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Key indicators

Single-crystal X-ray study

 $T = 85\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$ R factor = 0.037 wR factor = 0.090

Data-to-parameter ratio = 11.8

For details of how these key indicators were
automatically derived from the article, see
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1,5-Dimethyl-2-nitrimino-1,2-dihydropyridine

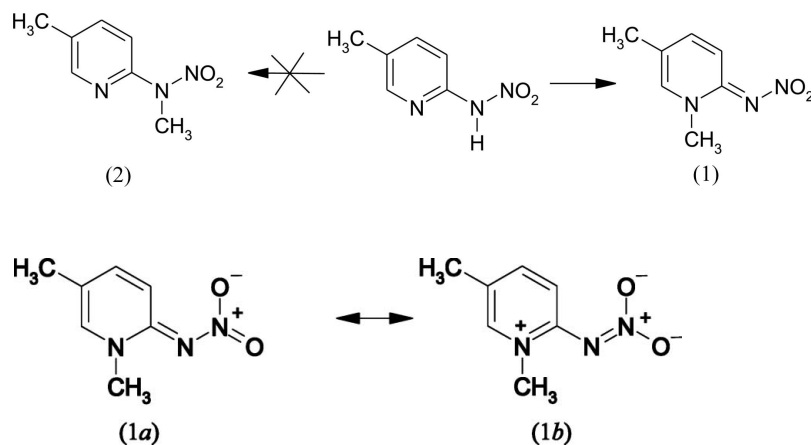
Methylation of 5-methyl-2-nitraminopyridine provides the title compound, $\text{C}_7\text{H}_9\text{N}_3\text{O}_2$, as the only product. The molecule consists of two planar fragments, *viz.* an aromatic ring and a nitrimino substituent. The NNO_2 group is twisted by $17(2)^\circ$ out of the plane of the pyridine ring. Despite a small torsion angle between these fragments, the geometry of the molecule indicates the participation of the π -electrons in the $\text{C}-\text{N}$ bond. The hydrogen bonds in the crystal structure seem to be too weak to generate any deformations observed in the molecule.

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Comment

Methylation of *N*-(2-pyridyl)nitramine under mild conditions provides the corresponding nitrimine in good yield (Daszkiewicz *et al.*, 1999). There are two nucleophilic centres in the nitramine anion; the site of methylation is influenced by the ring substituents. 2-Nitramino-5-methylpyridine gives 1,2-dihydro-1,5-dimethyl-2-nitriminopyridine, (1), as the only product when methylated in an alkaline medium.



The nitrimines, such as (1), and nitramines, *e.g.* (2), differ markedly in their chemical properties, especially regarding their susceptibility to the nitramine rearrangement (Daszkiewicz *et al.*, 1997). It may be of some interest to estimate the influence of *N*-methyl and *C*-methyl substituents on the aromaticity of the ring and the geometry of the NNO_2 group. The structure of (1) may be considered as a resonance hybrid of two canonical forms, (1a) and (1b), shown in the scheme.

In the resonance form (1b) the pyridine ring is presented as aromatic, while structure (1a) predicts significant deformations of the geometry of the ring. Comparison of the bond lengths within the ring does not resolve the problem of the participation of (1a) and (1b) in the electron distribution. The

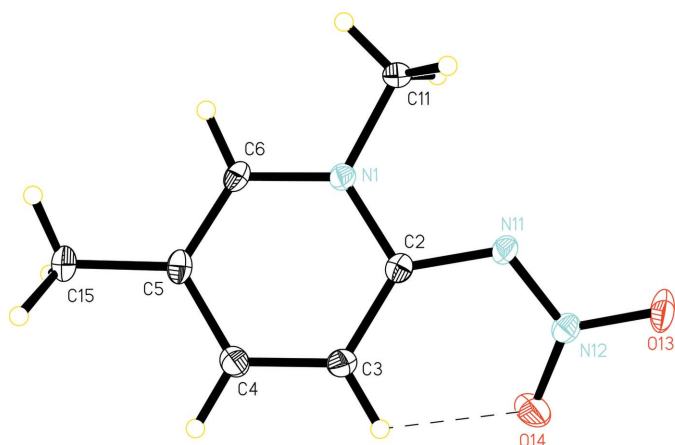


Figure 1
The molecular structure of (1). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates a hydrogen bond.

