

Table 3. First- and second-level graph-set descriptors involving hydrogen bonds designated (a)–(h) as described in the text

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
(a)	D	R ₂ ² (18)			C ₄ ¹ (18)	C ₄ ¹ (28)		
(b)		D			C ₄ ¹ (12)	C ₄ ¹ (30)		
(c)			R ₂ ² (14)					
(d)				D			C ₄ ¹ (30)	C ₄ ¹ (30)
(e)					D	R ₂ ² (30)		
(f)						D		
(g)							D	R ₂ ² (4)
(h)								D

Scan widths were $(1.20 + 0.35 \tan \theta)^\circ$ in ω , with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry indicated space group $P2_1/a$ (No. 14) and since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. Refined C—H distances range from 0.92 (2) to 0.99 (2) Å, with a mean value of 0.96 Å; refined O—H distances are given in Table 2. The refined water molecule angles are 106 (2) and 91 (4)°. The maximum effect of extinction was 7.2% of F_o for 202. The maximum positive residual peak was located near the midpoint of the C1—C13 bond; the maximum negative peak was located ~ 1.2 Å from C16 and ~ 1.6 Å from C9.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1049). Services for accessing these data are described at the back of the journal.

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1:1 Molecular Complex of 2-Amino-5-nitropyridine and 3-Nitro-2-pyridone

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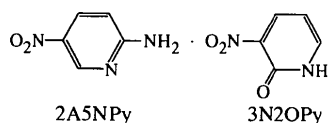
Abstract

The 2-amino-5-nitropyridine molecule of the title complex, C₅H₅N₃O₂·C₅H₄N₂O₃, is planar, while the nitro group in 3-nitro-2-pyridone is tilted away from the mean plane by 27.9 (3)°. The C—C bond distance between the substituted atoms in the pyridone ring, 1.439 (3) Å, is slightly lengthened due to the electron-withdrawing effect of the adjacent carbonyl and nitro groups. The molecules are linked into centrosymmetric tetramers which are stacked in layers along the *c* axis. The layers are held together by weak C—H···O hydrogen bonds and van der Waals interactions.

Comment

2-Amino-5-nitropyridine derivatives (Lehn, 1987; Nicoud & Twieg, 1987), its adducts (Masse, 1995; Hu, Shi, Huang, Li & Yang, 1994) and salts (Watanabe, Noritake, Hirose, Okada & Kurauchi, 1993; Pecaut & Masse, 1993) have been intensively examined in relation to their application as non-linear optical materials. We attempted to use a one-stage procedure for 2-aminopyridine nitration with a mixture of concentrated sulfuric and nitric acids (Lewis & Winfield, 1955), which usually gives a mixture of 3-nitro- and 5-nitro-2-aminopyridines in a ratio of 1:5 to 1:8 (Shoefield, 1967; Smith, 1985). The attempts to separate the two isomers by repeated fractionation from ethanol were unsuccessful because of the presence of an unknown phase. The structure analysis showed that under the experimental conditions

applied the main reaction product was a 1:1 molecular complex of 2-amino-5-nitropyridine (2A5NPy) and 3-nitro-2-pyridone (3N2OPy). The presence of the latter among the reaction products can be explained by the hydrolysis of 2-nitraminopyridine, formed during the first stage of the process, to 2-pyridone as a result of the relatively high water concentration in the nitration mixture. 2-Pyridone then undergoes further nitration to 3-nitro-2-pyridone. The characteristic features of nitraminopyridine rearrangement reactions in sulfuric acid have been discussed by Deady, Grimmet & Potts (1979).



The molecular geometry of 2A5NPy is in good agreement with that already determined for 2-amino-3-nitropyridine (Destro, Pilati & Simonetta, 1975). The molecule of 2A5NPy is planar within 0.010 (2) Å, with the O1A atom being furthest from its mean plane.

The keto form of the compound, 3N2OPy, was unequivocally established from the difference Fourier map after anisotropic refinement of the heavy atoms. A peak corresponding to the presence of a H atom was localized near the N1B rather than the O3B atom. The

bond lengths and angles are close to those found for the 2-pyridone derivatives (Almlöf, Kvick & Olovsson, 1971; Kvick & Booles, 1972). The C2B—C3B bond distance, 1.439 (3) Å, in 3N2OPy is slightly lengthened due to the electron-withdrawing effect of the adjacent carbonyl and nitro groups. The pyridone ring is planar, with the largest deviation of 0.021 (3) Å at the C3B atom. The nitro group is tilted away from this plane by 27.9 (3)°, which leads to a lengthening of the C—NO₂ bond to 1.457 (4) as compared with 1.436 (3) Å for the in-plane nitro group in 2A5NPy.

