

1-Nitroindoline

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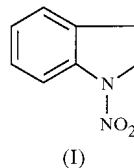
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In the title compound, $C_8H_8N_2O_2$, the nitramino group is planar and only slightly twisted with respect to the indoline rings. The bridgehead N—C bond is slightly shorter than in typical secondary aromatic nitramines. The N—N bond has some double-bond character. The molecules are connected by weak C—H \cdots O hydrogen bonds, forming chains parallel to the z direction.

Comment

Our studies on the molecular structure of secondary aromatic nitramines led to two conclusions. In the molecular structures of typical secondary aromatic nitramines, there are two planar π -electron fragments, *i.e.* the aromatic ring and the nitramino (NNO_2) group. These are not coplanar and the π -electron system of the nitramino group is not conjugated with the ring, as indicated by a large torsion angle about the Ar—N bond. The conformation of the nitramino group is determined by the four-cluster π -orbital system. The formally unshared electron pair on the amide nitrogen is shifted towards the electron-deficient nitrogen of the N -nitro group. The interaction of the N -methylnitramino group with the aromatic ring is of inductive character even in molecules containing a positively charged ring, as in 4-(N -methylnitramino)-1-methylpyridinium bromide (Zaleski *et al.*, 1999a) and 4-(N -methylnitramino)-pyridine 1-oxide (Zaleski *et al.*, 1999b). The twisted conformation of N -methyl- N -phenylnitramines



(Ejsmont *et al.*, 1998; Anulewicz *et al.*, 1993) may result from intermolecular interactions in the crystal network or from steric effects involving repulsion between the O atoms of the nitro groups and the H atoms in the *ortho* positions. To resolve this problem, we have prepared a model compound *viz.* 1-nitroindoline, (I).

It has been assumed that the five-membered ring constrains coplanarity of both π -electron systems. Conjugation between these systems should divert the charge distribution within the NNO_2 group and give rise to some observable changes in its geometry and in the spectral and chemical properties of the nitramine (I). The nitramino group in 1-nitroindoline (Fig. 1) is almost coplanar with C1 and C8. The N7—C1 bond [1.406 (1) Å] is slightly shorter than in typical secondary aromatic nitramines, where it always exceeds 1.42 Å. The N7—C8 bond [1.462 (2) Å] is longer than in analogous non-cyclic nitramines (usually 1.44–1.45 Å). The C1—N7—C8 valence angle [113.0 (1)°] is a compromise between the value characteristic of trigonal hybridization and the internal angle in a regular pentagon. The N—N and N—O bonds have typical lengths; on the other hand, comparison of the FT-IR spectra of (I) and its open-chain analogues (N -alkyl- N -phenylnitramines) suggests some differences in the geometry of the nitramino group since the characteristic bands are shifted. The asymmetric stretch gives a strong band at 1505 cm^{-1} (typically 1520–1525 cm^{-1}) and a symmetric stretching vibration at 1345 cm^{-1} is also out of the usually observed region of 1280–1300 cm^{-1} (Daszkiewicz *et al.*, 1995). The absorption bands may be shifted due to the steric interaction of the O11 and H6 atoms, which are very close to each other. Enlargement of some valence angles centred on C1, N7 and N10 [131.3 (1), 126.6 (1) and 118.4 (1)°, respectively] separates these atoms for the acceptable distance [C6 \cdots O11 2.849 (1) Å and H6 \cdots O11 2.31 Å]. It might have been enhanced more effectively by a twist along the N7—N10 bond, but this is not what is observed. The torsion angle C1—N7—N10—O11 amounts to only 10.4 (2)° and cannot seriously perturb the π -orbital system within the nitramino group. Consequently, the N—N bond [1.336 (1) Å] has some double-bond character, in spite of which it is longer than the corresponding bond in *e.g.* azobenzene (Harada *et al.*, 1997).

The five-membered ring is not planar, the geminal H atoms are in a different environment and their signals in the 1H NMR spectrum are not isochronous; consequently two unresolvable multiplets are observed. Considering that the sum of the internal valence angles is nearly exactly 540°, we may assume, on first sight, that the ring is planar. However, the torsion angles N7—C8—C9—C2 and C1—N7—C8—C9 are *ca* 7.0 (1)°, and suffice to make the aliphatic H atoms magneti-

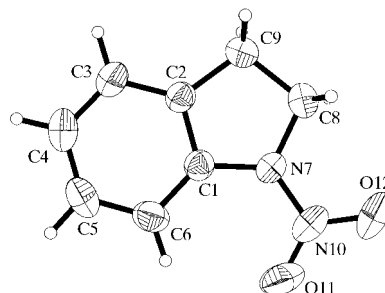


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

cally non-equivalent. It is worth noting that the chemical shift of the *N*-methylene group is nearly the same as observed in the spectrum of *N*-ethyl-*N*-phenylnitramine.

The molecules of (I) are arranged in the *xz* plane. They are connected to each other by weak C3—H3···O12¹ hydrogen bonds, forming chains parallel to the *z* direction (Fig. 2).

