

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.142$
 $S = 1.153$
 3476 reflections
 294 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.332 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.487 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)

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

| | | | |
|-------------|-----------|-------------|------------|
| C1—O2 | 1.183 (4) | C3—C4 | 1.517 (4) |
| C1—O1 | 1.380 (4) | C4—C5 | 1.340 (4) |
| C1—C2 | 1.476 (4) | C4—O1 | 1.382 (3) |
| C2—C3 | 1.527 (4) | C5—C7 | 1.473 (5) |
| C3—N1 | 1.484 (3) | C5—C6 | 1.515 (5) |
| O2—C1—O1 | 119.3 (3) | C4—C3—C2 | 101.9 (2) |
| O2—C1—C2 | 131.1 (3) | O1—C4—C3 | 109.1 (2) |
| O1—C1—C2 | 109.5 (3) | C1—O1—C4 | 110.7 (2) |
| C1—C2—C3 | 105.2 (2) | C3—N1—C9 | 118.5 (2) |
| C1—C2—C3—N1 | 94.9 (2) | C3—C4—C5—C6 | -173.5 (3) |
| C1—C2—C3—C4 | -17.8 (2) | C4—C5—C7—O3 | 163.3 (3) |
| N1—C3—C4—C5 | 77.0 (4) | C4—C3—N1—C9 | -179.4 (2) |

The absolute structure Flack (1983) parameter [$\chi = 1.8(17)$] was inconclusive; the absolute configuration was deduced from the known stereochemistry of the synthesis. H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, while methyl group H atoms were assigned $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. For the H atoms of the C6 methyl group, the torsion angle was also refined. The H atom on N1 was located from a difference map and refined isotropically.

Data collection: *DIF4* (Stoe & Cie, 1987a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1987b). Program used to solve structure: *SHELXS86* (Sheldrick, 1990). Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL93*. Other programs include *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1492). Services for accessing these data are described at the back of the journal.

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15,17-Di-2-propenylcalix[4]arene-25,26,27,28-tetrol: Self-Complexation and C—H...O Interactions

SYBOLT HARKEMA,^a JAN-DIRK VAN LOON,^b WILLEM VERBOOM^b AND DAVID N. REINHOUT^b

^aLaboratory of Chemical Physics, University of Twente, POB 217, 7500 AE Enschede, The Netherlands, and

^bLaboratory of Organic Chemistry, University of Twente, POB 217, 7500 AE Enschede, The Netherlands.

E-mail: s.harkema@tn.utwente.nl

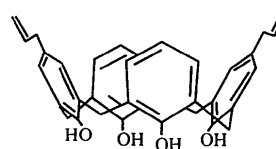
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Abstract

The crystal structure of 15,17-di-2-propenylcalix[4]arene-25,26,27,28-tetrol [systematic name: 15,17-di-2-propenylpentacyclo[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-dodecane-25,26,27,28-tetrol], $\text{C}_{34}\text{H}_{32}\text{O}_4$, was determined. The calix[4]arene molecule shows a cone conformation, stabilized by a ring-like hydrogen-bond pattern of the four hydroxyl H atoms. In the crystal structure, complexation of one of the propenyl side chains in the cavity of another calixarene molecule is found. The other side chain shows C—H...O interactions with a neighboring calixarene molecule.

Comment

Calix[4]arenes have received considerable attention in the field of supramolecular chemistry because they can form inclusion complexes with cations, anions or neutral molecules (Gutsche, 1989; Vicens & Böhmer, 1991; Böhmer, 1995). The conformation of calixarenes has been studied both in the solid state (Andreotti & Uguzzoli, 1991) and in solution (Groenen *et al.*, 1991). Four different conformations can be identified.



