organic papers

1,3-Di-2-pyridylthiourea monohydrate

Hui-Ping Zhong,[a] La-Sheng Long,[a] Rong-Bin Huang,[a] Lan-Sun Zheng[a] and Seik Weng Ng[b]*

[a]State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The title compound, $C_{11}H_{10}N_4S \cdot H_2O$, displays an intramolecular $N_{amido} \cdots N_{pyridyl}$ hydrogen bond [2.652 (2) Å] that locks the thiourea unit and one pyridyl ring into coplanarity [dihedral angle 2.7 (1)°]. The second pyridyl ring is also coplanar with the thiourea unit [dihedral angle 2.9 (1)°]. Its attached N atom interacts with the lattice water molecule to form a helical hydrogen-bonded chain that runs parallel to the b axis of the orthorhombic unit cell; adjacent chains are linked into a layer-like architecture by another hydrogen bond between the water molecule and the double-bonded S atom.

Comment

Previous attempts to prepare 1,3-di-2-pyridylthiourea, a compound that can be used for the separation of racemic mixtures of carboxylic acid derivatives, resulted in the isolation of the oxidation product. This fused four-ring compound features two pyridyl N atoms which are covalently linked to the S atom (Coles *et al.*, 2000). A modification of the synthesis, with carbon disulfide in place of carbonyl sulfide, gave the expected compound, which crystallizes as a monohydrate, (I) (Fig. 1).


(I)
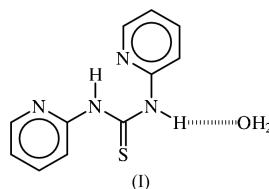
Selected geometric parameters are given in Table 1. The compound displays an $N_{amido} \cdots N_{pyridyl}$ intramolecular hydrogen bond [N2⋯N3 = 2.652 (2) Å; Table 2] that stabilizes the coplanarity of the thiourea unit with one pyridyl ring [dihedral angle 2.7 (1)°]. The second pyridyl ring is also coplanar with the thiourea unit [dihedral angle 2.9 (1)°]. Its attached N atom, N4, interacts with the lattice water molecule to form a helical hydrogen-bonded chain that runs parallel to the b axis (Fig. 2 and Table 2). Adjacent chains are linked into a layer-like architecture by another, somewhat weaker, hydrogen bond between the water molecule and the double-bonded S atom.

A similar intramolecular interaction [2.646 (4) Å] was also noted in 3-phenyl-1-(2-pyridyl)thiourea [dihedral angle 5.4 (1)°]; two molecules are linked across a centre of inversion to form a dimer (West *et al.*, 1999). Here the phenyl ring is inclined to the thiourea unit by 58.0 (1)°. On the other hand, in 1,3-diphenylthiourea (Ramnathan *et al.*, 1995), for which no such intramolecular interaction is possible, each ring is
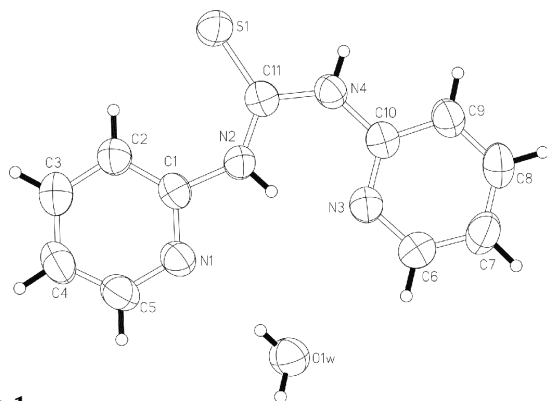
Figure 1
*ORTEP*II (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.
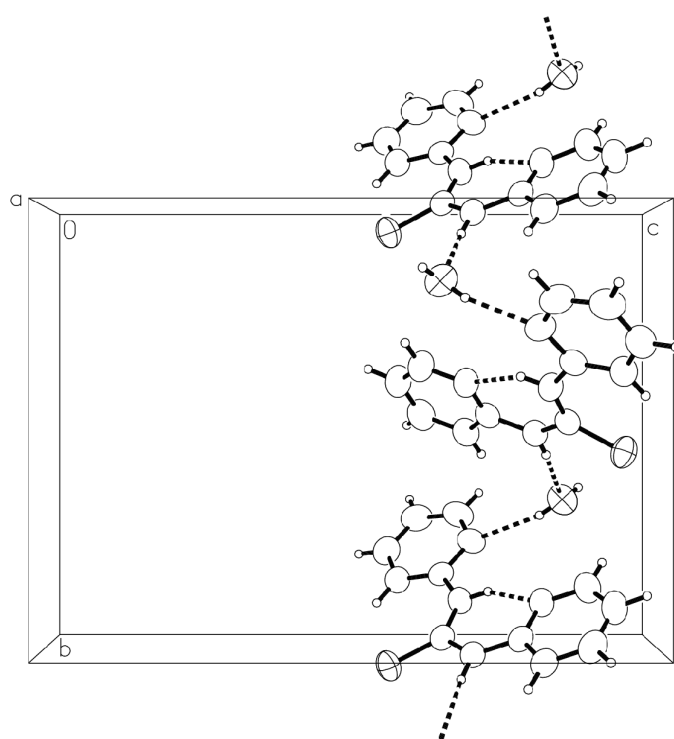
Figure 2
*ORTEP*II (Johnson, 1976) plot depicting the water–amide hydrogen bonding that leads to the formation of a helical chain running along the *b* axis.

