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5,11,17,23-Tetranitro-25,26,27,28-tetrapentyloxycalix[4]arene

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.082
wR factor = 0.247
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of the title compound, $C_{48}H_{60}N_4O_{12}$, is located on a crystallographic twofold rotation axis. It is found in the typical pinched cone conformation. The dihedral angles between the reference plane (defined by the C atoms of the methylene bridges) and the benzene rings are 83.33 (6) and 141.61 (5)°.

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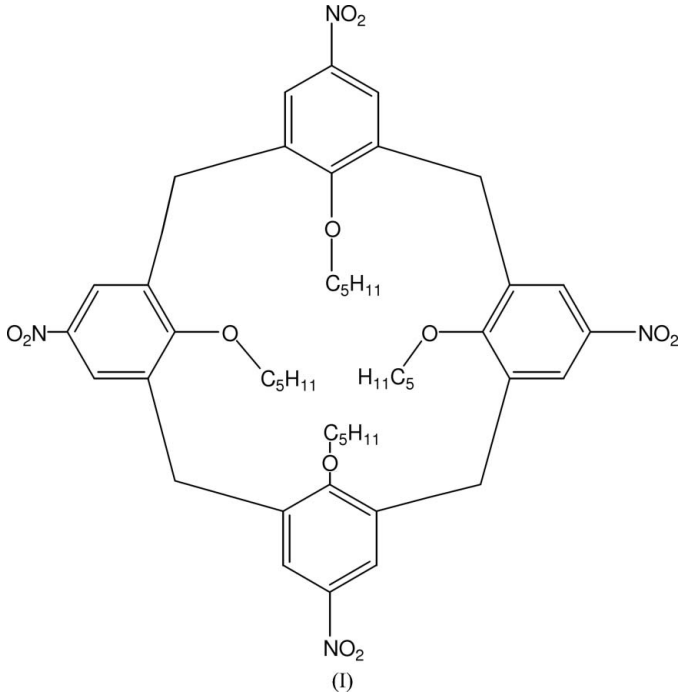
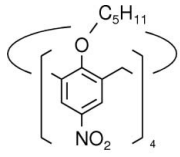
Comment

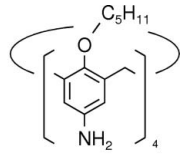
5,11,17,23-Tetranitro-25,26,27,28-tetrapentyloxycalix[4]arene, (I), was prepared by *ipso*-nitration of the corresponding tetrapentyloxycalix[4]arene with four *tert*-butyl groups at the wide rim (Jakobi *et al.*, 1996). It can be easily reduced to the tetraamino derivative, (II) (see scheme) (Jakobi *et al.*, 1996), the starting material for the synthesis of various derivatives, *e.g.* tetra-CMPO and tetraurea-calix[4]arenes.



(I)



(I)



(II)

CMPO (carbamoylmethylphosphineoxide) calix[4]arenes are highly efficient extractants for lanthanides and actinides

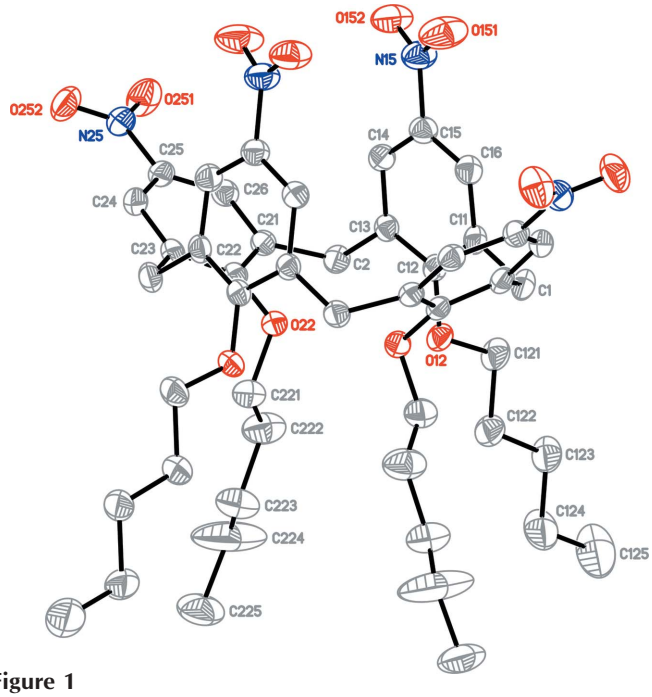


Figure 1
Perspective view of the title compound with the atom numbering; displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Unlabelled atoms are generated using the symmetry code $(-x+1, y, -z+\frac{3}{2})$.