The title compound, (I), has a regular cone conformation (Fig. 1), stabilized by four hydrogen bonds connecting the O atoms in a ring-like fashion. Hydrogen-bond data are included in Table 1. The regularity of the conformation is evidenced by the distances between neighboring O atoms [2.661 (3), 2.642 (3), 2.659 (3) and

2.699 (3) Å] and the angles between the best planes of the phenyl rings and the best plane fitted to the connecting methylene C atoms [51.6 (1), 59.8 (1), 48.0 (1) and 62.7 (1)°]. The packing diagram (Fig. 2) shows that

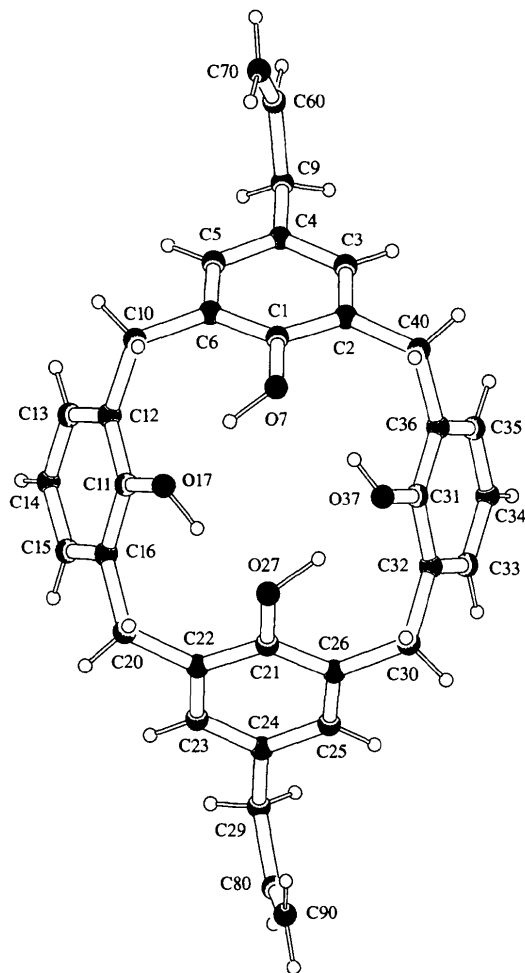


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing showing the atomic numbering.

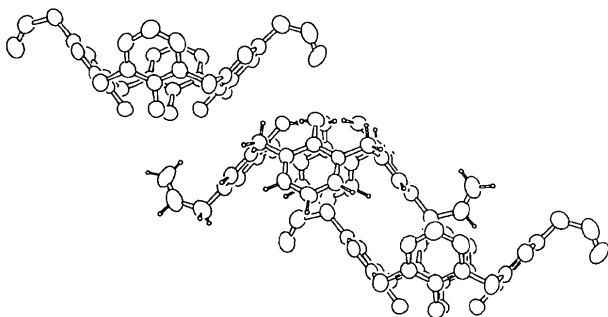


Fig. 2. *ORTEP* (Johnson, 1976) view showing part of the packing. H atoms have been omitted for clarity, except for those of the central molecule. Displacement ellipsoids are scaled to include 50% probability.

one of the propenyl chains is complexed in the apolar cavity of a neighboring calixarene molecule, forming centrosymmetric pairs. The other propenyl chain shows a short C—H···O contact of one of the vinylic H atoms with one of the O atoms of a different molecule (H90B···O27 2.82 Å and C90—H90B···O27 160°). The two molecules involved in this interaction are also related by a center of symmetry.

Experimental

The title compound was prepared according to van Loon (1992) and van Loon *et al.* (1990). Colorless crystals were obtained by recrystallization from dichloromethane. Only small crystals could be obtained, resulting in a rather small number of observed reflections.