inclined to the thiourea unit by 75.2 (1)°. This large twist is necessary for the molecule to use its two amide H atoms to bind to the S atom of an adjacent molecule to form a zigzag chain. The C=S distances in the three compounds are almost identical.

Experimental

An ethanol solution (50 ml) of 2-aminopyridine (0.19 g, 2 mmol) and carbon disulfude (9 ml, 1.4 mmol), kept at 273 K, was stirred for 2 h. The solution was then heated at reflux for 12 h. The reaction was carried out under an N_2 atmosphere. The solution was poured into water to afford a solid material that was recrystallized from aqueous ethanol.

Crystal data

$C_{11}H_{10}N_4S\cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 248.31$	Cell parameters from 1662
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.1921$ (1) Å	$\theta = 2.4$–23.3°
$b = 11.9609$ (3) Å	$\mu = 0.25$ mm^{-1}
$c = 16.5666$ (3) Å	$T = 298$ (2) K
$V = 1226.97$ (4) Å^3	Block, colourless
$Z = 4$	$0.37 \times 0.24 \times 0.22$ mm
$D_x = 1.344$ Mg m^{-3}	

Data collection

Bruker SMART APEX area-detector diffractometer	2320 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: none	$\theta_{max} = 27.5°$
7255 measured reflections	$h = -7 \rightarrow 7$
2724 independent reflections	$k = -15 \rightarrow 9$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
2724 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
170 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1119 Friedel pairs
	Flack parameter = 0.06 (8)

Table 1
Selected geometric parameters (Å, °).

S1—C11	1.688 (2)	N4—C11	1.381 (3)
N2—C11	1.348 (3)	N4—C10	1.412 (2)
N2—C1	1.408 (3)		
C11—N2—C1	132.8 (2)	N2—C11—S1	126.9 (2)
C10—N4—C11	131.0 (2)	N4—C11—S1	117.9 (2)
N2—C11—N4	115.2 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$n\cdots$N3	0.85 (1)	1.90 (2)	2.652 (2)	146 (2)
N4—H4$n\cdots$O1w^i	0.84 (1)	2.19 (1)	3.016 (2)	166 (2)
O1w—H1w1$\cdots$N1	0.85 (1)	2.18 (1)	3.008 (2)	166 (2)
O1w—H1w2$\cdots$S1^{ii}	0.84 (1)	2.61 (1)	3.414 (2)	161 (2)

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

The aromatic H atoms were placed at calculated positions (C—H = 0.93 Å) in a riding-model approximation; U_{iso}(H) values were set equal to $1.2U_{eq}$(parent C-atom). O- and N-bound H atoms were located and refined with an O—H = N—H = 0.86 (1) Å distance restraint.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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