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1,3-Bis(4-nitrophenyl)triazene

Manfredo Hörner,[a]* Leandro Bresolin,[a] Jairo Bordinhao,[a] Edmund Hartmann[b] and Joachim Strähle[b]

[a]Departamento de Quimica, Universidade Federal de Santa Maria, Caixa Postal 5071, 97110-900 Santa Maria, RS, Brazil, and [b]Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany
Correspondence e-mail: hoerner@base.ufsm.br

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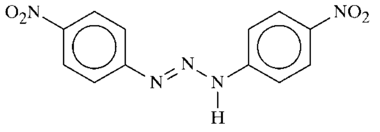
The structure of the title compound, $C_{12}H_9N_5O_4$, reveals an almost planar molecule (r.m.s. deviation = 0.061 Å), in which the interplanar angle between the phenyl rings is 5.7 (1)° and the largest interplanar angle is that between the phenyl ring and the nitro group of one of the 4-nitrophenyl substituents [8.8 (3)°]. The observed molecular conformation suggests a delocalization of π-electrons extended over the diazoamine group and the terminal aryl substituents. Intermolecular N—H···O interactions between the twofold screw-related molecules give rise to helical chains along the [010] direction. Intermolecular C—H···O interactions then generate sheets of molecules in the $(10\overline{1})$ plane, and these sheets are held together by N···C and O···O π–π interactions.

Comment

Numerous examples of free 1,3-disubstituted triazenes, *R*N═N—N(H)*R*, characterized by X-ray diffraction studies confirm a *trans* stereochemistry about the N═N double bond (Moore & Robinson, 1986). During the past few decades, asymmetric alkyl/aryl-substituted triazenes have been investigated for their biological activity. The resonance effect in the diazoamine group has been related to the antitumour activity of some triazene derivatives (Zhang *et al.*, 1999). On the other hand, studies of molecules with DNA binding affinity indicate that the planarity has a marked effect on the insertion between the base pairs (Mahadevan & Palaniandavar, 1998; Zhen *et al.*, 1999, 2000). We report here the synthesis and structural characterization of the title compound, (I), a symmetric disubstituted 1,3-diaryltriazene that has π acid nitro groups on the *para*-substituted terminal aryl (ar) rings.



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Deviations from typical N—N and C_{ar}—N bond lengths suggest that the delocalization of the π-electrons on the triazene group has extended to the terminal 4-nitrophenyl substituents. The N12═N13 bond [1.263 (2) Å] is longer than the characteristic value for a double bond (1.24 Å), whereas the N11—N12 bond [1.340 (2) Å] is shorter than the characteristic value for a single bond (1.44 Å; *International Tables for X-ray Crystallography*, 1985, Vol. III, p. 270). The N11—C11 [1.383 (2) Å] and N13—C21 [1.430 (2) Å] bonds are shorter than the length expected for a C_{ar}—N single bond and are in good agreement with the distances found in the related compound 1,3-bis(3-nitrophenyl)triazene [N4═N3 = 1.261 (2) Å, N2—N3 = 1.326 (2) Å, N2—C5 = 1.393 (2) Å and N4—C11 = 1.426 (2) Å; Zhang *et al.*, 1999].

The crystal structure contains molecules related by a twofold screw axis, which form helical chains along the [010] direction *via* N—H···O hydrogen bonds (Table 2). These chains are linked by C—H···O intermolecular interactions

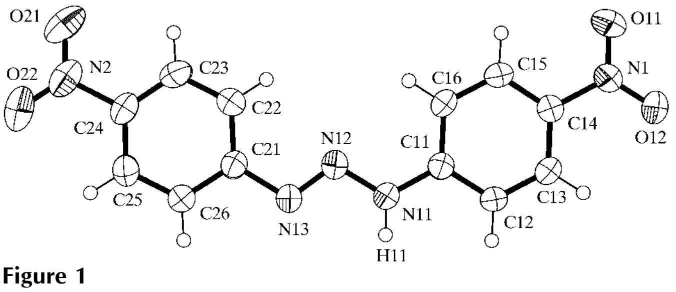


Figure 1
The molecular structure of (I), with displacement ellipsoids for non-H atoms drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

