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(I)

An Orthorhombic Phase of 3,6-Di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine

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Abstract

The title compound, $C_{12}H_{10}N_6$, crystallized in the orthorhombic system with space group $P2_12_12_1$. The N atoms of the two terminal pyridine rings are *trans* with respect to one another and the dihedral angle between the two least-squares planes of the pyridine rings is $22.6(2)°$. The central tetrazine ring has a boat conformation. Both intra- and intermolecular hydrogen bonds are observed.

Comment

The triclinic form of the title compound, (I), has been reported by Caira, Giles, Nassimbeni, Sheldrick & Hazell (1976). We report here on an orthorhombic form of this compound. The N atoms of the two pyridine rings were clearly identified by analyzing the displacement parameters of the possible positions. These two N atoms are *trans* with respect to one another, similar to the case in the previously reported triclinic structure. The central tetrazine ring has a boat conformation, with atoms N22 and N25 sitting at the bow and stern, respectively. Two short bond distances, C21—N26 of 1.284 (2) and N23—C24 of 1.276 (2) Å, and four long bond distances ranging from 1.385 (2) to 1.431 (2) Å were observed in this ring. The two short distances indicate that the double-bond character is localized between the C21/N26 and N23/C24 atom pairs.
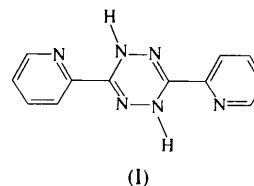
Only intramolecular hydrogen bonds were reported for the triclinic structure, whereas in the present orthorhombic structure, both intramolecular and weaker intermolecular hydrogen bonds are observed. Two intramolecular hydrogen-bonding distances are present between atoms N16 and H22, and atoms N36 and H25 [2.33 (2) and 2.32 (2) Å, respectively]. Two intermolecular hydrogen bonds occur between one molecule and a second molecule (*A*) related by the symmetry operation $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ (Fig. 1). The distances are 2.55 (2) for H22$\cdots$N26A and 2.50 (2) Å for H12$\cdots$N23A. There are no significant short intermolecular contacts between non-H atoms. The closest intermolecular distance observed is 3.262 (2) Å between atoms N22 and N26A. The dihedral angle between the two pyridine-ring planes is 22.6 (2)°, which is significantly smaller than that found in the triclinic structure (41.2°). This smaller angle is attributed to the combination effects of both intra- and intermolecular hydrogen bonds. Least-squares-planes data has been deposited as supplementary material.
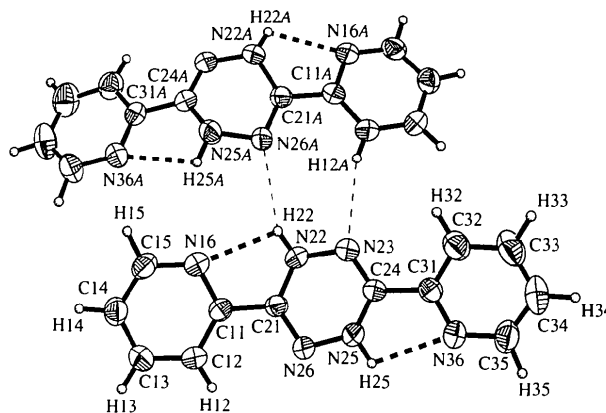

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the title compound showing 50% probability ellipsoids for non-H atoms and H atoms as spheres of arbitrary radii. Intramolecular hydrogen bonds are shown by broken lines and intermolecular hydrogen bonds by dashed lines. Molecule *A* is generated by the symmetry operation $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

Experimental

The title compound was synthesized according to the literature method of Geldard & Lions (1965). It was dissolved in a mixture of *n*-hexane and ethyl acetate (1:1 *v/v*). The orthorhombic crystals were grown by slow evaporation of the solvent mixture at room temperature.

$C_{12}H_{10}N_6$

Crystal data

$C_{12}H_{10}N_6$
$M_r = 238.3$
Orthorhombic
$P2_12_12_1$
$a = 7.3732 (7)$ Å
$b = 11.0354 (9)$ Å
$c = 13.820 (1)$ Å
$V = 1124.5 (2)$ Å^3
$Z = 4$
$D_x = 1.407$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 0.093$ mm^{-1}
$T = 298$ K
Prism
$0.70 \times 0.30 \times 0.25$ mm
Orange

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
  empirical via ψ scan ($P3$;
  Siemens, 1991)
$T_{min} = 0.8855$, $T_{max} = 0.9277$
3052 measured reflections
2589 independent reflections
1997 observed reflections
  $[F > 4\sigma(F)]$

$R_{int} = 0.0101$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 18$
3 standard reflections
  monitored every 300
  reflections
  intensity decay: $<2\%$

