

The crystals used in this investigation were prepared by Miss Britta Lundtoft.

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## 2-Amino-3-nitropyridine

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**Abstract.**  $C_5H_5N_3O_2$ , monoclinic, space group  $P2_1/n$ ;  $a=8.743(1)$ ,  $b=4.898(1)$ ,  $c=14.473(1)$  Å,  $\beta=106.57(1)^\circ$ ,  $V=594$  Å<sup>3</sup>,  $Z=4$ ,  $D_m=1.54(1)$ ,  $D_c=1.553$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha)=10.7$  cm<sup>-1</sup>. The molecule is closely planar, the nitro group being rotated by less than 3°. The structure features an off-set stacking of parallel pyridine rings at a separation of about 3.16 Å, and hydrogen bonding across centres of symmetry to form dimers.

**Introduction.** Crystals of 2-amino-3-nitropyridine are yellow needles elongated along **b**. Cell dimensions were obtained by a least-squares fit to the  $\sin^2 \theta$  values of 56  $hkl$  reflexions measured on a diffractometer. No corrections for eccentricity or absorption were made, and weights were assumed as inversely proportional to  $\sin^2 2\theta$ . The space group  $P2_1/n$  was indicated by the absences  $h0l$  with  $(h+l)$  odd and  $0k0$  with  $k$  odd. The

density was measured by flotation in dilute  $K_2HgI_4$  solution.

A crystal,  $0.30 \times 0.20 \times 0.15$  mm, sealed in a Lindemann glass capillary, was mounted on a computer-controlled Syntex  $P1$  diffractometer. Intensities were collected with Cu  $K\alpha$  radiation [ $\lambda(\text{Cu } K\alpha)=1.5418$  Å; graphite monochromator] and a variable rate  $\theta$ - $2\theta$  scan technique. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. A single standard reflexion was checked after each 45 intensity measurements; it showed no significant drift in intensity. A correction for coincidence losses at high counting rates was applied according to  $I_c = [1 - (1 - 4\tau I_o)^{1/2}] / 2\tau$ , where  $I_c$  and  $I_o$  are the corrected and observed intensities, respectively, and  $\tau$  is the dead time, for which a value of  $2.1 \times 10^{-6}$  was calculated from empirical data. The data set consisted of 985 observed reflexions (*i.e.*

Table 1. *Final atomic parameters and standard deviations (in parentheses)*

The anisotropic temperature coefficients are in the form  $T_i = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$ .

Fractional coordinates are  $\times 10^5$  for heavy atoms,  $\times 10^3$  for hydrogen atoms. Anisotropic temperature coefficients are  $\times 10^4$ , isotropic  $B$ 's  $\times 10$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>23</sub>
N(1)	40401 (23)	25785 (40)	56456 (13)	154 (3)	407 (10)	41 (1)	11 (5)	26 (1)	-1 (2)
C(2)	32173 (25)	16128 (49)	47594 (14)	128 (3)	355 (11)	40 (1)	55 (5)	25 (2)	8 (3)
C(3)	21437 (25)	-5798 (49)	46982 (14)	125 (3)	399 (12)	40 (1)	31 (5)	21 (2)	-3 (3)
C(4)	19416 (28)	-17417 (57)	55308 (17)	138 (4)	430 (13)	52 (1)	6 (6)	31 (2)	7 (4)
C(5)	27964 (30)	-7537 (58)	64098 (17)	177 (4)	524 (15)	43 (1)	7 (6)	36 (2)	18 (4)
C(6)	38186 (31)	13976 (59)	64219 (17)	172 (4)	493 (14)	41 (1)	-5 (7)	24 (2)	-6 (3)
N(2)	35207 (27)	29200 (50)	40207 (15)	181 (4)	471 (12)	41 (1)	-3 (6)	28 (2)	19 (3)
N(3)	12528 (24)	-17335 (46)	37890 (13)	152 (3)	491 (12)	47 (1)	21 (5)	18 (2)	-3 (3)
O(1)	14801 (23)	-8376 (45)	30413 (12)	268 (4)	682 (12)	40 (1)	-64 (6)	21 (1)	2 (3)
O(2)	2980 (21)	-35806 (44)	37814 (12)	180 (3)	651 (11)	71 (1)	-99 (5)	20 (2)	-25 (3)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	434 (3)	431 (6)	415 (2)	67 (7)
H(2)	307 (3)	228 (5)	344 (2)	55 (6)
H(4)	116 (3)	-325 (6)	545 (2)	63 (6)
H(5)	273 (3)	-149 (6)	702 (2)	65 (6)
H(6)	444 (3)	215 (5)	701 (2)	56 (6)

greater than zero) out of 1101 independent reflexions measured in the range  $0 < 2\theta < 140^\circ$ . Each reflexion was assigned a variance of  $\sigma^2(I)$  based on counting statistics plus a term  $(0.02 S)^2$ , where  $S$  is the scan count. Intensities and their standard deviations  $\sigma(I)$  were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the symbolic addition method based on the 183 reflexions with  $E \geq 1.50$ . The correct solution had the highest consistency (0.94) and required the fewest cycles to reach convergence. The resulting  $E$  map showed the location of all non-hydrogen atoms, which led to an  $R$  ( $= \sum |F_o - F_c| / \sum |F_o|$ ) of 0.29 for the 1101 measured reflexions. After three cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors, based on the 985 observed reflexions, a difference map indicated the location of all five H atoms.

