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N,*N*′-Diethyl-4,4′-dinitrohydrazobenzene

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There are two independent molecules, *A* and *B*, in the title compound, $C_{16}H_{18}N_4O_4$, and the asymmetric unit consists of one molecule *A* and one half-molecule *B*; a twofold axis runs through the centre of the N—N bond of molecule *B*. The crystal structure is stabilized mainly by van der Waals forces.

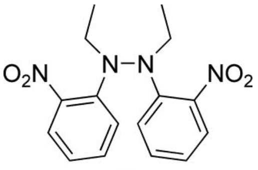
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.047
wR factor = 0.107
Data-to-parameter ratio = 7.8

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

Comment

In order to obtain more detailed information on the structural conformation of the title compound, (I), which may be useful for structure–activity relationship investigations, the X-ray crystal structure determination of (I) has been carried out and the results are presented here.



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. There are two independent molecules, *A* and *B*, in the crystal structure of (I). The asymmetric unit consists of one molecule *A* and half of molecule *B*; a twofold axis runs through the centre of the N—N bond of molecule *B*.

The main conformational difference between molecules *A* and *B* is the twist about the N—N bond. Comparison of the torsion angles around the N—N bonds shows some differences between molecules *A* and *B*: C1—N1—N2—C7 and C13—N1—N2—C15 for molecule *A* are −134.4 (4) and −56.7 (5)°, respectively, whereas C17—N5—N5^{i}—C17^{i} and C23—N5—N5^{i}—C23^{i} [symmetry code: (i) $1 - x, -y, z$] for molecule *B* are −86.2 (4) and −34.4 (4)°, respectively. The two benzene rings in each molecule are not coplanar; the dihedral angles between the planes of the rings are 66.3 (1) and 83.3 (1)° in molecules *A* and *B*, respectively.

The N—N bond distance is 1.421 (4) and 1.403 (6) Å in molecules *A* and *B*, respectively. The value found in free 2,4-dinitrophenylhydrazine is 1.405 (4) Å (Okabe *et al.*, 1993), and 1.449 Å in hydrazine (Morino *et al.*, 1960). The sums of the angles around the N atoms are 350.1° for atom N1, 343.6° for atom N2 and 354.5° for atom N5.

Experimental

The reaction was performed at a controlled anode potential of 1.5 V *versus* SCE (saturated calomel electrode) in an undivided cell with platinum plate electrodes having an area of 3 cm^2 and a magnetic stirrer bar in the cell, at room temperature, in methanolic sodium cyanide solution (*N*,*N*-diethyl-*o*-nitroaniline, 0.02 *M*; cyanide, 0.08 *M*). The reaction was terminated after passage of 3 F mol^{-1} of added amine. The electrolyte was worked up by distillation of the methanol. Saturated aqueous NaCl was then added and the mixture was extracted with diethyl ether. The organic layer was dried with Na_2SO_4 and concentrated. The product was purified by column chromatography on silica gel (ethyl acetate–petroleum ether 1:5). It was crystallized from a mixture of ethyl acetate and petroleum ether (m.p. 395 K). ^{1}H NMR ($CDCl_3$,δ, p.p.m.): 7.68 (*dd*, *J* = 1.5 Hz, 2H), 7.43 (*t*, *J* = 8.6 Hz, 2H), 7.33 (*d*, *J* = 1.4 Hz, 2H), 6.96 (*t*, *J* = 8.9 Hz, 2H), 3.42 (*dd*, *J* = 7.3 Hz, 4H), 1.19 (*t*, *J* = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 141.9, 139.9, 132.8, 126.3, 120.7, 119.2, 46.2, 12.7.