The molecules are linked into centrosymmetric tetramers (Fig. 1) by three types of hydrogen bonds, *i.e.* N—H···O, N—H···N and C—H···O (Table 2). The 2A5NPy and pyridone rings are coplanar, making a dihedral angle of 5.0 (1)°. The eight-membered hydrogen-bonded ring formed by the *endo*-imino HN1B and amino HN31A atoms is similar to that found in the structure of 2-pyridone:6-chloro-2-hydroxypyridine (Almlöf, Kvick & Olovsson, 1971). In addition, the second amino HN32A atom closes another eight-membered ring, which is further stabilized by two C3A—H3A···O2B hydrogen bonds. The H···O and C···O distances, on average 2.45 (2) and 3.26 (3) Å, respectively, fall within the same ranges already observed for the coordinated water molecules in the structures of certain hydrated alkaloids (Steiner, 1995).

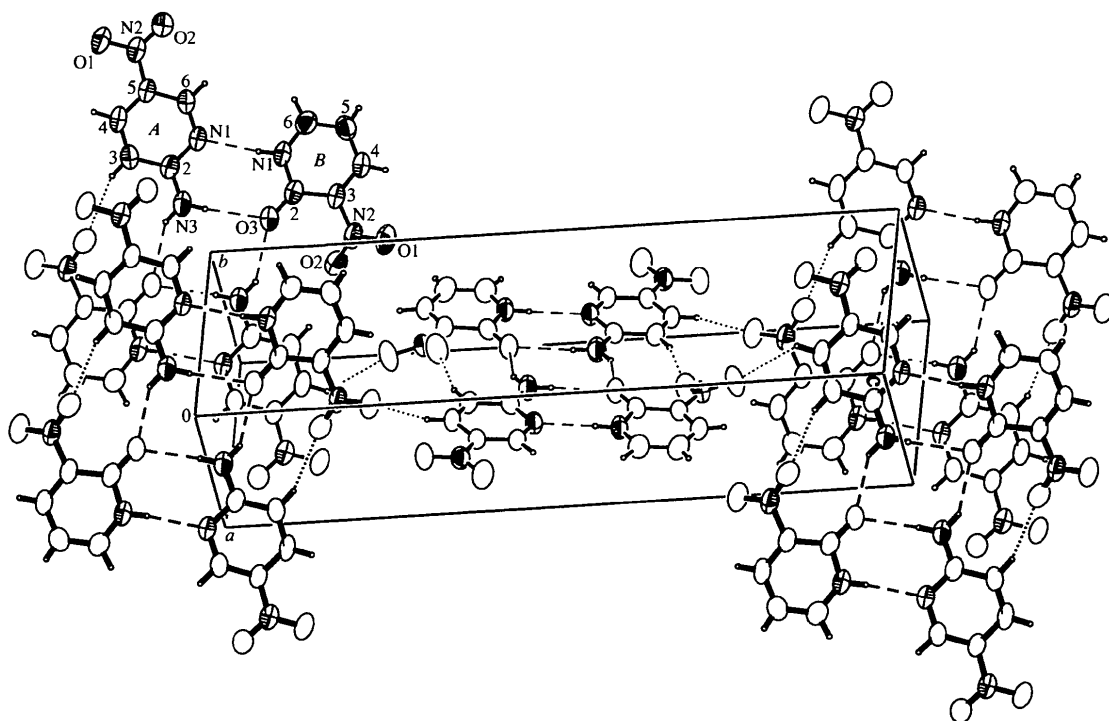


Fig. 1. A view of the packing of the tetramers in the unit cell. Displacement ellipsoids are drawn at the 40% probability level. Dashed lines denote N—H···N and N—H···O hydrogen bonds, and dotted lines denote C—H···O hydrogen bonds. N atoms are represented as inner-shaded ellipsoids.

The tetramers are stacked in layers along the *c* axis. Within the layers, the closest contacts between the tetramers are H6A···O2A(-*x*, -1 - *y*, 1 - *z*) and H6B···O2A(1 + *x*, 1 + *y*, *z*). In addition, there is a close and oriented disposition between the carbonyl group and the pyridine ring from adjacent tetramers at 3.341 (3) Å, which possibly facilitates their parallel arrangement.

The layers are held together by weak C4A—H4A···O1B($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) hydrogen bonds as well as van der Waals interactions. The planes of 2A5NPY from adjacent layers make an angle of 57.60 (4)°.

