

Software. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1085). Services for accessing these data are described at the back of the journal.

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1,3-Bis(3-nitrophenyl)triazene

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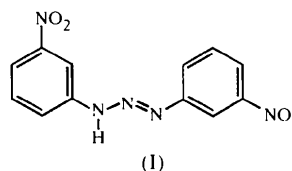
Abstract

The title molecule, C₁₂H₉N₃O₄, has *trans* geometry about the azo linkage. The dihedral angle between the two phenyl rings is 6.2(2)°. The whole molecule is

almost planar and the maximum deviation from the mean plane is 0.166(3) Å. The resonance effect in the triazene group which might explain the antitumour activity of some triazene derivatives is discussed. In the crystal structure, while the twofold screw-related molecules are packed in a simple herringbone pattern, the inversion-centre-related molecules form hydrogen-bonded dimers which are held together through $\pi \cdots \pi$ interactions along the [010] direction.

Comment

It has been reported that 1,3-diphenyltriazene shows antitumour activity comparable to that of 3,3-dimethyl-1-aryltriazenes. 1,3-Diaryltriazenes can act as pro-drugs, or 'carriers' of diazonium compounds, since they undergo hydrolysis to form aryl diazonium compounds (Nifontov *et al.*, 1988, 1994). Surprisingly few X-ray structural studies of these compounds have been reported. As part of the X-ray structural studies of substituted triazene compounds, we have synthesized the title compound, (I), and confirmed its structure by X-ray analysis.



Within the limits of accuracy, the bond lengths and angles of the two nitrophenyl rings are in agreement with each other, but the whole molecule is asymmetric. N3=N4 [1.261(2) Å] is longer than expected for a double bond, N2=N3 [1.326(2) Å] is shorter than expected for a single bond, and C5=N2 and C11=N4 are both short for single C_{ar}—N bonds; there is clear evidence of a resonance effect in this part of the molecule. In view of the carcinogenic activity of some azobenzene derivatives (Kurosaki *et al.*, 1976) closely related to their conjugation structure (Arcos & Arcos, 1962), we think that the resonance effect in the triazene group in triazene derivatives might be related to their antitumour activity. While the nitro groups O3=N5—O4 and O1=N1—O2 are twisted by 3.3(2) and 6.7(2)° from their benzene planes, the dihedral angle between the two phenyl rings is 6.2(2)°, and the torsion angles C5=N2=N3=N4 and N2=N3=N4—C11 are 179.4(1) and 179.6(1)°, respectively, showing the near coplanarity of the whole molecule. The shortest distance between the intermolecular mean planes is 3.27(3) Å.

In the crystal structure, the twofold screw-related molecules are packed in a simple herringbone pattern; interactions between them include the close contact O3 \cdots N5 (Table 2). The molecules related by inversion centres are linked together to form dimers by O4 \cdots H—

N2 hydrogen bonds (O4 at $1-x, 2-y, -z$), and the dimers are held together by strong $\pi \cdots \pi$ interactions. Some short contacts less than 3.40 Å are presented in Table 2.

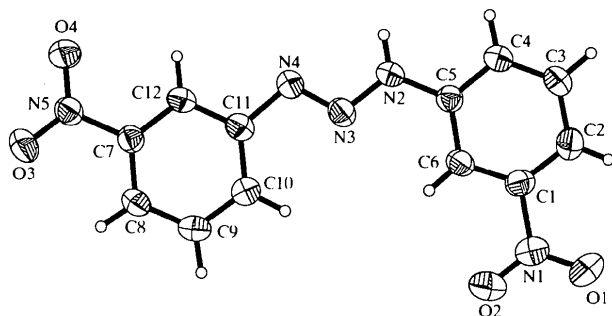


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids for non-H atoms. H atoms are shown as small spheres of an arbitrary radius.