The final least-squares refinement included, in a single matrix, 112 parameters: coordinates and anisotropic temperature coefficients  $B_{ij}$  for the ten heavy atoms, coordinates and isotropic  $B$ 's for the five H atoms, a scale factor, and a secondary extinction parameter  $g$  (Larson, 1967, equation 3; Zachariasen, 1963). During the last least-squares cycle, the shifts in atomic parameters were less than  $0.2\sigma$  (with the exception of  $b_{33}$  for C(2) and N(1), the shift being  $< 0.3\sigma$ ), and convergence was assumed. A final difference map showed no unusual features. The final  $R$  was 0.057 for 985 reflexions having net intensities greater than zero, the weighted  $R$   $\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} \}$  0.052, and the goodness-of-fit, based on 985 weighted reflexions and 112 parameters, was 2.41. The secondary extinction coefficient,  $g$ , assumed a final value of  $14.5 (2.5) \times 10^{-6}$ . Form factors for C, N and O were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , with  $w = 1/\sigma^2(F_o)$  [where  $\sigma^2(F_o) = \sigma^2(F_o^2) / 4F_o^2$ ]. The final parameters are in Table 1.\*

**Discussion.** In the investigation of the e.s.r. spectra of nitroaminopyridine radical anions it appeared that the theoretical interpretation of the spectra is possible only through the knowledge of the accurate geometry of the parent compounds. To this aim the crystal structure determination of 2-amino-3-nitropyridine has

been carried out. The results are shown on the thermal ellipsoid plot of Fig. 1, which includes bond distances and angles (the formal e.s.d.'s are in parentheses), and the numbering of atoms.

The pyridine ring is substantially planar (Table 2); N(2) lies on the ring plane, while N(3) is displaced

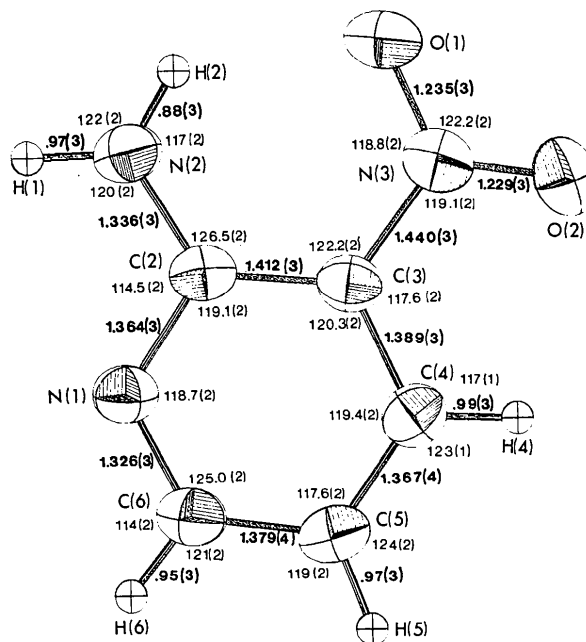


Fig. 1. The 2-amino-3-nitropyridine molecule. The atoms are represented by temperature-factor ellipsoids drawn at the 40% probability level (Johnson, 1965).

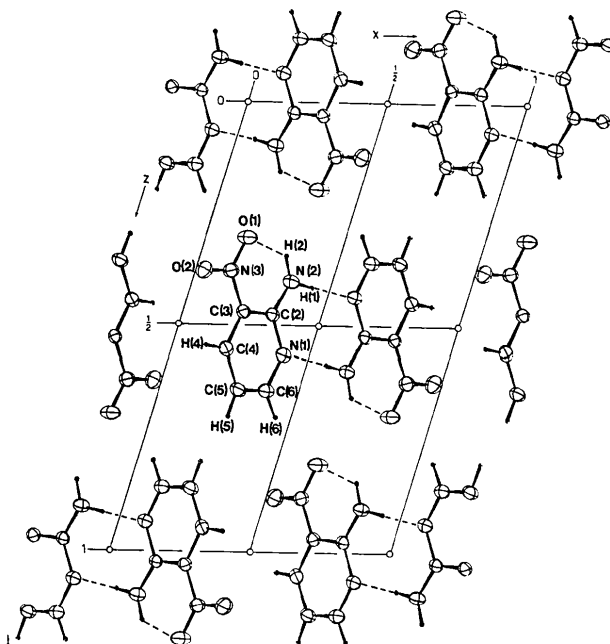


Fig. 2. A drawing of the structure viewed down *b*. Dashed lines represent hydrogen bonds.

\* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31240 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

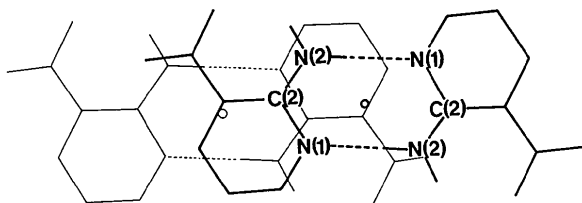


Fig. 3. A drawing of the dimer stacking, viewed perpendicular to the planes of the pyridine rings.

from the plane by  $> 10\sigma$ . From torsion angles involving O(1), O(2), N(3), C(3), C(2) and C(4) a slight rotation ( $< 3^\circ$ ) of the nitro group can be inferred. C(3), N(3), O(1) and O(2) are coplanar within 0.002 Å; this plane makes an angle of  $3.7^\circ$  with the plane of the pyridine ring.

Table 2. Deviations from the least-squares plane of the pyridine ring

The direction cosines of the least-squares plane of N(1)–C(6), weighted equally, are 0.7630,  $-0.6460$  and  $-0.1961$  relative to the crystal axes  $a$ ,  $b$  and  $c$ ; the origin-to-plane distance is 0.281 Å.

N(1)	$-0.004$ Å	N(2)	$0.003$ Å	H(1)	$0.07$ Å
C(2)	$0.004$	N(3)	$0.028$	H(2)	$0.07$
C(3)	$-0.001$	O(1)	$0.109$	H(4)	$-0.02$
C(4)	$-0.004$	O(2)	$-0.022$	H(5)	$0.02$
C(5)	$0.004$			H(6)	$0.01$
C(6)	$0.002$				

A drawing of the structure is shown in Fig. 2. Centres of symmetry are utilized in forming dimers linked by N(2)–H(1)···N(1) hydrogen bonds [N(2)···N(1) = 3.009; H(1)···N(1) = 2.04 Å]. The second H atom of the amino group is involved in an intramolecular hydrogen bond [H(2)···O(1) = 2.03 Å].

Molecules related to one another by translation along  $b$  form a column of relatively close, off-set stacked dimers; the stacking distance is 3.16 Å. The shortest heavy-atom contacts within the stacked dimers are: O(2)···N(2), 3.231; N(3)···N(2), 3.244; C(4)···N(1), 3.311; C(2)···N(1), 3.333; C(6)···N(2), 3.338; N(1)···N(2), 3.383; and C(2)···C(2), 3.385 Å.

A drawing of one of these columns, viewed perpendicular to the planes of the dimers, is shown in Fig. 3. The shortest contacts between atoms in different stacks involve atoms of the nitro group. They include: N(2)···O(1) (at  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ), 3.046; C(4)···O(2) (at  $-x, -1 - y, 1 - z$ ), 3.345; and C(5)···O(2) (at  $-x, -y, 1 - z$ ), 3.388 Å.

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## 3-Cyano-2-phenylglyoxyl-*N*-methoxyaziridine (*E*)

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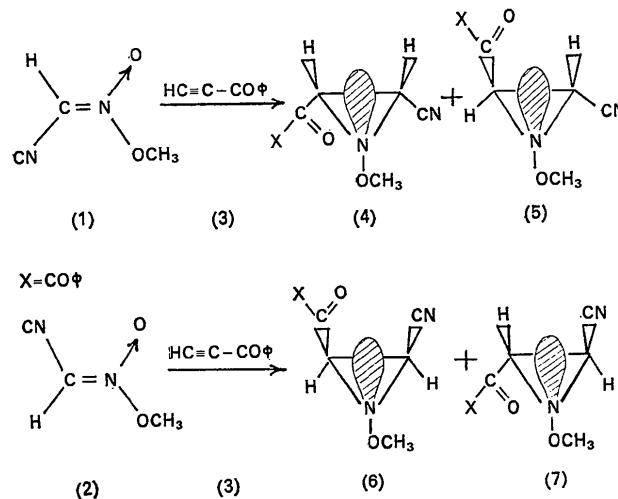
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**Abstract.** C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>, orthorhombic, *Pbca*,  $a = 15.70$  (2),  $b = 6.45$  (1),  $c = 23.19$  (2),  $Z = 8$ ,  $D_c = 1.30$  g cm<sup>-3</sup>.

This determination has been carried out to establish unambiguously the stereochemistry at the nitrogen atom N(1). The methoxy group bonded to N(1) is *cis* with respect to the cyano group and *trans* to the phenylglyoxyl group.

**Introduction.** The addition of nitronic esters (1) and (2) to benzoylacetylene (3) leads to a quantitative yield of stable nitrogen invertomers of aziridines (4) to (7).<sup>\*</sup> This reaction is stereoselective (Grée & Carrié, 1975); (1) gives only (4) and (5), and (2) leads to (6) and (7):



\* It is well known that the nitrogen inversion barrier of aziridines is considerably raised when this nitrogen bears a methoxy substituent (Brois, 1970; Lehn, 1970; Rauk, Allen & Mislow, 1970).