Crystal data

C₃₄H₃₂O₄
M_r = 504.6
 Monoclinic
*P*2₁/*c*
a = 16.206 (2) Å
b = 8.991 (4) Å
c = 18.665 (2) Å
 β = 102.91 (2)°
V = 2651 (2) Å³
Z = 4
D_x = 1.264 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 7.0–14.1°
 μ = 0.076 mm⁻¹
T = 293 K
 Parallelepiped
 0.50 × 0.20 × 0.20 mm
 Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4810 measured reflections
 4666 independent reflections
 2444 reflections with $I > \sigma(I)$

*R*_{int} = 0.018
 θ_{\max} = 25°
h = 0 → 18
k = 0 → 10
l = -22 → 22
 3 standard reflections
 frequency: 60 min
 intensity decay: <3%

Refinement

Refinement on *F*²
R(*F*) = 0.096
 $wR(F^2)$ = 0.101
S = 1.073
 4666 reflections
 360 parameters
 H atoms treated as riding atoms except for hydroxyl H atoms
 $w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{\max}$ = 0.02
 $\Delta\rho_{\max}$ = 0.32 e Å⁻³
 $\Delta\rho_{\min}$ = -0.40 e Å⁻³
 Extinction correction: Zachariasen (1963)
 Extinction coefficient: 2.5 (4) × 10⁻⁷
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|---------|-----------|---------|-----------|
| O7—C1 | 1.400 (4) | C14—C15 | 1.390 (5) |
| O7—H7 | 1.05 (4) | C15—C16 | 1.386 (5) |
| O17—C11 | 1.392 (4) | C16—C20 | 1.517 (4) |
| O17—H17 | 1.03 (4) | C20—C22 | 1.514 (4) |
| O27—C21 | 1.382 (4) | C21—C22 | 1.400 (4) |
| O27—H27 | 1.11 (5) | C21—C26 | 1.397 (4) |

| | | | |
|-------------|-----------|---------------|-----------|
| O37—C31 | 1.392 (3) | C22—C23 | 1.392 (5) |
| O37—H37 | 0.91 (5) | C23—C24 | 1.374 (4) |
| C1—C2 | 1.386 (4) | C24—C25 | 1.390 (5) |
| C1—C6 | 1.383 (4) | C24—C29 | 1.506 (5) |
| C2—C3 | 1.394 (4) | C25—C26 | 1.387 (5) |
| C2—C40 | 1.512 (5) | C26—C30 | 1.520 (4) |
| C3—C4 | 1.386 (5) | C29—C80 | 1.511 (6) |
| C4—C5 | 1.388 (4) | C30—C32 | 1.517 (4) |
| C4—C9 | 1.501 (4) | C31—C32 | 1.389 (4) |
| C5—C6 | 1.395 (4) | C31—C36 | 1.397 (4) |
| C6—C10 | 1.511 (4) | C32—C33 | 1.404 (4) |
| C9—C60 | 1.483 (6) | C33—C34 | 1.386 (5) |
| C10—C12 | 1.521 (5) | C34—C35 | 1.382 (5) |
| C11—C12 | 1.387 (5) | C35—C36 | 1.381 (4) |
| C11—C16 | 1.399 (4) | C36—C40 | 1.518 (5) |
| C12—C13 | 1.389 (5) | C60—C70 | 1.277 (5) |
| C13—C14 | 1.378 (5) | C80—C90 | 1.249 (6) |
| O7—C1—C2 | 117.9 (3) | C21—C22—C23 | 117.5 (3) |
| C2—C1—C6 | 122.9 (3) | C22—C23—C24 | 122.7 (4) |
| O7—C1—C6 | 119.3 (2) | C23—C24—C29 | 120.8 (3) |
| C1—C2—C40 | 122.7 (3) | C23—C24—C25 | 117.9 (4) |
| C3—C2—C40 | 120.3 (2) | C25—C24—C29 | 121.2 (3) |
| C1—C2—C3 | 117.0 (3) | C24—C25—C26 | 122.4 (3) |
| C2—C3—C4 | 123.1 (3) | C25—C26—C30 | 121.4 (3) |
| C3—C4—C5 | 117.0 (3) | C21—C26—C30 | 120.9 (3) |
| C3—C4—C9 | 121.4 (3) | C21—C26—C25 | 117.8 (3) |
| C5—C4—C9 | 121.7 (3) | C24—C29—C80 | 115.8 (3) |
| C4—C5—C6 | 122.7 (3) | C26—C30—C32 | 113.0 (3) |
| C1—C6—C10 | 122.7 (3) | O37—C31—C32 | 117.7 (3) |
| C5—C6—C10 | 119.8 (3) | C32—C31—C36 | 122.7 (3) |
| C1—C6—C5 | 117.4 (2) | O37—C31—C36 | 119.7 (3) |
| C4—C9—C60 | 115.3 (3) | C30—C32—C31 | 123.3 (2) |
| C6—C10—C12 | 113.2 (2) | C30—C32—C33 | 119.5 (3) |
| O17—C11—C16 | 118.7 (3) | C31—C32—C33 | 117.3 (3) |
| C12—C11—C16 | 122.8 (3) | C32—C33—C34 | 121.0 (4) |
| O17—C11—C12 | 118.6 (3) | C33—C34—C35 | 119.6 (3) |
| C10—C12—C13 | 121.1 (3) | C34—C35—C36 | 121.6 (4) |
| C10—C12—C11 | 121.3 (3) | C31—C36—C40 | 122.0 (2) |
| C11—C12—C13 | 117.7 (3) | C31—C36—C35 | 117.9 (3) |
| C12—C13—C14 | 121.3 (3) | C35—C36—C40 | 120.2 (3) |
| C13—C14—C15 | 119.7 (4) | C2—C40—C36 | 112.3 (3) |
| C14—C15—C16 | 121.3 (4) | C9—C60—C70 | 129.6 (3) |
| C15—C16—C20 | 120.2 (3) | C29—C80—C90 | 129.0 (4) |
| C11—C16—C20 | 122.5 (3) | C1—O7—H7 | 118 (2) |
| C11—C16—C15 | 117.3 (3) | C11—O17—H17 | 106 (3) |
| C16—C20—C22 | 113.2 (2) | C21—O27—H27 | 115 (2) |
| O27—C21—C26 | 119.8 (3) | C31—O37—H37 | 112 (2) |
| O27—C21—C22 | 118.5 (3) | O7—H7...O17 | 166 (4) |
| C22—C21—C26 | 121.7 (3) | O17—H17...O27 | 165 (3) |
| C20—C22—C23 | 121.2 (3) | O27—H27...O37 | 168 (4) |
| C20—C22—C21 | 121.3 (3) | O7—H37...O37 | 164 (4) |

