2-(2-Pyridylimino)-2H-1,2,4-thia-diazolo[2,3-a]pyridine

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The title compound, $C_{11}H_8N_4S$, is found to have a symmetrical resonance structure in which both pyridyl-N atoms interact with the S atom forming hemi-bonds. This also results in the formation of a delocalized diimine region and disturbance of the aromaticity in the pyridyl rings.

Comment

The efficient and economical production of enantiomerically pure compounds, particularly from racemic mixtures, is a major challenge facing the modern chemical industry. Recent developments in supramolecular chemistry (Webb & Wilcox, 1993) suggest the development of enantioselective receptors capable of strongly binding substrates as an alternative approach to the resolution of racemates. Thiourea derivatives
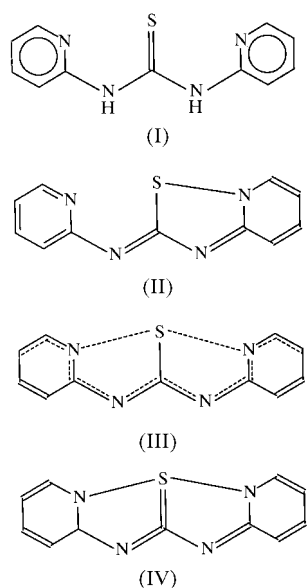
have been synthesized as carboxylic acid binding sites during a scheme of research investigating the separation of racemic mixtures of carboxylic acid derivatives.

Attempts to prepare N,N'-dipyridylthiourea, (I), as a carboxylic acid binding site resulted in the formation of 2-(2-pyridylimino)-2H-1,2,4-thiadiazolo[2,3-b]pyridine, (II), shown in Fig. 1. It is presumed that oxidation of the expected product has occurred during the synthesis, causing a loss of amide protons in the thiourea moiety. This compound has been reported previously (Harris, 1972) where spectroscopic data was interpreted in terms of a resonance structure, (III), which is now confirmed by our work.
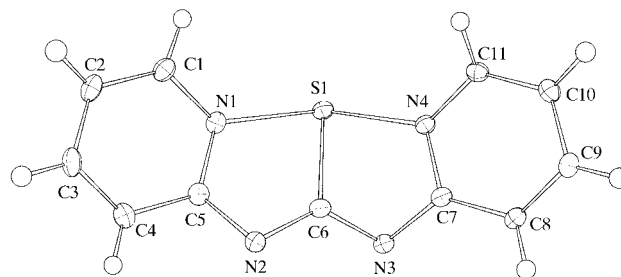
Figure 1
View of the title compound. Ellipsoids of all atoms are drawn at the 50% probability level.

The fused four-ring molecule formed by this interaction is essentially planar, with the sulfur–nitrogen separations [1.8926 (11) and 1.9653 (11) Å] significantly less than the sum of the van der Waals radii, 3.35 Å (Bondi, 1964). These interactions may be considered as hemi-bonds, as in a resonance structure they must be reversibly formed to account for changes in equilibrium and consequently in the solid-state structure a bond averaged over two canonical forms is observed. The length of the C—S bond [1.7915 (12) Å] is greatly increased from the double-bond length normally observed in thiourea derivatives, 1.67 Å (West et al., 1999) and, from literature values (Allen et al., 1987) may be considered to be a formal single bond. This indicates that the canonical form, (IV), suggested by Harris (1972), is not a significant contributor to the electronic structure. A search of the Cambridge Structural Database (Allen et al., 1983) revealed few cases of sulfur in a similar coordination environment and none with aromatic moieties. The two structures most relevant for comparison, POXYOQ (Kobayashi et al., 1998) and ROBPON (Iwasaki et al., 1996) both contain bonds to sulfur longer than those in (III).

