Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.103$
$S = 1.093$
2433 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.1711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.214$ e Å^{-3}
$\Delta\rho_{\min} = -0.187$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN* and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

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Acta Cryst. (1997). C**53**, 1644–1647

5,11,17,23-Tetra-*tert*-butyl-26,28-dihydroxy-25,27-bis[2-(*p*-nitrobenzylideneamino)-ethoxy]calix[4]arene

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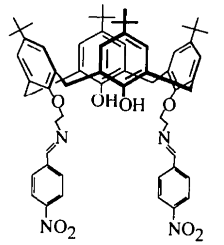
Abstract

The title compound, $C_{62}H_{72}N_4O_8$, has a cone conformation. The planes of the individual phenyl rings are inclined at angles of 97.49 (7), 142.24 (10), 92.78 (7) and 143.14 (11)° to the plane of the methylene C atoms linking these aromatic rings. There are intramolecular hydrogen bonds between the proximal hydroxy and ether functional groups, with O···O non-bonded contacts of 2.862 (3) and 2.892 (3) Å, respectively. The cones are linked to one another along the *a* axis by two weak intermolecular C—H···O hydrogen bonds [C···O contacts of 3.303 (7) and 3.377 (7) Å] to form an infinite polymeric chain.

Comment

Calixarenes are currently enjoying considerable interest in the field of supramolecular chemistry because their derivatives can form inclusion complexes with cations or with neutral molecules (Gutsche, 1989; Vicens & Böhmer, 1991). As a result of selective 1,3-dialkylation of *p*-*tert*-butylcalix[4]arene (Gutsche, 1989; Vicens & Böhmer, 1991), conformationally stable modified tetrameric structures with the 2+2′ functional group disposition and distal 1,3-regiochemistry have been developed. They are synthesized by treatment of *p*-*tert*-butylcalix[4]arene with various electrophiles such as ethyl bromoacetate, chloroacetone, bromopinacolone and chloroacetonitrile under basic conditions (Collins, McKervey & Harris, 1989; Collins *et al.*, 1991). We report here an efficient method for synthesizing the title compound, (I), by reacting *p*-nitrobenzaldehyde with calix[4]areneamine.



(I)

The molecule has a distorted cone conformation. Four *tert*-butyl groups have high thermal motion and are rotationally disordered. This is a relatively common occurrence and a similar situation has been observed in other *tert*-butylcalixarene systems such as 1,3-dicyanomethoxy-*p*-*tert*-butylcalix[4]arene (Collins *et al.*, 1991), the ethanol complex of 1,3-diethoxy-*p*-*tert*-butylcalix[4]arene (Bugge, Verboom, Reinhoudt & Harkema, 1992) and pentahydroxy-*p*-*tert*-butylcalix[5]arene (Gallagher, Ferguson, Böhmer & Kraft, 1994). The molecular geometry can be described by the interplanar angles between the individual phenyl-ring planes and the plane (*R*) of the methylene C atoms linking these aromatic rings. In compound (I), the reference plane *R* consists of atoms C11, C41, C61 and C91, the phenyl rings containing C1, C31, C51 and C81 being denoted *A*, *B*, *C* and *D*, respectively. The dihedral angles between *R* and *A*, *B*, *C* and *D* are 97.49 (7), 142.24 (10), 92.78 (7) and 143.14 (11)°, respectively. These values indicate that the aromatic ring system is tilted so that its *tert*-butyl group is directed away from the ring cavity. The two aromatic rings *A* and *C* bearing 2-(*p*-nitrobenzylideneamino)ethoxy moieties are approximately parallel to each other, with an interplanar angle of 10.3 (2)°. The two remaining rings (*B* and *D*) are significantly tilted so as to place the hydroxy groups inside the cavity. This structural arrangement enhances the formation of the intramolecular hydrogen bonds between the proximal hydroxy and ether functional groups [O42(H)···O12 2.862 (3) and O92(H)···O62 2.892 (3) Å]. The other two important phenolate O···O intramolecular contacts are O42···O62 of 3.039 (3) and O92···O12 of 3.008 (3) Å. The O···O non-bonded contacts mentioned above give the size of the cavity base. An alternative way of describing calixarene conformations involves the torsion angles, φ and χ, about each of the independent C(aromatic)—CH$_2$ bonds, as suggested by Ugozzoli & Andreetti (1992). Table 1 lists the corresponding φ and χ values, in which φ ranges from 68.1 (4) to 102.9 (4)° and χ ranges from -57.2 (4) to -111.5 (3)°. These torsion angles are in good agreement with those reported in *p*-*tert*-butylcalix[4]arene dimethyl ether crown(5); $\varphi = 60$ (2) to 103 (2)° and $\chi = -62$ (2) to -106 (2)° (Ugozzoli & Andreetti, 1992). Both compounds show two phenolic units almost perpendicular to the mean plane through the C atoms of the CH$_2$ bridges and their cone conformations can be denoted by symbolic representation as $C_1 \pm,\pm,\pm,\pm$, suggested by Ugozzoli & Andreetti (1992).