Data were collected in the $\omega/2\theta$ -scan mode [scan width (ω): $1.3 + 0.35 \tan \theta$], using graphite-monochromated Mo $K\alpha$ radiation. The intensity data were corrected for Lorentz and polarization effects and for long time-scale variation. No absorption correction was applied. The structure was solved with *MULTAN* (Germain *et al.*, 1971) and refined by full-matrix least squares. Refinements (on F^2) were made, using all reflections. Weights for each reflection in the refinement were $w = 1/[\sigma^2(F_o^2)]$, $\sigma(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined as 0.04. All calculations were performed with *SDP* (B. A. Frenz & Associates Inc., 1983). All heavy atoms were refined with anisotropic displacement parameters. H atoms were placed at calculated positions (C—H 0.95 Å) and treated as riding atoms, except for the hydroxyl H atoms, which were found from a difference Fourier synthesis and refined with isotropic displacement parameters.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CAD-4 EXPRESS*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1242). Services for accessing these data are described at the back of the journal.

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3-Methyl-1,5-dinitro-3-azabicyclo[3.3.1]non-7-ene

O. V. SHISHKIN,^a YU. M. ATROSCHENKO,^b S. S. GITIS,^b
E. N. ALIFANOVA^b AND I. V. SHAKHKELDYAN^b

^aA. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 28 Vavilov Str., Moscow 117813, Russia, and ^bTula State Pedagogical University, 125 Lenina Ave., Tula 300026, Russia. E-mail: oleg@xray.ineos.ac.ru

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Abstract

The 3-azabicyclo[3.3.1]non-7-ene skeleton of the title compound, C₉H₁₃N₃O₄, has a sofa-chair conformation. There are two molecules in the asymmetric unit with different orientations of their nitro groups.