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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.043
 wR factor = 0.129
Data-to-parameter ratio = 17.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

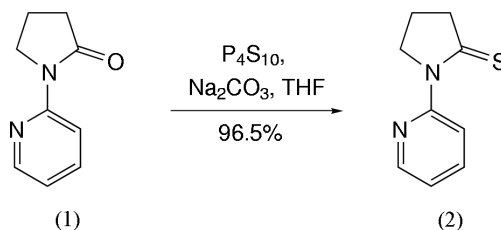
1-(2-Pyridyl)pyrrolidine-2-thione

The title compound, $\text{C}_9\text{H}_{10}\text{N}_2\text{S}$, was prepared by thionation of 1-(2-pyridyl)pyrrolidin-2-one with phosphorus pentasulfide. In the crystalline state, the plane of the pyrrolidine-2-thione ring is twisted by about 21° relative to the pyridine ring. In the crystal structure, molecules are associated by π - π stacking.

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Comment

1-Arylpyrrolidin-2-ones and 1-arylpiperidine-2-thiones are pivotal intermediates in our investigations into the synthesis of various nitrogen-containing heterocyclic systems (Michael *et al.*, 1988), including analogues of the quinolone antibacterials (Michael, de Koning, Hosken & Stanbury, 2001) and aziridinomitosenes (Michael, de Koning, Petersen & Stanbury, 2001). We have previously reported the X-ray crystal structures of several 1-arylpiperidin-2-ones, the results showing that substituents on the aromatic ring influence the torsion angles between the lactam and aryl rings (Billing, Boeyens, Denner *et al.*, 1991; Billing, Boeyens, Levendis & Michael, 1991). Our interest in 1-pyridyl analogues stemmed both from our ongoing investigations into the synthesis of antibiotic systems and also from their potential as scaffolds for ligand synthesis.



Thiolactams are generally prepared by treating the corresponding lactams with thionating agents such as phosphorus pentasulfide or Lawesson's reagent (Thomsen *et al.*, 1984, and references therein; Jesberger *et al.*, 2003). In the present case, the known precursor 1-(2-pyridyl)pyrrolidin-2-one, (1) (Renger, 1985), was thionated by prolonged treatment at ambient temperature with phosphorus pentasulfide and sodium carbonate in tetrahydrofuran (Brillon, 1990) to give the title compound, (2), in 96.5% yield. Crystals suitable for X-ray diffraction were grown at the interface of a two-phase hexane-ethyl acetate system.

Bond lengths and angles in the molecular structure of (2) (Fig. 1) are unexceptional. The *N*-aryl bond length ($\text{N1}-\text{C2}'$) is 1.420 (2) \AA , which is virtually the same as the average distance, 1.419 \AA , observed in eight 1-arylpiperidin-2-ones that were previously reported (Billing, Boeyens, Denner *et al.*, 1991; Billing *et al.*, 1991). The implication is that resonance