The conformation of the two OCH$_2$CH$_2$–N=CH–C$_6$H$_4$NO$_2$ chains may be revealed clearly by the torsion angles C1—O12—C13—C14 and C51—O62—C63—C64 which are 165.6 (3) and 167.2 (3)°, respectively. Therefore, two oxygenated side chains are almost parallel to each other, with their methylene groups pointing outside to reduce the steric crowding in the narrow calix[4]arene ring. The phenyl ring defined by atoms

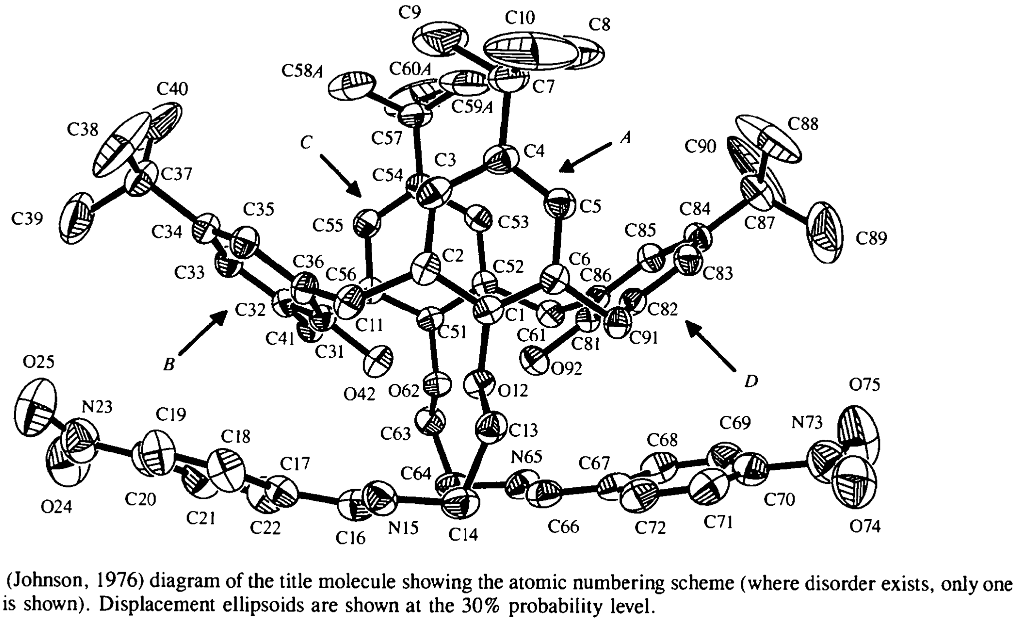


Fig. 1. An *ORTEPII* (Johnson, 1976) diagram of the title molecule showing the atomic numbering scheme (where disorder exists, only one of the disordered atoms is shown). Displacement ellipsoids are shown at the 30% probability level.

