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

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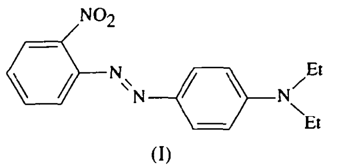
Abstract

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 $\pi\cdots\pi$ 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-

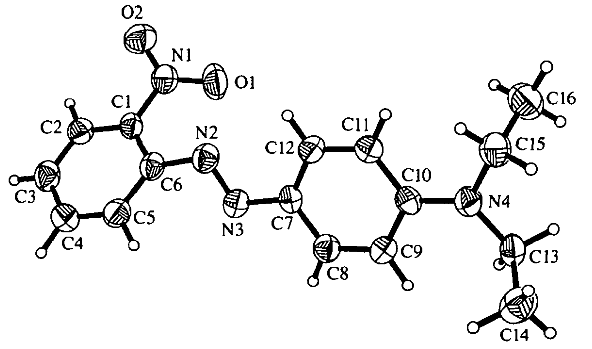


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

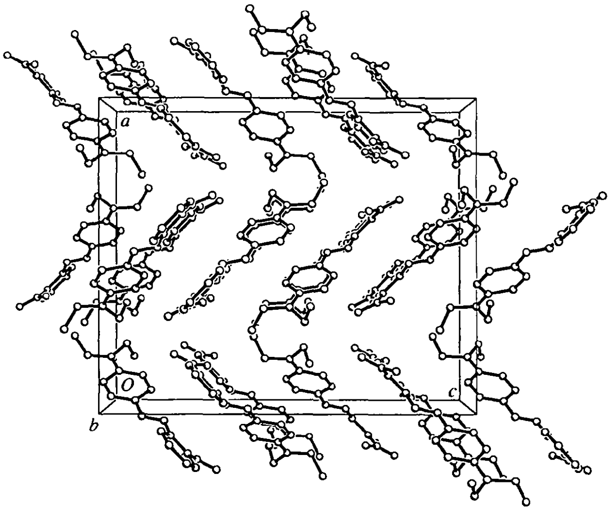


Fig. 2. Packing diagram viewed down the *b* axis.

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

spectively, and the torsion angle C6—N2—N3—C7 being −176.9 (2)°. We believe that the non-planarity of the skeleton of the molecule and the rotation of the nitro group out of the ring plane result from the interaction between atoms O1 and N2. The O1···N2 distance of 2.647 (5) Å is in agreement with that of the related compound 2-nitro-4′-[*N*,*N*-bis(β-hydroxyethyl)amino]azobenzene (2.648 Å; Mcintosh, Freeman & Singh, 1989). It is possible that the closeness of O1 and N2 leads to the formation of an azoxy intermediate (Mcintosh, Freeman & Singh, 1989).

In this crystal, molecules are packed in a simple herring-bone pattern. The strongest interactions between molecules are listed in Table 2.

Experimental

To a solution formed by dissolving 0.69 g (5.0 mmol) 2-nitroaniline in 5 ml water and 2 ml hydrochloride and cooled below 273 K, 0.35 g (5.1 mmol) sodium nitrite was added. The solution was stirred for 15 min and cooled to below 278 K, whereupon 0.79 ml (5.0 mmol) *N*,*N*-diethylaniline and 1 ml hydrochloride were added to the above diazotized solution. After dry acetic sodium (3 g) was added, the reaction was continued for 20 min at ambient temperature, yielding a sticky product. The product was recrystallized twice from ethanol and once from acetone. Red hexagonal prismatic crystals were obtained by slow evaporation from a dichloromethane–tetrahydrofuran solution after 2 d.

Crystal data

$C_{16}H_{18}N_4O_2$
$M_r = 298.34$
Orthorhombic
Pbcn
$a = 17.366\,(3)$ Å
$b = 8.196\,(2)$ Å
$c = 20.999\,(4)$ Å
$V = 2988.8\,(11)$ Å^3
$Z = 8$
$D_x = 1.326$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 2.35$–$15.48°$
$\mu = 0.091$ mm^{-1}
$T = 291\,(2)$ K
Hexagonal prism
0.54 × 0.54 × 0.46 mm
Red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2188 measured reflections
2080 independent reflections
1288 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.011$

$\theta_{\max} = 24°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 7$
$l = -24 \rightarrow 1$
3 standard reflections every 97 reflections
intensity decay: 1.40%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.075$
$S = 0.875$
2080 reflections
272 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.134$ e Å^{-3}
$\Delta\rho_{\min} = -0.113$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0047 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—N1	1.217 (2)	N3—C7	1.410 (2)
O2—N1	1.227 (2)	N4—C10	1.362 (2)
N1—C1	1.462 (3)	N4—C13	1.458 (3)
N2—N3	1.268 (2)	N4—C15	1.463 (3)
N2—C6	1.422 (2)		
O1—N1—C1	119.2 (2)	C5—C6—N2	121.7 (2)
O2—N1—C1	117.9 (2)	C1—C6—N2	121.1 (2)
N3—N2—C6	112.5 (2)	C8—C7—N3	116.1 (2)
N2—N3—C7	114.8 (2)	C12—C7—N3	125.5 (2)
C10—N4—C13	121.9 (2)	N4—C10—C9	121.9 (2)
C10—N4—C15	122.5 (2)	N4—C10—C11	122.0 (2)
C2—C1—N1	117.2 (2)	N4—C13—C14	113.6 (2)
C6—C1—N1	120.8 (2)	N4—C15—C16	112.7 (2)
C6—N2—N3—C7	−176.9 (2)		

Table 2. *Intermolecular interactions*

E (kJ mol^{-1})^a	DP (Å)^b	DC (Å)^c	Symmetry code
−28.03 (5)	3.53 (3)	3.85 (2)	$-x, y, \frac{3}{2} - z$
−34.61 (5)	3.72 (3)	4.25 (3)	$-x, 1 - y, 2 - z$

Notes: (*a*) interaction energy between the reference molecule and the molecule specified by the symmetry code listed, calculated by *OPEC* (Gavezzotti, 1983); (*b*) the shortest interplanar distance between the parallel ring planes; (*c*) the distance between the centres of the corresponding ring planes.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1041). Services for accessing these data are described at the back of the journal.

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