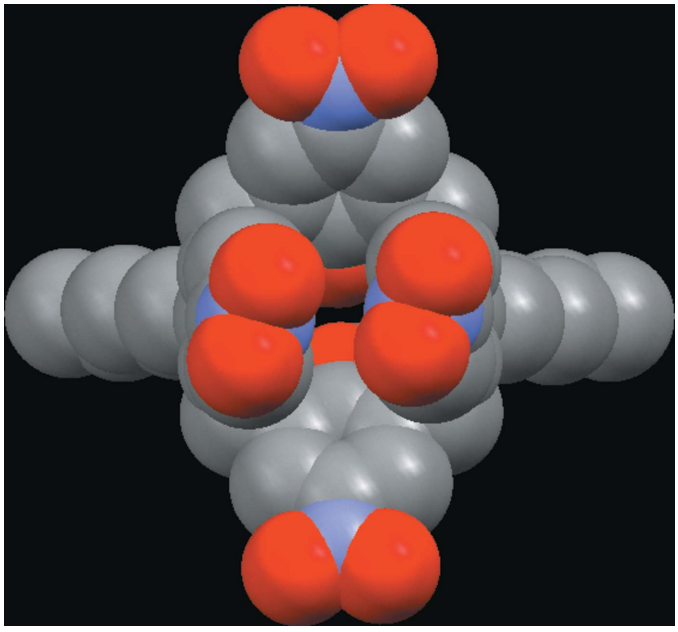


Figure 2
Space-filling model of the title compound showing the pinched cone conformation; H atoms have been omitted for clarity.

(Arnaud-Neu *et al.*, 1996); tetraurea-calix[4]arenes are able to form hydrogen-bonded dimeric capsules in apolar aprotic solvents (Rebek, 2000) *via* self-assembly. Both areas have been intensively studied during the last decade.

A perspective view of the title compound is shown in Fig. 1. The molecule is located on a crystallographic twofold rotation axis. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 1.6 plus three updates; MOGUL Version 1.0; Allen, 2002).

The molecule adopts the typical pinched cone conformation of tetraether derivatives. The reference plane of the calixarene, defined as the mean plane of the bridging C atoms [here C1, C2, C1^{i} and C2^{i}; symmetry code: (i) $1-x, y, \frac{3}{2}-z$], is almost planar (r.m.s. deviation = 0.0536 Å); the rings C11–C16 and C21–C26 subtend angles of 83.33 (6) and 141.61 (5)°, respectively, with this plane. Thus, the former rings are slightly bent inwards, whereas the others are clearly bent outwards. The rings C11–C16 and C11^{i}–C16^{i} are almost coplanar [13.34 (14)°], whereas the other two are almost perpendicular to each other [75.94 (7)°]. In Table 1, the torsion angles describing the orientation of the aromatic rings with respect to the reference plane are listed.

Both pentyloxy chains adopt all *trans* conformations.

Experimental

The title compound was synthesized according to Jakobi *et al.* (1996). The single crystals were obtained by slow evaporation of a solution in chloroform/methanol.

Crystal data

$C_{48}H_{60}N_4O_{12}$
$M_r = 885.00$
Monoclinic, $C2/c$
$a = 22.5587$ (11) Å
$b = 11.8751$ (4) Å
$c = 19.2336$ (11) Å
$\beta = 112.057$ (4)°
$V = 4775.3$ (4) Å^3
$Z = 4$
$D_x = 1.231$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31383 reflections
$\theta = 1.9$–25.2°
$\mu = 0.09$ mm^{-1}
$T = 173$ (2) K
Block, light yellow
0.38 × 0.35 × 0.29 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: none
39302 measured reflections
4859 independent reflections
3906 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 26.4°$
$h = -28 \rightarrow 28$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.247$
$S = 1.07$
4859 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1304P)^2 + 6.4471P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}

Table 1
Selected torsion angles (°).

C23^{i}—C1—C11—C12	−120.1 (3)	C12—C13—C2—C21	122.7 (2)
C22^{i}—C23^{i}—C1—C11	66.6 (3)	C13—C2—C21—C22	−69.1 (3)

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

Although the displacement ellipsoids of some atoms of the pentyl chains are rather large, the structure was refined without employing a disorder model because the current model does not show any significant peak in the final difference map (the highest peak is 0.714 e$^-$ Å^{-3}). Furthermore, a disorder model did not refine satisfactorily, because several restraints had been necessary to drive the

geometric parameters to sensible values and some atoms had to be refined isotropically to prevent them from becoming non-positive definite. H atoms were located in a difference electron-density map, but refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C)] using a riding model with C—H distances ranging from 0.95 to 0.99 Å.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991) and *MERCURY* (Version 1.4; Bruno *et al*., 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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