Experimental

2-Aminopyridine (4.7 g, 0.05 mol) was added carefully to 10 ml cooled sulfuric acid (*d* 1.84) below 293 K. 10 ml of a 1:1 mixture of sulfuric acid (*d* 1.84) and nitric acid (*d* 1.41) were added dropwise to this solution, which was cooled to 278–283 K. The solution was stirred for 10 min and warmed continuously to 308 K. The temperature increased spontaneously to about 338 K. The solution was stirred at 323 K for 4 h to complete the reaction. The resulting solution was poured over ice and neutralized with concentrated ammonia. The precipitate was filtered and dried at 343 K. The yield of the raw product was 4.52 g (65.2%). The powder diffraction pattern of the raw product showed the presence of a 1:1 complex of 2-amino-5-nitropyridine and 3-nitro-2-pyridone as well as traces of 2-amino-5-nitropyridine. After two recrystallizations from ethanol, the yield was 3.0 g (48%). A single crystal was grown by slow evaporation from ethanol solution.

Crystal data

C ₅ H ₅ N ₃ O ₂ ·C ₅ H ₄ N ₂ O ₃	Mo K α radiation
<i>M_r</i> = 279.21	λ = 0.71073 Å
Monoclinic	Cell parameters from 18 reflections
<i>P</i> ₂ ₁ / <i>n</i>	θ = 20.09–21.83°
<i>a</i> = 7.643 (3) Å	μ = 0.128 mm ⁻¹
<i>b</i> = 6.509 (2) Å	<i>T</i> = 292 K
<i>c</i> = 24.140 (1) Å	Prismatic
β = 97.76 (3)°	0.26 × 0.23 × 0.16 mm
<i>V</i> = 1190 (1) Å ³	Brown
<i>Z</i> = 4	
<i>D_x</i> = 1.558 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.053
$\omega/2\theta$ scans	θ_{\max} = 25.91°
Absorption correction: none	<i>h</i> = 0 → 9
4853 measured reflections	<i>k</i> = -8 → 8
2279 independent reflections	<i>l</i> = -29 → 29
1212 reflections with <i>I</i> > 2 σ (<i>I</i>)	3 standard reflections
	frequency: 120 min
	intensity decay: 1.5%

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} = -0.001
<i>R</i> (<i>F</i>) = 0.042	$\Delta\rho_{\max}$ = 0.192 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.104	$\Delta\rho_{\min}$ = -0.153 e Å ⁻³

S = 1.132
2275 reflections
209 parameters
Only coordinates of H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.277P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0021 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

O1A—N2A	1.231 (3)	N1B—C6B	1.339 (4)
O2A—N2A	1.225 (3)	N1B—C2B	1.372 (4)
N2A—C5A	1.436 (3)	N2B—C3B	1.457 (4)
N3A—C2A	1.322 (4)	C2B—C3B	1.439 (3)
O1B—N2B	1.212 (3)	C3B—C4B	1.354 (4)
O2B—N2B	1.215 (3)	C4B—C5B	1.371 (4)
O3B—C2B	1.236 (3)	C5B—C6B	1.350 (4)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N3A—HN31···O3B'	0.79 (2)	2.19 (2)	2.978 (3)	176 (2)
N3A—HN32···O3B''	0.84 (2)	2.21 (2)	2.964 (4)	150 (2)
C3A—H3A···O2B''	0.88 (2)	2.40 (2)	3.245 (4)	161 (2)
C4A—H4A···O1B'''	0.86 (2)	2.44 (2)	3.078 (3)	132 (2)
C6A—H6A···O2A''	0.89 (2)	2.46 (2)	3.337 (4)	173 (2)
N1B—HN1B···N1A'	0.82 (2)	2.08 (2)	2.896 (3)	174 (2)
C6B—H6B···O2A'	0.88 (2)	2.49 (2)	3.363 (4)	171 (2)

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

H atoms were localized from difference Fourier maps and refined with fixed *U*_{iso} = 0.0506 Å².

Data collection: CAD-4 Manual (Enraf–Nonius, 1988). Data reduction: DATARED (Vassilev, 1997; unpublished). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: KAPPA (Macíček, 1992; unpublished).

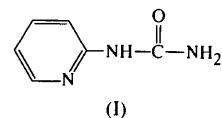
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1296). Services for accessing these data are described at the back of the journal.