Experimental

3-Nitroaniline (0.69 g, 5.0 mmol) was dissolved in 5 ml water and 2 ml HCl, and the resulting solution was cooled to below 273 K. Sodium nitrite (0.35 g, 5.1 mmol) was added and the solution stirred for 15 min before being cooled to below 278 K. 0.69 g (5.0 mmol) 3-nitroaniline and 1 ml HCl were then added to the above diazotized solution. After adding dry sodium acetate (3 g), the reaction continued for 20 min at ambient temperature and yielded a yellow product. The product was recrystallized twice from ethanol/water (1:1). Bar-shaped crystals were obtained by slow evaporation from a 95% ethanol solution after a week.

Crystal data

$C_{12}H_9N_5O_4$
 $M_r = 287.24$
 Monoclinic
 $P2_1/n$
 $a = 12.676(2) \text{ \AA}$
 $b = 5.341(1) \text{ \AA}$
 $c = 19.493(2) \text{ \AA}$
 $\beta = 107.42(1)^\circ$
 $V = 1259.2(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.515 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction:
 empirical (North *et al.*, 1968)
 $T_{\min} = 0.901$, $T_{\max} = 0.961$
 3571 measured reflections
 3004 independent reflections
 1891 reflections with
 $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 28 reflections
 $\theta = 3.22\text{--}18.23^\circ$
 $\mu = 0.118 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Bar
 $0.68 \times 0.68 \times 0.20 \text{ mm}$
 Red

$R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 28^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 7$
 $l = -25 \rightarrow 24$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.11%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.118$
 $S = 0.901$
 3002 reflections
 227 parameters
 All H-atom parameters
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.194 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.152 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL93
 Extinction coefficient:
 0.0153(17)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

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

| | | | |
|--------------|----------|---------------|-----------|
| N1—C1 | 1.477(2) | N3—N4 | 1.261(2) |
| N2—N3 | 1.326(2) | N4—C11 | 1.426(2) |
| N2—C5 | 1.393(2) | N5—C7 | 1.465(2) |
| N3—N2—C5 | 119.8(1) | N2—C5—C6 | 121.1(1) |
| N4—N3—N2 | 113.6(1) | C12—C11—N4 | 115.9(1) |
| N3—N4—C11 | 111.8(1) | C10—C11—N4 | 124.5(1) |
| C4—C5—N2 | 119.2(1) | | |
| C5—N2—N3—N4 | 179.4(1) | N3—N2—C5—C6 | -8.0(2) |
| N2—N3—N4—C11 | 179.6(1) | N3—N4—C11—C12 | -176.2(1) |
| N3—N2—C5—C4 | 173.3(1) | N3—N4—C11—C10 | 4.0(2) |

Table 2. Intermolecular hydrogen bonds and other contacts (\AA)

| | | | |
|------------------------------|----------|------------------------------|----------|
| O1 \cdots C9 ⁱ | 3.323(3) | O3 \cdots C4 ⁱⁱ | 3.332(3) |
| O3 \cdots O3 ⁱⁱ | 3.327(3) | O4 \cdots N4 ^{iv} | 3.304(3) |
| O3 \cdots O4 ⁱⁱ | 3.182(3) | N3 \cdots C1 ^{iv} | 3.387(3) |
| O3 \cdots N5 ⁱⁱ | 2.992(2) | O4 \cdots C3 ^v | 3.335(3) |
| O3 \cdots C7 ⁱⁱ | 3.277(3) | O4 \cdots N2 ^v | 3.023(2) |

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

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SHELXTL (Sheldrick, 1993a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993b). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1224). Services for accessing these data are described at the back of the journal.

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25,27-Dihydroxyethoxy-26,28-dipropoxy-*tert*-butylcalix[4]arene

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Abstract

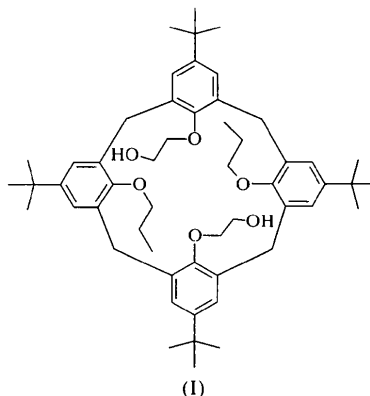
In the solid state, the title compound, C₅₄H₇₆O₆, adopts a pinched cone conformation, which is somewhat distorted.