longest bond [C2—C3 = 1.4225 (17) Å] is presented as a single in both structures, while the double bond [C5—C6 = 1.3810 (17) Å] is the shortest one. The planarity of the ring favours the aromatic structure (1*b*). The largest deviation from the plane [0.0203 (8) Å for atom C2] and the location of the N1—C11 bond in the plane indicates that an unshared electron pair on atom N1 is lacking.

The nitrimino group is nearly planar, with atom N12 only 0.0199 (13) Å from the N11/O13/O14 plane, but the N11—C2 bond is rather far from this plane. Another way of lengthening the H3...O14 distance to the sum of the van der Waals radii (2.60 Å; Pauling & Pauling, 1975) is deformation of the valence angles. The C3—C2—N11 angle is enlarged to 130.91 (11)° at the expense of the N1—C2—N11 angle [112.04 (10)°]. Analogously, the N11—N12—O14 angle [123.84 (11)°] is greater than another one centred on N12 [115.96 (10)°]. The observed deviations from coplanarity of the nitrimino group and pyridine ring may also result from steric factors. Small torsion angles along the C2—N1 [N1—C2—N11—N12 19.4 (2)° and C3—C2—N11—N12 -165.40 (10)°] and N11—N12 bonds [C2—N11—N12—O14 6.81 (18)° and C2—N11—N12—O13 -176.28 (11)°] are also observed. Such an arrangement decreases the effectiveness of π -electron delocalization but does not suppress it completely.

Four intermolecular hydrogen bonds are present in the crystal structure, with the O atoms of the nitro groups acting as acceptors. They are, in general, weak in nature, since H atoms bonded to C atoms participate in this interaction. Aromatic C atoms are better H-atom donors than methyl groups. The strongest hydrogen bond is the intramolecular C3—H3...O14 interaction, illustrated in Fig. 2.

Experimental

5-Methyl-2-nitraminopyridine (1.53 g, 0.01 mol) and anhydrous sodium carbonate (2.10 g, 0.02 mol) were dissolved in water (80 ml). Dimethyl sulfate (1.1 ml, 11.6 mmol) was added and the mixture was stirred for 6 h at room temperature. It was then cooled on an ice bath and a precipitate (0.84 g, m.p. 465–467 K) was collected by filtration.

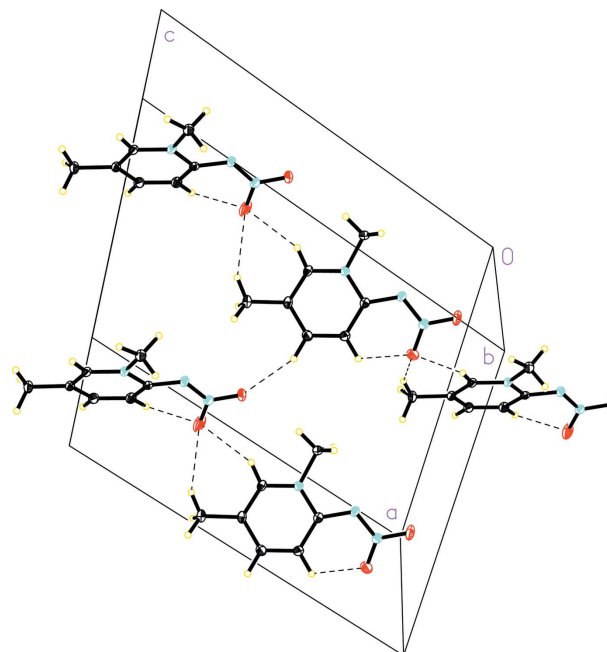


Figure 2
A packing diagram for (1), showing the intermolecular hydrogen-bonding scheme (dashed lines).

