Acta Cryst. (1998). C**54**, 441–442

2-(Nitroamino)pyridine

Olyana Angelova,[a] Rosica Petrova[a] and Vladimir Atanasov[b]

[a]*Bulgarian Academy of Sciences, CL Mineralogy & Crystallography, Rakovski str. 92, 1000 Sofia, Bulgaria, and* [b]*University of Sofia, Chemistry Department, J. Bauchier 1, 1027 Sofia, Bulgaria. E-mail: jmacicek@bgcict.acad.bg*

(*Received 28 May 1997; accepted 5 November 1997*)

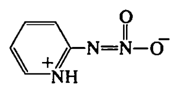
Abstract

In the title compound, $C_5H_5N_3O_2$, the amino H atom was localized in the vicinity of the endocyclic N atom at a distance of 0.94 (2) Å, showing that the compound exists in the form of a zwitterion. Bond lengths and molecular planarity [within 0.048 (1) Å] correspond to an overall π-conjugated system. The molecules are coupled as centrosymmetric dimers through short N_{endo}—H···N_{exo} hydrogen bonds.

Comment

2-(Nitroamino)pyridine is of potential interest as a non-linear material due to its overall conjugation and molecular polarity. Also, it is an effective reagent for the synthesis of 3- and 5-nitro-2-aminopyridines (Deady *et al.*, 1979, 1982); knowledge of its structure could throw light on the reaction mechanism.

The title compound undergoes an intramolecular amino H-atom rearrangement to give a zwitterion, (I), in the solid state.



(I)

Bond lengths and molecular planarity [within 0.048 (1) Å] correspond to an overall π-conjugated system (Allen *et al.*, 1987). The intramolecular C3—H3···O1 hydrogen bond stabilizes the molecular planarity and is a factor facilitating nucleophilic attack at position 3 in the pyridinium ring. The molecules are coupled to form centrosymmetric dimers through short N1—H1···N2 and C6—H6···O2 bonds (Table 3). The dimers are further hydrogen bonded by relatively short C—H···O-type interactions. The molecules are plane-to-plane stacked along the *b* axis, with an interplanar distance of 3.678 (3) Å.

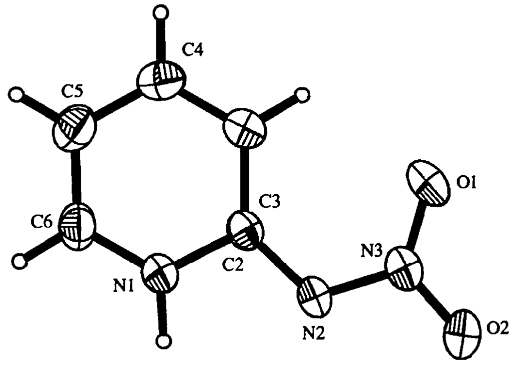


Fig. 1. View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

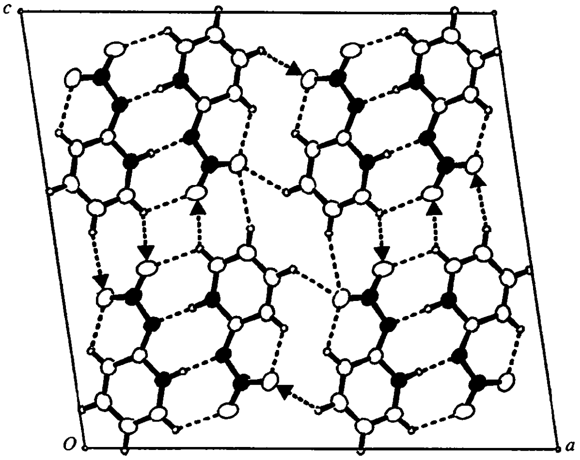


Fig. 2. Projection of the structure down the *b* axis. Dotted lines denote hydrogen bonds. Arrows are for bonds to symmetry-equivalent atoms.

Experimental

2-(Nitroamino)pyridine was synthesized from 2-aminopyridine following the procedure of Deady *et al.* (1982). 2-Aminopyridine was treated with concentrated H_2SO_4–HNO_3 (1:1) at 273 K for 1 h. The mixture was neutralized with aqueous NH_3 to pH 3. The crude product was recrystallized from aqueous ethanol. Single crystals were grown by slow evaporation of an acetonitrile solution.

