condensation of *p*-cresol and acetic aldehyde or of *p*-*tert*-butylphenol and *p*-nitrobenzaldehyde (Grüttner, Böhmer, Assmus & Scherf, 1995). The *cis* and *trans* isomers of (2) were separated by column chromatography. Yield (*cis* isomer) 15%, m.p. 595–597 K ($\text{CHCl}_3/\text{MeOH}$); ^1H NMR (CDCl_3 , 298 K) 10.03 (*s*, 4H, OH), 8.15 (*d*, 2H, H *ortho* to NO_2), 7.52 (*d*, 2H, H *meta* to NO_2), 7.01 (*s*, 2H, ArH), 6.96 (*s*, 2H, ArH), 6.93 (*s*, 2H, ArH), 6.87 (*s*, 2H, ArH), 6.14 (*s*, 1H, CH), 4.72 (*q*, 1H, CH), 4.23 (*d*, 2H, CH_2), 3.50 (*d*, 2H, CH_2), 2.18 (*s*, 6H, CH_3), 1.69 (*d*, 3H, CH_3), 1.12 (*s*, 18 H, CMe_3). Crystals of (2) suitable for X-ray analysis were obtained by recrystallization from chloroform/methanol.

Crystal data

$\text{C}_{45}\text{H}_{49}\text{NO}_6 \cdot 0.5\text{CHCl}_3$
 $M_r = 759.54$
 Triclinic
 $P\bar{1}$
 $a = 10.3121(12)$ Å
 $b = 13.9765(12)$ Å
 $c = 14.973(2)$ Å
 $\alpha = 101.622(8)^\circ$
 $\beta = 104.206(10)^\circ$
 $\gamma = 99.248(8)^\circ$
 $V = 1998.3(4)$ Å³
 $Z = 2$
 $D_x = 1.262$ Mg m⁻³
 D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 6962 measured reflections
 6962 independent reflections
 2071 reflections with
 $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 25
 reflections
 $\theta = 5.6\text{--}17.4^\circ$
 $\mu = 0.179$ mm⁻¹
 $T = 294(1)$ K
 Needle
 $0.40 \times 0.14 \times 0.10$ mm
 Very pale yellow

$\theta_{\text{max}} = 25^\circ$
 $h = -12 \rightarrow 11$
 $k = 0 \rightarrow 16$
 $l = -17 \rightarrow 17$
 3 standard reflections
 frequency: 120 min
 intensity variation: 1.0%

Refinement

Refinement on F^2
 $R(F) = 0.0536$
 $wR(F^2) = 0.1803$
 $S = 0.847$
 6962 reflections
 513 parameters
 H atoms riding (C—H 0.93–
 0.98 and O—H 0.82 Å)
 $w = 1/[\sigma^2(F_o^2) + (0.0871P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.304$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.290$ e Å⁻³
 Extinction correction:
 SHELXL93
 Extinction coefficient:
 0.0070 (13)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C11	1.394 (5)	O51—N51	1.222 (7)
O2—C21	1.390 (5)	O52—N51	1.199 (7)
O3—C31	1.395 (5)	N51—C54	1.487 (7)
O4—C41	1.381 (5)	O2—O3	3.250 (5)
C16—C17—C22	114.7 (4)	C36—C37—C42	112.5 (4)
C26—C27—C32	108.0 (3)	C12—C47—C46	110.1 (3)

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>
O1—H1 $\cdots$ O4	0.82	1.86	2.674 (5)
O2—H2 $\cdots$ O1	0.82	1.84	2.637 (4)
O3—H3 $\cdots$ O2 ⁱ	0.82	2.21	2.828 (4)
O4—H4 $\cdots$ O3	0.82	1.91	2.703 (4)

Symmetry code: (i) $1-x, 1-y, -z$.

During the solution of the structure it became apparent that there was a set of electron-density maxima centred around the origin which could be interpreted as a disordered chloroform molecule. Initial refinement of an occupancy factor for this molecule led to a value which was not significantly different from 0.5 and in subsequent cycles the occupancy was fixed at 0.5. The C—Cl distances were fixed at 1.768 Å (Orpen *et al.*, 1994) and the intramolecular Cl $\cdots$ Cl distances restrained to have similar values to give approximately tetrahedral

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 *SHELXL93* (Sheldrick, 1993).

Data collection: *CAD-4/PC* (Enraf-Nonius, 1992). Cell refinement: *SET4* and *CELDIM* (Enraf-Nonius, 1992). Data reduction: *DATRD2 NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX94* and *SHELXL93*. Molecular graphics: *NRCVAX94*, *ORTEP-II* (Johnson, 1976), *PLATON* (Spek, 1996a) and *PLUTON* (Spek 1996b). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* 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.

References

- Andreotti, G. D., Ungaro, R. & Pochini, A. (1979). *J. Chem. Soc. Chem. Commun.* pp. 1005–1007.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1994). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Biali, S. E., Böhmer, V., Cohen, S., Ferguson, G., Grüttner, C., Grynszpan, F., Paulus, E. F., Thondorf, I. & Vogt, W. (1996). *J. Am. Chem. Soc.* **118**, 12938–12949.
- Böhmer, V., Goldmann, H., Vogt, W., Paulus, E. F., Tobiasson, F. L. & Thielman, M. J. (1990). *J. Chem. Soc. Perkin Trans. 2*, pp. 1769–1775.
- Böhmer, V., Merkel, L. & Kunz, U. (1987). *J. Chem. Soc. Chem. Commun.* pp. 896–897.
- Enraf-Nonius (1992). *CAD-4/PC Software*. Version 1.1. Enraf-Nonius, Delft, The Netherlands.
- Ferguson, G. (1996). *PREPCIF. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs*. University of Guelph, Canada.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Gallagher, J. F., Ferguson, G., Böhmer, V. & Kraft, D. (1994). *Acta Cryst. C50*, 73–77.
- Goldmann, H., Vogt, W., Paulus, E. F. & Böhmer, V. (1989). *J. Am. Chem. Soc.* **110**, 6811–6817.
- Grüttner, C., Böhmer, V., Assmus, R. & Scherf, S. (1995). *J. Chem. Soc. Perkin Trans. 1*, pp. 93–94.
- Grüttner, C., Böhmer, V., Vogt, W., Thondorf, I., Biali, S. E. & Grynszpan, F. (1994). *Tetrahedron Lett.* **35**, 6267–6270.
- Johnson, C. K. (1976). *ORTEP-II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlations*, Vol. 2, edited by H.-B. Burgi & J. D. Dunitz. Weinheim, Germany: VCH.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1996a). *PLATON. Molecular Geometry Program*. Version of August 1996. University of Utrecht, The Netherlands.
- Spek, A. L. (1996b). *PLUTON. Molecular Graphics Program*. Version of August 1996. University of Utrecht, The Netherlands.
- Ungaro, R., Pochini, A., Andreotti, G. D. & Sangermano, V. (1984). *J. Chem. Soc. Perkin Trans. 2*, pp. 1979–1985.

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A Calix[4]arene with Diethylthiocarbamoylmethoxy 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-dihydropentacyclo[19.3.1.1^{3,7}.-19,13.1^{15,19}]octacos-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene-25,27-diylbis(oxythioacetamide), C₅₆H₇₈N₂O₄S₂, 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; McKerver, 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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