Sodium carbonate and dimethyl sulfate, in the same amounts, were added to the filtrate and stirring was continued for 4 h. The second crop of the crude product was combined with the first one (1.37 g, 82%) and crystallized from water. Recrystallization from methanol provided crystals of 1,5-dimethyl-2-nitrimino-1,2-dihydropyridine, (1), suitable for X-ray diffraction studies (0.89 g, 53%; m.p. 464–465 K). ^1H NMR (DMSO-*d*₆, δ , p.p.m.): 8.23 (*dd*, $^3J = 9.4$ Hz, $^4J = 2.3$ Hz, ^1H , H4), 8.11 (*d*, $^4J = 2.3$ Hz, ^1H , C6), 7.90 (*d*, $^3J = 9.4$ Hz, ^1H , H3), 3.79 (*s*, 3H, *N*-methyl group), 2.24 (*s*, 3H, Ar-methyl group); ^{13}C NMR (DMSO-*d*₆, δ , p.p.m.): 155.1 (C2), 144.0 (C6), 140.5 (C4), 124.6 (C5), 117.6 (C3), 42.4 (*N*-methyl group), 16.7 (Ar-methyl group); IR (KBr, ν , cm^{-1}): 1412, 1257 (*N*-nitro group).

Crystal data

$\text{C}_7\text{H}_9\text{N}_3\text{O}_2$
 $M_r = 167.17$
Monoclinic, $C2/c$
 $a = 14.3053$ (17) Å
 $b = 7.6741$ (10) Å
 $c = 15.790$ (2) Å
 $\beta = 114.586$ (12)°
 $V = 1576.3$ (4) Å³

$Z = 8$
 $D_x = 1.409$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 85.0$ (1) K
Block, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
 ω scans
Absorption correction: none
5421 measured reflections

1713 independent reflections
1456 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 27.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.07$
1713 reflections
145 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 1.7281P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C6	1.3633 (16)	C4—C5	1.4141 (18)
N1—C2	1.3824 (16)	C5—C6	1.3810 (17)
C2—N11	1.3716 (15)	N11—N12	1.3359 (15)
C2—C3	1.4225 (17)	N12—O14	1.2463 (14)
C3—C4	1.3787 (17)	N12—O13	1.2518 (14)
N11—C2—N1	112.04 (10)	N12—N11—C2	117.78 (10)
N11—C2—C3	130.91 (11)	O14—N12—N11	123.84 (11)
N1—C2—C3	116.89 (11)	O13—N12—N11	115.96 (10)
N1—C6—C5	122.14 (11)		
N1—C2—N11—N12	−165.40 (10)	C2—N11—N12—O14	6.81 (18)
C3—C2—N11—N12	19.4 (2)	C2—N11—N12—O13	−176.28 (11)

Table 2

Hydrogen-bond 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>
C11—H1C...O14 ⁱ	0.99 (2)	2.50 (2)	3.2217 (17)	129 (1)
C3—H3...O14	0.97 (2)	2.17 (2)	2.7009 (16)	113 (1)
C4—H4...O13 ⁱⁱ	0.99 (2)	2.36 (2)	3.2738 (16)	154 (1)
C15—H5A...O14 ⁱⁱⁱ	0.98 (2)	2.57 (2)	3.4285 (18)	147 (1)
C6—H6...O14 ⁱⁱⁱ	0.95 (2)	2.39 (2)	3.2576 (16)	152 (1)

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

H atoms were located in a difference Fourier map and refined freely. Refined C—H distances converged between 0.947 (15) and 1.000 (18) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

References

- Daszkiewicz, Z., Domański, A. A. & Kyzioł, J. B. (1997). *Chem. Pap.* **51**, 22–28.
- Daszkiewicz, Z., Kyzioł, J. B. & Zaleski, J. (1999). *J. Mol. Struct.* **513**, 69–77.
- Oxford Diffraction (2002). *CrysAlis CCD* (Version 1.170) and *CrysAlis RED* (Version 1.170.16). Oxford Diffraction, Wrocław, Poland.
- Pauling, L. & Pauling, P. (1975). *Chemistry*, p. 163. San Francisco: W. H. Freeman and Company. Polish Edition.
- Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.