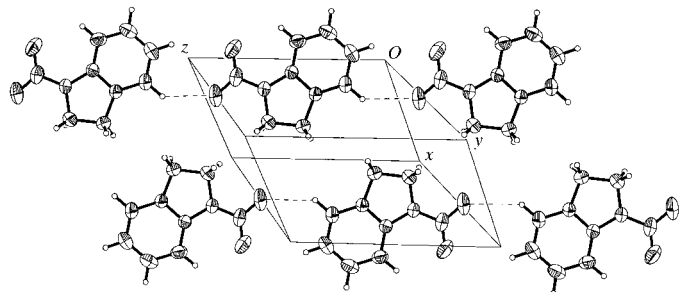


Figure 2
The packing diagram of (I) showing the hydrogen-bonding scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

For the preparation of compound (I), indoline (3.58 g, 0.03 mol) and sodium hydride (3.00 g of 60% NaH, 0.075 mol) were heated in boiling toluene for 2 h under a nitrogen atmosphere. The mixture was cooled to room temperature, *n*-butyl nitrate (5.30 g, 0.045 mol) was added and the suspension was stirred for 1 h at 298 K. Water (20 ml) was added, the layers were separated and the toluene layer was extracted (3 × 20 ml) with aqueous 10% sodium hydrogen sulfate to remove unreacted amine. The solution was dried over anhydrous magnesium sulfate and evaporated in a vacuum at 313 K. The residue (3.31 g, 67%) was crystallized from ethyl ether–*n*-hexane, yielding colourless crystals melting at 363–366 K. Recrystallization from methylene chloride–*n*-hexane gave 1-nitroindoline (1.30 g, 26%) (m.p. 362.5–363.5 K). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a methylene chloride solution at room temperature; the compound is light sensitive. IR (KBr, cm⁻¹): 1505, 1345 (*N*-nitro group stretching vibrations). ¹H NMR (DMSO-*d*₆, p.p.m.): 7.90, *dd*, ³*J* = 8.0 Hz, ⁴*J* = 0.9 Hz, 1H (proton in *ortho* position); 7.11–7.39, *m*, 3H (remaining aromatic H atoms); 4.32–4.48, *m*, 4H and 3.11–3.31, *m*, 4H (aliphatic H atoms).

Crystal data

C ₈ H ₈ N ₂ O ₂	<i>Z</i> = 2
<i>M_r</i> = 164.16	<i>D_x</i> = 1.450 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 5.886 (2) Å	Cell parameters from 19 reflections
<i>b</i> = 8.402 (3) Å	<i>θ</i> = 15–26°
<i>c</i> = 8.923 (3) Å	<i>μ</i> = 0.107 mm ⁻¹
<i>α</i> = 116.80 (3)°	<i>T</i> = 293 (2) K
<i>β</i> = 104.04 (3)°	Plate, colourless
<i>γ</i> = 92.53 (3)°	0.60 × 0.50 × 0.25 mm
<i>V</i> = 376.1 (2) Å ³	

Data collection

Kuma KM-4 diffractometer	<i>h</i> = -8 → 8
<i>ω</i> scans	<i>k</i> = -10 → 8
2196 measured reflections	<i>l</i> = -10 → 12
2063 independent reflections	2 standard reflections
1643 reflections with <i>I</i> > 2σ(<i>I</i>)	every 50 reflections
<i>R</i> _{int} = 0.006	intensity decay: 4.05%
<i>θ</i> _{max} = 30.06°	

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.0575P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	(Δ/σ) _{max} = 0.010
<i>S</i> = 1.012	$\Delta\rho_{max} = 0.25 \text{ e } \text{Å}^{-3}$
2063 reflections	$\Delta\rho_{min} = -0.17 \text{ e } \text{Å}^{-3}$
142 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.042 (10)

Table 1

Selected geometric parameters (Å, °).

C1—C6	1.383 (2)	C5—C6	1.384 (2)
C1—C2	1.388 (1)	N7—N10	1.336 (1)
C1—N7	1.406 (1)	N7—C8	1.462 (2)
C2—C3	1.376 (2)	C8—C9	1.523 (2)
C2—C9	1.499 (2)	O11—N10	1.226 (2)
C3—C4	1.381 (2)	O12—N10	1.231 (2)
C4—C5	1.374 (2)		
C1—N7—C8—C9	-7.0 (1)	C1—N7—N10—O11	10.4 (2)
C3—C2—C9—C8	175.5 (1)	C8—N7—N10—O11	-179.4 (1)
C1—C2—C9—C8	-5.0 (1)	C1—N7—N10—O12	-170.4 (1)
N7—C8—C9—C2	6.9 (1)	C8—N7—N10—O12	-0.3 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C3—H3···O12 ¹	0.98 (2)	2.57 (2)	3.335 (2)	134 (1)

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

All H-atom parameters were refined and C—H distances ranged from 0.924 (18) to 0.994 (19) Å.

Cell refinement: *Kuma Diffraction Software* (Kuma, 1997); data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1117). Services for accessing these data are described at the back of the journal.

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