Refinement

Refinement on F
$R = 0.0313$
$wR = 0.0379$
$S = 0.91$
1997 reflections
204 parameters
All H-atom parameters
  refined
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction:
$F^* = F/[1.0 + 0.002\chi \times F^2/\sin(2\theta)]^{1/4}$
Extinction coefficient:
$\chi = 0.0026 (5)$
Atomic scattering factors
  from International Tables
  for X-ray Crystallography
  (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
C11	0.1118 (2)	0.1308 (1)	0.3673 (1)	0.0381 (4)
C12	0.1060 (3)	0.0292 (2)	0.4264 (1)	0.0441 (5)
C13	0.1721 (3)	0.0388 (2)	0.5190 (1)	0.0490 (5)
C14	0.2418 (3)	0.1476 (2)	0.5500 (1)	0.0491 (6)
C15	0.2427 (3)	0.2435 (2)	0.4868 (1)	0.0488 (5)
N16	0.1778 (2)	0.2380 (1)	0.3961 (1)	0.0438 (4)
C21	0.0314 (2)	0.1285 (1)	0.2691 (1)	0.0379 (5)
N22	−0.0075 (3)	0.2387 (1)	0.2257 (1)	0.0457 (5)
N23	0.0158 (2)	0.2412 (1)	0.1235 (1)	0.0449 (4)
C24	−0.0410 (2)	0.1434 (1)	0.0846 (1)	0.0387 (4)
N25	−0.1099 (2)	0.0488 (1)	0.1402 (1)	0.0436 (4)
N26	−0.0117 (2)	0.0283 (1)	0.2280 (1)	0.0424 (4)
C31	−0.0399 (2)	0.1297 (1)	−0.0219 (1)	0.0396 (4)
C32	0.0245 (3)	0.2200 (2)	−0.0820 (1)	0.0540 (6)
C33	0.0206 (4)	0.2005 (2)	−0.1804 (1)	0.0701 (8)
C34	−0.0463 (3)	0.0930 (2)	−0.2149 (1)	0.0707 (8)
C35	−0.1079 (3)	0.0084 (2)	−0.1501 (1)	0.0599 (7)
N36	−0.1061 (2)	0.0248 (1)	−0.0542 (1)	0.0483 (4)

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

C11—C12	1.388 (2)	C35—N36	1.337 (2)
C11—N16	1.340 (2)	C11—C12	1.388 (2)
C12—C13	1.374 (2)	C11—C21	1.482 (2)
C21—N22	1.385 (2)	C13—C14	1.373 (3)
N22—N23	1.424 (2)	C14—C15	1.373 (3)
N23—C24	1.276 (2)	C15—N16	1.342 (2)
C24—C31	1.479 (2)	C21—N26	1.284 (2)
C31—N36	1.334 (2)	C24—N25	1.392 (2)
C32—C33	1.376 (3)	N25—N26	1.431 (2)
C33—C34	1.371 (4)	C31—C32	1.382 (2)
C34—C35	1.370 (3)		
C12—C11—N16	123.4 (1)	C24—C31—C32	121.8 (1)
N16—C11—C21	115.6 (1)	C32—C31—N36	123.4 (1)
C11—C12—C13	118.3 (2)	C31—C32—C33	118.3 (2)
C13—C14—C15	118.5 (2)	C33—C34—C35	118.8 (2)
C12—C11—C21	120.9 (1)	C11—C21—N26	121.2 (1)
C12—C13—C14	119.4 (2)	C21—N22—N23	114.9 (1)
C14—C15—N16	123.9 (2)	N23—C24—N25	121.4 (1)
C11—N16—C15	116.5 (1)	N25—C24—C31	118.3 (1)
C11—C21—N22	117.7 (1)	C21—N26—N25	111.3 (1)
N22—C21—N26	120.9 (1)	C24—C31—N36	114.9 (1)
N22—N23—C24	111.3 (1)	C32—C33—C34	119.1 (2)
N23—C24—C31	120.3 (1)	C34—C35—N36	123.5 (2)
C24—N25—N26	113.7 (1)	C31—N36—C35	116.9 (2)

Due to the non-centrosymmetric space group ($P2_12_12_1$), the quadrant data were collected (h $-9\rightarrow9$, k $0\rightarrow15$, l $0\rightarrow18$). The general hkl and $\overline{hkl}$ pairs were not merged, but the $h00$ and $\overline{h}00$, $h0l$ and $\overline{h}0l$, and $hk0$ and $\overline{hk}0$ pairs were merged because of the $C2$ symmetry. The structure was solved by direct methods. All non-H atoms were revealed by the first trail. H atoms were located from the successful difference Fourier syntheses. A full-matrix least-squares method was used to refine the structure. The atoms of the two pyridine rings were treated as C atoms during the first few cycles of refinement. One pyridine ring atom (C16) showed a smaller displacement parameter ($U_{eq} = 0.0345$ Å^2) compared with the average displacement parameter ($U_{eq} = 0.0512$ Å^2) of atoms C12, C13, C14 and C15. A similarly small displacement parameter ($U_{eq} = 0.0381$ Å^2) was observed for atom C36 of the second pyridine ring (average $U_{eq} = 0.0676$ Å^2 for atoms C32, C33, C34 and C35). The C16 and C36 positions were therefore assigned as N atoms, i.e. N16 and N36, in the final refinement. All H atoms were refined as normal atoms and C and N atoms were refined anisotropically.