C17–C22 in the side chain is nearly parallel to the aromatic ring *B* of the cone, the dihedral angle between them being 19.8 (2)°. Similarly, the phenyl ring defined by atoms C67–C72 makes an angle of 24.5 (2)° to the aromatic ring *D*.

The cones are linked to one another along the *a*-axis direction by two weak intermolecular C—H···O hydrogen bonds to form an infinite one-dimensional polymeric chain. In one chain, all the cones have their aperture in the same direction parallel to the $[0\bar{1}1]$ axis. Table 2 lists the hydrogen-bonding parameters. In fact, these hydrogen bonds [C21···O74^{i} 3.303 (7) and C71^{i}···O24 3.377 (7) Å; symmetry code: (i) $x-1, y, z$] form a ten-membered ring of H21—C21—C20—N23—O24···H71^{i}—C71^{i}—C70^{i}—N73^{i}—O74^{i}···H21, which enhances the stability of crystal packing. There are no direct hydrogen bonds between adjacent polymeric chains. In the *bc* plane, the polymeric chains form layers parallel to the $(0\bar{1}1)$ plane. Two adjacent cone chains are related to each other by an inversion center along both the [011] and $[0\bar{1}1]$ directions. A packing diagram viewed along the *a* axis has been deposited with the supplementary data.

Experimental

The title compound, (I), was prepared by reacting 5,11,17,23-tetra-*tert*-butyl-25,27-diaminoethoxy-26,28-dihydroxycalix[4]-arene with *p*-nitrobenzaldehyde (2 equivalents) in hot ethanol for 10 min. The product formed as fine yellow crystals from the reaction solution (m.p. 530–531 K) in *ca* 92% yield. Crystals suitable for X-ray diffraction were obtained by slow evaporation at 298 K of a chloroform–ethanol solution. The nature of the 2+2′ functional group and the cone conformation were deduced initially from solution ^{1}H NMR: two *tert*-butyl singlets at 0.91 and 1.29 p.p.m., and a single *AB* system for the bridging methylene groups at 3.25 and 4.22 p.p.m. (J_{AB} = 13.2 Hz).

Crystal data

$C_{62}H_{72}N_4O_8$
$M_r = 1001.24$
Triclinic
$P\bar{1}$
$a = 12.702\ (3)$ Å
$b = 14.653\ (3)$ Å
$c = 17.715\ (2)$ Å
$\alpha = 88.722\ (12)°$
$\beta = 77.38\ (2)°$
$\gamma = 66.64\ (2)°$
$V = 2946.1\ (11)$ 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 35 reflections
$\theta = 5.0$–$12.5°$
$\mu = 0.074$ mm^{-1}
$T = 293$ K
Prism
0.40 × 0.30 × 0.20 mm
Yellow

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
12 260 measured reflections
10 351 independent reflections
4216 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 15$
$k = -16 \rightarrow 17$
$l = -20 \rightarrow 21$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.153$
$S = 1.146$
10 351 reflections
700 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.018$

$\Delta\rho_{\rm max} = 0.546$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.256$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0173 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O12—C1	1.400 (4)	O62—C51	1.403 (3)
O42—C31	1.376 (3)	O92—C81	1.373 (3)
C3—C2—C11—C36	72.7 (4)	C53—C52—C61—C86	68.1 (4)
C2—C11—C36—C35	−110.7 (4)	C52—C61—C86—C85	−111.5 (3)
C33—C32—C41—C56	102.9 (4)	C83—C82—C91—C6	102.3 (4)
C32—C41—C56—C55	−57.2 (4)	C82—C91—C6—C5	−61.4 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O42—H42···O12	0.82	2.06	2.862 (3)	164
O92—H92···O62	0.82	2.10	2.892 (3)	164
C21—H21···O74^{i}	0.93	2.50	3.303 (7)	144
C71—H71···O24^{ii}	0.93	2.57	3.377 (7)	146

Symmetry codes: (i) $x-1, y, z$; (ii) $1+x, y, z$.

