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4′-(Dimethylamino)-4-nitroazobenzene

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The title compound [systematic name: (4-dimethylaminophenyl)(4-nitrophenyl)diazene], $C_{14}H_{14}N_4O_2$, has *trans* geometry about the azo linkage and is planar. Although the crystal structure is non-centrosymmetric, the overall net dipole moment is minimized by antiparallel arrangement of chains of molecules related by translation ($1 + x$, y, $2 + z$) and by marked orientational disorder in the azo moiety, through rotation about the C$\cdots$C axis that it bridges. The chains are connected by weak C—H$\cdots$O hydrogen bonding between nitro and dimethylamino groups. They lie perpendicular to the (103) plane and form stacks through π–π interaction, propagating along the crystallographic *a* axis. The stacks interact through a combination of van der Waals interactions and edge-to-face π–π interaction to give a herring-bone appearance in the view along their long axis.

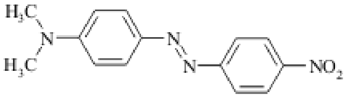
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–N) = 0.005 Å
Disorder in main residue
R factor = 0.071
wR factor = 0.204
Data-to-parameter ratio = 9.9

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

Comment

Azo dyes incorporating 'push–pull' donor–acceptor aryl rings are of much commercial importance for the dyeing of textiles (Zollinger, 1994), and some exhibit second- or third-order non-linear optical properties (Barachevsky, 1998). As part of a study on the production of such dyes in microfluidic reactors, we have chosen the title compound, (I), as a reference material for prototype system parameterization, due to its relative ease of synthesis and analysis by HPLC and colorimetric detection (Salimi-Moosavi *et al.*, 1997). We have synthesized and characterized (I) to confirm its identity and purity, and have determined its structure by X-ray crystallography.



(I)

The bond distances observed are very similar to those in related compounds, such as the isomeric 4′-(dimethylamino)-2-nitroazobenzene [(II); Zhang *et al.*, 1998], although the NO_2 group exhibits slightly longer N—O distances [(I): 1.226 (4) Å; (II): 1.211 (3) and 1.190 (3) Å]. The absence of steric effects between the NO_2 and azo N atoms in (I) accounts for the small dihedral angle between the NO_2 group and its parent ring of 7.8 (7)°, compared with 63.9 (2)° in (II). No non-H atom deviates significantly from the mean plane of the two benzene rings, and the dihedral angle between these rings is 2.1 (4)°, so the molecule is essentially planar (Table 1).

Hydrogen bonding between NO_2 and $N(CH_3)_2$ groups is responsible for the formation of chains of molecules in the

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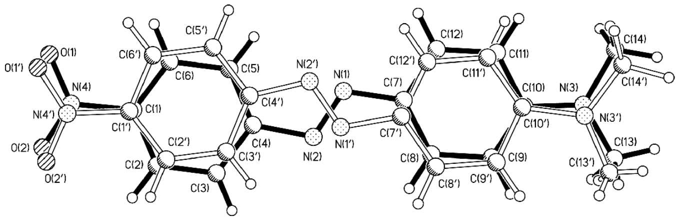

Figure 1
The disordered molecular structure of (I).

[101] direction. Evidence for these weak interactions lies in their geometric parameters: O1···C13^i = 3.391 (2) Å, O1···H13C^i—C13^i = 160°, O2···C14^i = 3.650 (2) Å and O1···H14C^i—C14^i = 170% [symmetry code: (i) $1 + x, y, 2 + z$]. Parallel stacking of these chains is achieved by π–π interaction, as indicated by the perpendicular separation of <3.5 Å for the mean planes through the rings of adjacent molecules.

The crystal was found to exhibit significant disorder in the orientation of the azo moiety, —N1═N2—. This disorder was modelled as a rotation of 180° about the C4···C7 axis, the minor part being ∼ 25% occupied. This rotation induces a small change of orientation in the remainder of the molecule. Therefore, whole-molecule disorder was modelled.

This investigation indicates that the title compound crystallizes in a non-centrosymmetric space group which may be advantageous in studies of non-linear optical behaviour. We intend to determine better methods for its crystallization, with the aim of reducing the degree of disorder in the crystal structure.

Experimental

A solution of 4-nitrobenzenediazonium tetrafluoroborate (0.10 g, 0.42 mmol) in 10 ml methanol was added to a solution of *N,N*-dimethylaniline (0.051 g, 0.42 mmol) in 10 ml methanol, and stirred at room temperature for 10 min. The resulting red–orange precipitate was filtered off and recrystallized from methanol. Crystals for structure determination were grown by slow evaporation of a chloroform solution of the product.

Crystal data

$C_{14}H_{14}N_4O_2$
$M_r = 270.29$
Monoclinic, $P2_1$
$a = 7.590$ (4) Å
$b = 10.532$ (6) Å
$c = 8.101$ (4) Å
$\beta = 100.248$ (9)°
$V = 637.3$ (6) Å^3
$Z = 2$

$D_x = 1.409$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2320 reflections
$\theta = 5.1$–53.2°
$\mu = 0.10$ mm^{-1}
$T = 150$ (2) K
Block, red
0.43 × 0.42 × 0.19 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.959$, $T_{\max} = 0.982$
6858 measured reflections

1183 independent reflections
1183 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.071$
$wR(F^2) = 0.204$
$S = 1.21$
1183 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1146P)^2 + 0.2904P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N4	1.226 (4)	N3—C10	1.371 (5)
N1—N2	1.258 (6)	N3—C13	1.453 (5)
N1—C7	1.400 (5)	N4—C1	1.434 (5)
N2—C4	1.422 (6)		
N2—N1—C7	115.0 (5)	C2—C1—N4	118.2 (3)
N1—N2—C4	112.5 (4)	C6—C1—N4	121.8 (3)
C10—N3—C13	119.4 (5)	C5—C4—N2	123.7 (3)
C10—N3—C14	121.0 (5)	C3—C4—N2	116.3 (3)
C13—N3—C14	119.6 (5)	C8—C7—N1	125.5 (3)
O2—N4—O1	123.7 (5)	C12—C7—N1	114.5 (3)
O2—N4—C1	118.6 (5)	N3—C10—C11	115.2 (4)
O1—N4—C1	117.6 (4)	N3—C10—C9	124.7 (4)
C7—N1—N2—C4	−180.0 (4)	N1—N2—C4—C5	1.6 (6)
O2—N4—C1—C2	−8.9 (8)	N2—N1—C7—C8	−3.6 (6)
O1—N4—C1—C2	171.4 (5)	C13—N3—C10—C11	−171.3 (5)
O2—N4—C1—C6	173.8 (5)	C14—N3—C10—C11	9.4 (8)
O1—N4—C1—C6	−5.9 (8)	C13—N3—C10—C9	5.1 (9)
C6—C1—C2—C3	0.0	C14—N3—C10—C9	−174.2 (5)

Due to whole-molecule disorder in the structure, with substantial overlap of atoms, the constituent benzene rings were constrained to ideal hexagonal geometry, and isotropic displacement parameters were refined for all non-H atoms. Although the crystal is non-centrosymmetric, the absolute configuration could not be determined in the absence of significant anomalous scattering effects; Friedel pairs were merged. H atoms were positioned geometrically and refined with a riding model (including torsional freedom for methyl groups), with C—H = 0.95–0.98 Å, and with $U_{\rm iso}$(H) values constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); 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); software used to prepare material for publication: *enCIFer* (CCDC, 2003).

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