Crystal data

$C_5H_5N_3O_2$
$M_r = 139.11$
Monoclinic
$I2/a$
$a = 18.331\ (4)$ Å
$b = 3.678\ (3)$ Å
$c = 17.052\ (1)$ Å
$\beta = 98.43\ (2)°$
$V = 1137.3\ (7)$ Å^3
$Z = 8$
$D_x = 1.624$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 21.54$–$22.25°$
$\mu = 0.12$ mm^{-1}
$T = 292$ K
Prismatic
0.53 × 0.33 × 0.33 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6136 measured reflections
1692 independent reflections
1220 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 30.0°$
$h = -25 \rightarrow 25$
$k = -5 \rightarrow 5$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 1.6%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.071$
$S = 1.232$
1220 reflections
95 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + (0.045F)^2]$
$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 0.143$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.095$ e Å^{-3}
Extinction correction: Stout & Jensen (1968), formula 17.16
Extinction coefficient: $3.976(6) \times 10^{-6}$
Scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.41131 (6)	−0.1925 (4)	0.15292 (7)	0.0545 (3)
O2	0.31355 (7)	0.0426 (4)	0.08584 (7)	0.0601 (3)
N1	0.31503 (6)	0.0694 (3)	0.34356 (6)	0.0311 (2)
N2	0.32041 (6)	0.0516 (4)	0.21382 (6)	0.0342 (3)
N3	0.35095 (7)	−0.0373 (4)	0.14993 (7)	0.0378 (3)
C2	0.35668 (7)	−0.0279 (3)	0.28721 (7)	0.0281 (3)
C3	0.42603 (7)	−0.1823 (4)	0.31444 (8)	0.0339 (3)
C4	0.44784 (8)	−0.2285 (4)	0.39414 (9)	0.0391 (3)
C5	0.40256 (8)	−0.1269 (4)	0.44970 (9)	0.0412 (4)
C6	0.33611 (8)	0.0230 (5)	0.42173 (8)	0.0375 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—N3	1.239 (2)	N2—C2	1.360 (2)
O2—N3	1.237 (2)	C2—C3	1.407 (2)
N1—C2	1.360 (2)	C3—C4	1.370 (2)
N1—C6	1.343 (2)	C4—C5	1.399 (2)
N2—N3	1.336 (2)	C5—C6	1.358 (2)
N3—N2—C2	119.4 (1)	O2—N3—N2	114.7 (1)
O1—N3—O2	121.4 (1)	N1—C2—N2	110.1 (1)
O1—N3—N2	123.9 (1)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—HN1$\cdots$N2$^{\rm i}$	0.95 (2)	1.95 (2)	2.890 (3)	175.7 (18)
C3—H3$\cdots$O1	0.95	2.18	2.728 (2)	115.4
C4—H4$\cdots$O1$^{\rm ii}$	0.95	2.56	3.291 (2)	134.3
C5—H5$\cdots$O1$^{\rm iii}$	0.95	2.60	3.509 (2)	160.3
C6—H6$\cdots$O2$^{\rm iv}$	0.95	2.54	3.300 (2)	137.5
C6—H6$\cdots$O2$^{\rm i}$	0.95	2.55	3.161 (2)	122.1

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

The H atoms bonded to C atoms were constrained to idealized positions, while the amino H atom was located from a difference Fourier map and further included in the refinement. All H atoms were assigned isotropic U values of 0.0506 Å^2.

Data collection: *CAD*-4 *Users Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work was supported by the Bulgarian Academy of Sciences and the Bulgarian National Science Fund (Projects Ch-402 and Ch-588).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1128). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Deady, L. W., Grimmett, M. R. & Potts, C. H. (1979). *Tetrahedron*, **35**, 2895–2900.

Deady, L. W., Korytsky, O. L. & Rowe, J. E. (1982). *Aust. J. Chem.* **35**, 2025–2034.

Enraf–Nonius (1985). *Structure Determination Package. SDP/PDP Users Guide.* Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1988). *CAD-4 Users Manual.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Macíček, J. (1992). *KAPPA. Program for the Preparation of Material for Publication from a CIF File.* Bulgarian Academy of Sciences, Sofia, Bulgaria.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Stout, G. H. & Jensen, H. (1968). In *X-ray Structure Determination.* New York: MacMillan.

Acta Cryst. (1998). **C54**, 442–444

5-Amino-3-trifluoromethyl-1*H*-1,2,4-triazole

O. Ya. Borbulevych,[a] O. V. Shishkin,[a] S. M. Desenko,[b] V. N. Chernenko[b] and V. D. Orlov[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 28 Vavilov str., Moscow 117813, Russia, and* [b]*Kharkov State University, 4 Svobodi sq., Kharkov 310077, Ukraine. E-mail: shil@xrpent.ineos.ac.ru*

(Received 10 July 1997; accepted 23 October 1997)

Abstract

The bond lengths in the five-membered ring of the title compound, $C_3H_3F_3N_4$, (1), are equal within three standard deviations to those in 5-amino-3-nitro-1*H*-1,2,4-triazole. The amino group in (1) has a trigonal-