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Bond lengths and angles in (I) fall within the expected ranges for urea and its derivatives (Blessing, 1983; Allen *et al.*, 1987). It is worth noting the chemical and geometric non-equivalence of the two ureido N—C bonds [1.379 (1) and 1.325 (2) Å for the imino and amino groups, respectively] caused by resonance effects from the π -conjugated system of the pyridyl ring. The same distance variations have been observed in the structure of monophenylurea [1.375 (10) and 1.326 (10) Å, respectively; Kashino & Haisa, 1977]. The C(pyridyl)—N2 bond distance [1.389 (2) Å] is 3σ shorter than the C(phenyl)—N distance of 1.419 (9) Å in monophenylurea and 25σ shorter than the C(methyl)—N bond length of 1.439 (2) Å in monomethylurea (Huiszoon & Tiemessen, 1976).

The molecule is planar, with the largest deviation [0.065 (1) Å] at the amino N3 atom. This corresponds well with other pyridylurea and thiourea compounds {*N*-(*n*-pyridyl)-*N'*-(4-chlorophenyl)urea, where *n* = 2, 3, 4 (Le Magueres, Ouahab, Hocquet & Fournier, 1994); *N*-(*n*-pyridyl)-*N'*-phenylurea, where *n* = 3, 4, *N*-(*n*-chloro-4-pyridyl)-*N'*-phenylurea, where *n* = 2, 3 (Yamaguchi & Shudo, 1991); tetra[1-allyl-3-(2-pyridyl)thiourea-*S*]-di- μ -chlorotetrachlorodibismuth(III) and hexa[1-allyl-3-(2-pyridyl)thiourea-*S*]bismuth(III) nitrate (Battaglia & Corradi, 1981); chloro(triphenylphosphine)[1-phenyl-3-(2-pyridyl)-2-thiourea]copper(II) and chlorobis[1-phenyl-3-(2-pyridyl)-2-thiourea]copper(II) (Ferrari, Fava, Pelizzi & Tarasconi, 1985); trichlorotris[1-phenyl-3-(2-pyridyl)-2-thiourea-*S*]bismuth(III) (Battaglia & Corradi, 1983)}. In all 2-pyridyl derivatives, the planarity of the molecule is promoted by an intramolecular *endo*-N··H—N(ureido) hydrogen bond. In (I), the geometry of this bond is N1··HN3 1.99 (2), N1··N3 2.714 (2) Å and N1··HN3—N3 135 (2)°. The 3- and 4-pyridyl compounds also retain planarity in contrast to the phenylurea and thiourea derivatives where the phenyl ring can freely rotate. Thus, the phenyl ring in monophenylurea is tilted to the urea plane by 47.4°, in 3- and 4-tolylurea by 54.4 (5) and 52.1 (4)°, respectively (Ciajolo, Lelj, Tancredi, Temussi & Tuzi, 1982), in 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea by 13.3° (Cruse, 1978), in *N*-(*n*-pyridyl)-*N'*-(4-chlorophenyl)urea, where *n* = 2, 3, 4, by 6, 3 and 11°, in *N*-(2,3,5,6-tetrafluoropyridyl)-*N'*-phenylurea by 32.1 (4)° (Yamaguchi, Matsumura, Haga & Shudo, 1992) and in *N*-methyl-*N'*-phenylurea by 30° (Brett, Rademacher & Boese, 1990). Correspondingly, the phenyl rings in the symmetrically disubstituted urea and thiourea compounds are also bent from the central plane, for example, in diphenylurea by 43.0 (2)° (Dannecker, Kopf & Rust, 1979), in bis(3,4-dichlorophenyl)urea by 16.32 and 29.53° for molecule

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N-(2-Pyridyl)urea

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Abstract

The structure of the title compound, C₆H₇N₃O, is built of layers stacked along the *c* axis and each layer consists of parallel zigzag ribbons of hydrogen-bonded molecules extended along the *ab* diagonals. Within the layers, the molecules are plane-to-plane coupled at distances of 3.330 (2) Å. The molecular planes from adjacent layers make an angle of 68.0 (1)°.

Comment

Recently, we have begun to examine the design and chemical and structural characterization of new non-linear optical materials based on unsymmetrical urea and thiourea derivatives with π -conjugated substituents. The polar structure of monophenylurea (Kashino & Haisa, 1977) encouraged us to examine the structure of *N*-(2-pyridyl)urea, (I), where the *endo*-N atom was expected to induce a non-centrosymmetric arrangement in the crystalline state. However, the crystal structure is centrosymmetric, but with interesting cyclic hydrogen-bonding bridges and molecular plane-to-plane coupling.