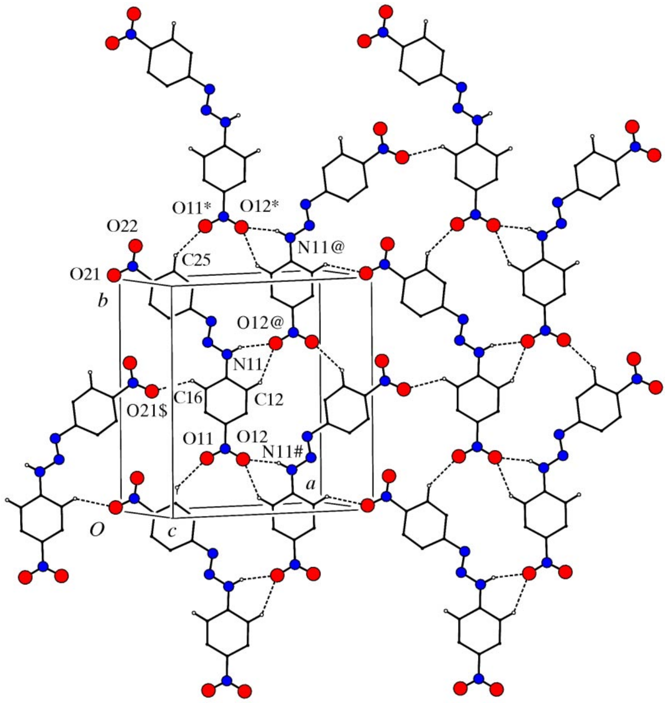


Figure 2
A view of a sheet of molecules of (I), showing the N—H···O and C—H···O interactions. Atoms marked with an 'at' sign (@), a dollar sign ($) or a hash (#) are at the symmetry positions ($1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), ($-x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) and ($1 - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), respectively.

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(Table 2), generating sheets in the $(10\overline{1})$ plane (Fig. 2), and these sheets are then linked into a three-dimensional molecular array by N···C and O···O π–π interactions [N11···C21^{iv} = 3.388 (3) Å and O21···O21^{v} = 3.117 (4) Å; symmetry codes: (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x, -y+2, -z$]. These values are in good agreement with the π–π contacts found in 1,3-bis(3-nitrophenyl)triazene [N···C = 3.387 (3) Å and O···O = 3.182 (3) Å; Zhang *et al.*, 1999].

Because of the strong π acidity of the nitro groups, which favours the delocalization of the π-electrons and the conjugation between the C11–C16 and C21–C26 phenyl rings and the N═N—N(H) moiety, the whole molecule is almost planar [interplanar angles O11—N1—O12/C11–C16 = 7.3 (1)°, O21—N2—O22/C21–C26 = 8.8 (3)°, C11–C16/H11—N11—N12—N13 = 6.4 (1)° and C21–C22/N13—N12—N11—H11 = 3.7 (1)°]. The weak intermolecular C16···O21^{ii} contact [3.194 (3) Å; see Table 2 for symmetry code] causes the C11–C16 phenyl ring to deviate by an angle of 6.4 (1)° from the plane defined by the N13═N12—N11—H11 moiety, while the C21–C26 phenyl ring remains nearly coplanar with the diazoamine group.

Experimental

4-Nitroaniline (21.5 g, 155 mmol) was dissolved in glacial acetic acid (40 ml) and cooled to below room temperature. A sodium nitrite solution (5.4 g, 78 mmol) in water (100 ml) was added slowly with continuous stirring. The yellow reaction mixture was then neutralized with an aqueous solution (10%) of $NaHCO_3$ and a yellow precipitate was observed. The crude yellow product was isolated by filtration and dried over P_2O_5 in a vacuum and the product was recrystallized from a tetrahydrofuran/*n*-hexane mixture (1:1). Yellow column-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent mixture (yield 15.1 g, 67.5%; m.p. 506 K).

Crystal data

$C_{12}H_9N_5O_4$
$M_r = 287.24$
Monoclinic, $P2_1/c$
$a = 13.452$ (1) Å
$b = 13.671$ (2) Å
$c = 7.034$ (2) Å
$\beta = 93.442$ (11)°
$V = 1291.2$ (4) Å^3
$Z = 4$

$D_x = 1.478$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.1$–25.4°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Column, yellow
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2581 measured reflections
2375 independent reflections
1405 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

$\theta_{\rm max} = 25.4°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.124$
$S = 0.98$
2375 reflections
191 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.0938P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.015 (2)

Table 1
Selected geometric parameters (Å, °).

O12—N1	1.221 (2)	N11—N12	1.340 (2)
O11—N1	1.215 (2)	N11—C11	1.383 (2)
O22—N2	1.216 (3)	N12—N13	1.263 (2)
O21—N2	1.217 (2)	N13—C21	1.430 (2)
N12—N11—C11	120.09 (16)	N12—N13—C21	112.14 (15)
N13—N12—N11	112.32 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O12^{i}	0.86	2.11	2.929 (2)	159
C12—H12···O12^{i}	0.93	2.49	3.248 (3)	139
C16—H16···O21^{ii}	0.93	2.50	3.194 (3)	131
C25—H25···O11^{iii}	0.93	2.46	3.222 (3)	140

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

The H-atom positional parameters were obtained geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and refined as riding on the respective C and N atoms, with $U_{\rm iso}$ values of 1.2 times the $U_{\rm eq}$ values of the attached Csp^2 and Nsp^2 atoms. The nitro atoms show a large thermal motion, as indicated by their elongated displacement ellipsoids (Fig. 1). Split peaks for these atoms were not observed and consequently a disorder model was not used.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1694). Services for accessing these data are described at the back of the journal.

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