It can be seen from the bond lengths shown in Table 1 that there has been a breakdown in the aromaticity of the pyridyl rings and some delocalization about the diimido moiety. The bond lengths between C5, N1, C1, C2 and those of C7, N4, C11, C10 are all conjugated, whilst C2, C3, C4, C5 and C7, C8, C9, C10 show a degree of alternation.

Weak intermolecular interactions exist between C11—H11···N2($\frac{1}{2}+x, y-\frac{1}{2}, z$) and C9—H9···N3($\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$) [$D-A$ = 3.283 (3) and 3.455 (3) Å, respectively]. These give rise to an infinite three-dimensional array of two interwoven herring-bone structures.

Experimental

Thiophosgene (0.4 ml, 5.3 mmol) was slowly added to a mixture of 2-aminopyridine (1.00 g, 10.6 mmol) in chloroform (20 ml). After addition of 0.4 *M* aqueous potassium carbonate (23.8 ml, 9.5 mmol), the mixture was heated under reflux for 24 h. After cooling to room temperature, the organic layer was concentrated *in vacuo* to afford a brown solid which was purified by recrystallization from methanol to produce pale-yellow plates suitable for X-ray diffraction (1.65 g, 7.2 mmol, 68%). The product was characterized by ^{1}H and ^{13}C NMR and mass spectrometry, giving results consistent with those in the literature (Harris, 1972).

Crystal data

$C_{11}H_8N_4S$
$M_r = 228.27$
Monoclinic, $C2/c$
$a = 10.970$ (2) Å
$b = 8.986$ (2) Å
$c = 20.881$ (4) Å
$\beta = 103.66$ (3)°
$V = 2000.2$ (7) Å^3
$Z = 8$

$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 42 625 reflections
$\theta = 2.01–27.5°$
$\mu = 0.297$ mm^{-1}
$T = 150$ (2) K
Plate, pale yellow
$0.1 \times 0.1 \times 0.025$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scans (*SORTAV*; Blessing, 1995)
$T_{min} = 0.957$, $T_{max} = 0.994$
42 625 measured reflections
2294 independent reflections

2164 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -11 \rightarrow 11$
$l = -27 \rightarrow 27$
Intensity decay: none

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.7915 (12)	N4—C11	1.3546 (16)
S1—N4	1.8926 (11)	C1—C2	1.3671 (19)
S1—N1	1.9653 (11)	C2—C3	1.403 (2)
N1—C5	1.3480 (16)	C3—C4	1.3737 (19)
N1—C1	1.3534 (16)	C4—C5	1.4126 (18)
N2—C6	1.3276 (16)	C7—C8	1.4132 (17)
N2—C5	1.3598 (16)	C8—C9	1.3711 (18)
N3—C6	1.3366 (15)	C9—C10	1.4092 (19)
N3—C7	1.3518 (16)	C10—C11	1.3687 (18)
N4—C7	1.3561 (15)		
C6—S1—N4	83.40 (5)	N4—S1—N1	165.42 (5)
C6—S1—N1	82.05 (5)		

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.065$
$S = 1.162$
2294 reflections
177 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 1.9948P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1993).

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–469.
Harris, R. L. N. (1972). *Aust. J. Chem.* **25**, 993–1001.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Iwasaki, F., Yasui, M., Yoshida, S., Nishiyama, H., Shimamoto, S. & Matsumura, N. (1996). *Bull. Chem. Soc. Jpn*, **69**, 2759–2762.
Kobayashi, K., Sato, S., Horn, E. & Furukawa, N. (1998). *Tetrahedron Lett.* **39**, 2593–2596.
Otwinowski, Z. & Minor, W. (1997). *Macromolecular Crystallography*, Part A, p. 307. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.
Webb, T. H. & Wilcox, C. S. (1993). *Chem. Soc. Rev.* **22**, 383–395.
West, D. X., Hermetet, A. K., Ackerman, L. J., Valdés-Martínez, J. & Hernández-Ortega, S. (1999). *Acta Cryst.* C**55**, 811–813.