Comment

Calixarenes are readily synthesized by the condensation of *tert*-butylphenol and formaldehyde, and are easily modified on both the narrow (lower) rim and the wide (upper) rim by further chemical reactions (Böhmer, 1995). *o*-Alkylation or *o*-acylation of calix[4]arenes by residues larger than ethyl results in one of four basic conformations. Various X-ray structural analyses of tetraethers, with identical or different ether residues, have been reported (Guelzim *et al.*, 1993; Arnaud-Neu *et al.*, 1992), showing the molecule to be usually in a so-called 'pinched' cone conformation, where two opposite aromatic rings are nearly parallel, while the other two rings are bent away from the cavity. No inclusion of guests is usually observed in this conformation.

The title calixarene, (I), adopts this pinched-cone conformation, leading to an O1···O3 separation of 5.538 (2) Å and an O2···O4 separation of 3.668 (2) Å. The shape of the calix cavity can be described by the dihedral angles between the aromatic rings and the mean molecular plane of the four methylene-C atoms (C25–C28) linking them. These angles, facing the cavity (Perrin & Oehler, 1991), are 86.80 (5), 136.61 (6), 93.72 (5) and 133.39 (6)° for rings C1–C6, C7–C12, C13–C18 and C19–C24, respectively. The dihedral angles between opposite rings demonstrate that rings C7–C12 and C19–C24 are perpendicular to each other,

with a dihedral angle of 89.99 (6)°, while rings C1–C6 and C13–C18 are nearly parallel, with a dihedral angle of 1.0 (1)°. The dihedral angles between two adjacent aromatic rings are 88.12 (6), 87.16 (6), 86.19 (6) and 85.93 (6)°. Similar behaviour concerning the shape of the cavity is observed in several tetraethers reported previously (Guelzim *et al.*, 1993; Arnaud-Neu *et al.*, 1992).



The hydroxyethyl ether groups are oriented inwards, and the two hydroxy groups (O5 and O6/O6B) form intramolecular hydrogen bonds to the O atoms (O1 and O3/O5) of the adjacent propoxyphenyl units. The O5···O3 distance is in the usual hydrogen-bonding range [2.719 (2) Å], while the O6···O1 and O6B···O5 distances of 2.939 (2) Å and 2.951 (1) Å, respectively, are slightly longer. The hydrophobic propyl ether residues, on the other hand, are directed outwards from the cavity, and all the ether residues are oriented in roughly the same direction. The conformation of the

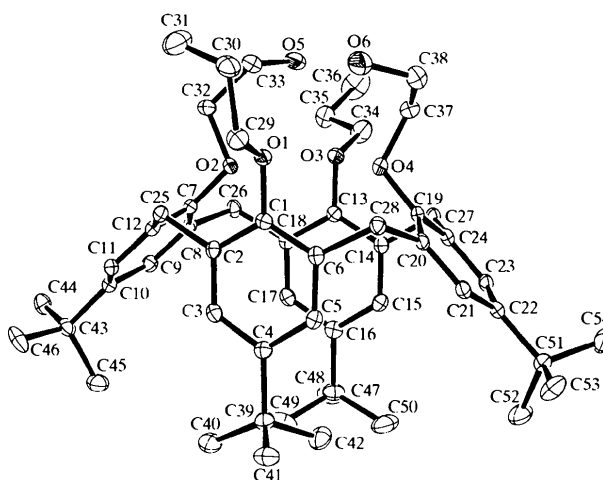


Fig. 1. An ORTEP III (Burnett & Johnson, 1996) plot of the title compound, showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.