All non-H atoms were refined anisotropically. H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter. The 12 terminal C atoms of the *tert*-butyl groups were found to be disordered. Treating each of these C atoms as two split positions leads to an unstable refinement. Therefore, in the final cycle, only one *tert*-butyl group including atoms C58, C59 and C60, which have the largest equivalent isotropic displacement parameters ($U_{\rm eq}$) ranging from 0.31 to 0.40 Å^2, was refined as two orientations with the same occupancy.

Data collection: *P*3/*P*4-*PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P*3/*P*4-*PC Diffractometer Program*. Data reduction: *XSCANS* (Fait, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1340). Services for accessing these data are described at the back of the journal.

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2-Nitro-4′-(*N*,*N*-diethylamino)azobenzene,† $C_{16}H_{18}N_4O_2$

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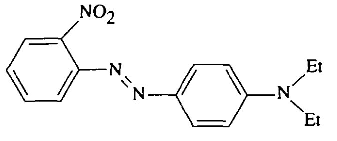
Abstract

The title molecule has *trans* geometry about the azo linkage. The dihedral angle between the two phenyl rings is 47.1 (5)° and the twist angle for the nitro group is 24.4 (3)°. The effect of the nitro group on the geometry of the molecule is discussed. In this crystal structure, the molecules pack through π···π and van der Waals interactions.

Comment

Some azobenzene compounds containing donor–acceptor groups have non-linear optical properties (Bauers & Yilwaz, 1993; Holland & Treliant, 1992), which prompted us to undertake a systematic study. During the process, we isolated the title compound, (I).



(I)

Within the limits of accuracy, bond lengths and angles (Table 1) are in agreement with those of other azobenzene compounds (Howard, Batsanov, Bryce & Chesney, 1994; Preut, Wicenes & Neumann, 1991; Moreiras, Solans, Solans, Miravitlles, Germain & Declercq, 1980). While the whole molecule is non-planar, atoms N3 and N4 are nearly coplanar with the C7–C12 ring, the torsion angles N3—C7—C12—C11, N3—C7—C8—C9, N4—C10—C11—C12 and N4—C10—C9—C8 being 179.3 (2), −179.8 (2), −179.3 (2) and 178.9 (2)°, re-

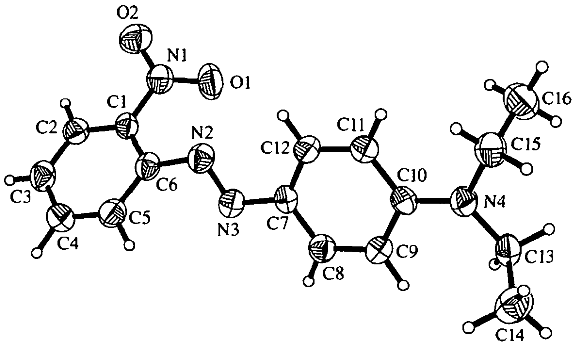


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

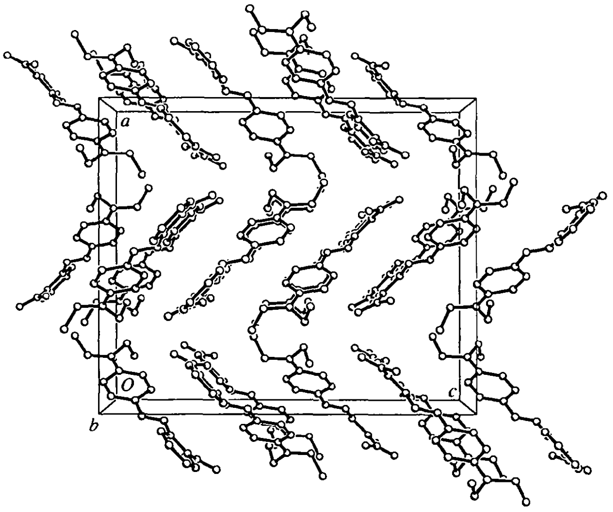


Fig. 2. Packing diagram viewed down the *b* axis.

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† IUPAC name: (4-diethylaminophenyl)(2-nitrophenyl)diazene.