Crystal data

$C_{16}H_{18}N_4O_4$
$M_r = 330.34$
Orthorhombic, $P2_12_12$
$a = 7.8212\ (16)$ Å
$b = 46.154\ (4)$ Å
$c = 6.7885\ (8)$ Å
$V = 2450.5\ (6)$ Å^3
$Z = 6$
$D_x = 1.343$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 60 reflections
$\theta = 1.8$–12.5°
$\mu = 0.10$ mm^{-1}
$T = 295\ (2)$ K
Prism, red
0.4 × 0.4 × 0.2 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: none
6045 measured reflections
2550 independent reflections
1594 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$

$\theta_{\rm max} = 25.0^\circ$
$h = -9 \rightarrow 9$
$k = -54 \rightarrow 54$
$l = -8 \rightarrow 8$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.107$
$S = 1.03$
2550 reflections
325 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.394 (5)	N5—C17	1.398 (5)
N1—N2	1.420 (4)	N5—N5$^{\rm i}$	1.405 (6)
N1—C13	1.487 (5)	N5—C23	1.504 (7)
N2—C7	1.412 (5)		
C1—N1—N2	114.7 (3)	C17—N5—N5$^{\rm i}$	114.4 (3)
C1—N1—C13	118.6 (3)	C17—N5—C23	120.9 (3)
N2—N1—C13	116.8 (3)	N5$^{\rm i}$—N5—C23	119.1 (2)
C7—N2—N1	113.0 (3)	N1—C13—C14	113.3 (4)
C7—N2—C15	118.2 (3)	N2—C15—C16	112.7 (4)
N1—N2—C15	112.4 (3)	C24—C23—N5	110.9 (5)
C1—N1—N2—C7	−134.4 (4)	N5$^{\rm i}$—N5—C17—C18	157.5 (4)
C13—N1—N2—C7	80.3 (4)	N5$^{\rm i}$—N5—C17—C22	−19.3 (6)
C13—N1—N2—C15	−56.7 (5)	N5$^{\rm i}$—N5—C23—C24	143.3 (5)
C7—N2—C15—C16	147.1 (4)	N5$^{\rm i}$—N5—C23—C24	−64.3 (6)

Symmetry code: (i) $-x+1, -y, z$.

H atoms were positioned geometrically and refined as riding on their parent atoms, with C—H = 0.93 Å for aromatic CH, 0.97 Å for CH$_2$ and 0.96 Å for methyl groups. Isotropic displacement parameters for the H atoms were set to $1.2U_{\rm eq}$(C) for aromatic and methylene H atoms and $1.5U_{\rm eq}$(C) for methyl groups.

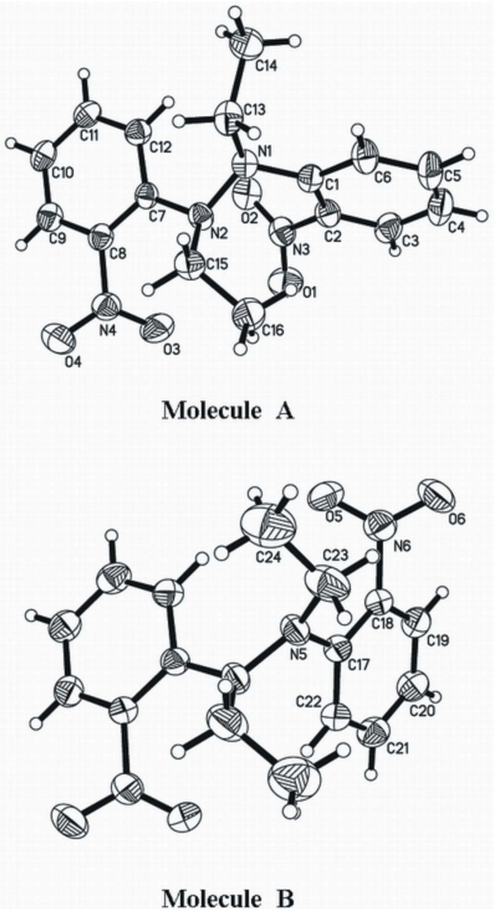


Figure 1
The two independent molecules, *A* and *B*, of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary size. Unlabelled atoms in molecule *B* are related to labelled atoms by the symmetry operator ($1 - x$, $-y$, z).

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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