Data collection, cell refinement and data reduction used the $P3$ program (Siemens, 1991). The structure solution and refinement were carried out using *SHELXTL-Plus* (Sheldrick, 1991), which was also used for the preparation of material for publication. Molecular graphics used *ORTEP* (Johnson, 1965) in *SHELXTL-Plus*.
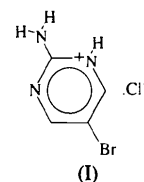
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2-Amino-5-bromopyrimidinium Chloride

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Abstract

The title compound, $C_4H_5BrN_3^+.Cl^-$, crystallized from water as flat plates. The structure is held together by extensive hydrogen bonding between the chloride ions and both the amino and pyrimidinium H atoms. In addition, the pyrimidinium ions are linked *via* hydrogen bonding of one of the amino H atoms and the non-protonated ring N atoms. The molecules packs as sheets, with the sheets at a distance of 3.3 Å from one another.

Comment

We are interested in the packing of halometallate anions with protonated organic bases, especially amino-pyridines and aminopyrimidines. The interactions between the protonated organic molecules, such as π stacking or hydrogen bonding, may make substantial contributions to the formation of the crystal lattice. We have recently begun preparing compounds using 2-amino-5-bromopyrimidine and were therefore interested in what kind of interactions we might expect between the organic groups. Accordingly, we have determined the structure of 2-amino-5-bromopyrimidine as its hydrochloride salt, (I). The structure of 2-amino-pyrimidine has been reported previously (Furberg, Grogaard & Smedsrud, 1979), as well as its hydrochloride hemihydrate (Furberg & Grogaard, 1980). The structure of 2-amino-5-bromopyrimidine has been reported as the free base (Watton, Low, Tollin & Howie, 1988).

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(I)

The bond lengths and angles within the ring (Fig. 1) are, in general, comparable to those of the non-brominated species (Furberg & Grogaard, 1980). The C4—C5—C6 angle is somewhat larger than that of the non-brominated species, and the N3—C4—C5 and C5—C6—N1 angles are correspondingly smaller (all by about 1°). A slight shortening of both the C5—C6 and C4—N3 bonds (0.01–0.02 Å) is observed in comparison with the free base (Watton, Low, Tollin & Howie, 1988).
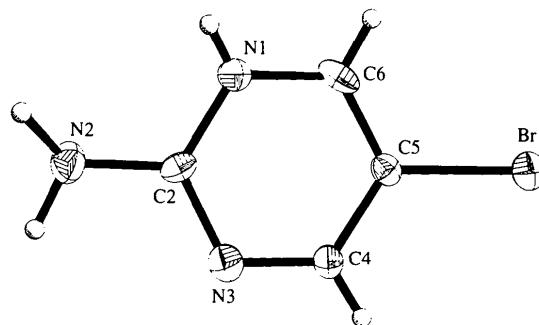

Fig. 1. The molecular structure of 2-amino-5-bromopyrimidinium chloride showing 50% probability ellipsoids.

A slight lengthening of the N2—C2 bond (*ca* 0.02 Å) is also observed. A significant structural difference appears in the packing of the 5-bromo derivative compared with the parent molecule as a result of the large Br atom and the loss of the solvent water molecule. 2-Amino-5-bromopyrimidine packs in sheets (Fig. 2), with an average separation of 3.3 Å. Within the sheets,
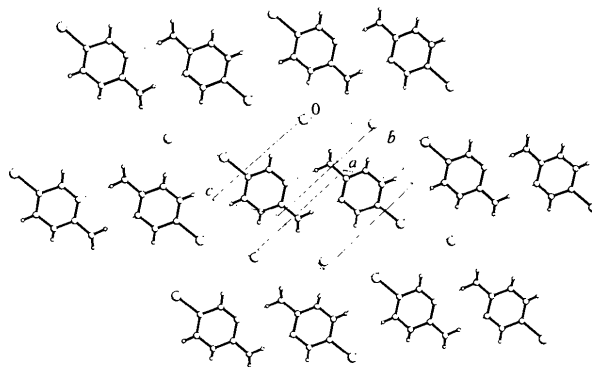

Fig. 2. Packing diagram viewed perpendicular to the planes of the pyrimidinium rings.