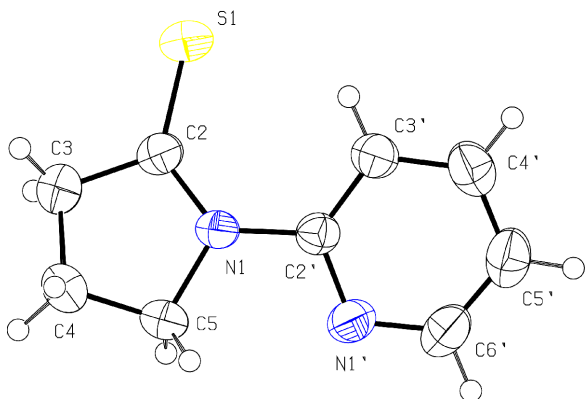


Figure 1
A view of (2) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

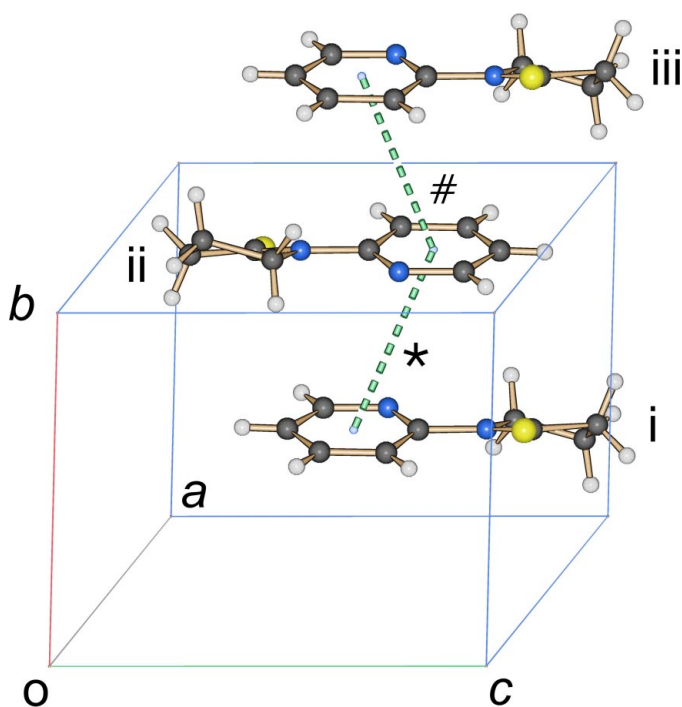


Figure 2
Part of the crystal structure of (2), showing the π - π stacking along the b axis. Ring-centroid separation distances marked with a hash (#) or asterisk (*) are 3.9141 (12) and 4.0815 (13) Å, respectively. Symmetry codes for the various molecules are as follows: (i) $2 - x, 1 - y, 1 - z$; (ii) x, y, z ; (iii) $2 - x, 2 - y, 1 - z$.

effects between the thioamide and heteroaromatic moieties are insignificant. This is also borne out by the torsion angle of -158.79 (18°) for the $C2-N1-C2'-N1'$ sequence, which clearly indicates that the two π -bonded systems are far from coplanar. This torsion angle also reveals an anticlinical disposition of the negatively polarized N and S sites on the pyridyl and thiolactam rings, respectively, as one would expect on electrostatic grounds. The thiolactam ring itself adopts an envelope conformation with C4 0.437 (3) Å out of the plane defined by $C5-N1-C2-C3$, the torsion angle for which is 3.9 (2°). The crystal structure is reinforced by aromatic π - π stacking interactions along the b axis (Fig. 2). No hydrogen

bonding or other obvious weak interactions exist in this structure.

Experimental

A solution of 1-(2-pyridyl)pyrrolidin-2-one (1.65 g, 10.2 mmol) in dry tetrahydrofuran (THF, 10 ml) was added to a solution of P_4S_{10} (2.26 g, 10.2 mmol) and Na_2CO_3 (1.08 g, 10.2 mmol) in dry THF (60 ml). The resulting mixture was stirred at room temperature under an atmosphere of N_2 for 9 d. Aqueous Na_3PO_4 solution (10%, 100 ml) was then added. The aqueous layer was extracted with EtOAc/hexane (1:1, 1×50 ml) and EtOAc (2×50 ml). The organic fractions were combined, dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure to yield a yellow residue. The product was purified by column chromatography on silica gel using EtOAc/hexane (1:1) as eluant to yield pale yellow plates (1.75 g, 96.5%; m.p. 363–368 K). Crystals suitable for X-ray crystallography were obtained by slow growth at the interface of a two-phase solvent system in which hexane was carefully floated above a solution of the compound in ethyl acetate. IR (thin film on NaCl plate, cm^{-1}): $\bar{\nu}$ 1645 (s), 1215 (m), 759 (m); 1H NMR (300 MHz, $CDCl_3$): δ 2.16 (2H, quintet, $J = 7.8$ Hz, 4- CH_2), 3.27 (2H, t, $J = 7.8$ Hz, $CH_2C=S$), 4.42 (2H, t, $J = 7.2$ Hz, N CH_2), 7.19 (1H, ddd, $J = 7.4, 4.9$ and 1.0 Hz, 5'-H), 7.77 (1H, ddd, $J = 8.4, 7.4$ and 2.0 Hz, 4'-H), 8.46 (1H, ddd, $J = 4.9, 2.0$ and 1.0 Hz, 6'-H), 8.81 (1H, td, $J = 8.4$ and 1.0 Hz, 3'-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.0 (C-4), 48.5 (C-3), 56.1 (C-5), 118.4 (C-3' or C-5'), 121.6 (C-3' or C-5'), 137.0 (C-4'), 147.9 (C-6'), 152.3 (C-2'), 203.0 (C=S); m/z (EI) 178 (M^+ , 100%); 177 (54), 150 (15), 137 (4), 136 (5), 120 (25), 119 (58), 107 (15), 105 (5) (found: $M^+ = 178.0565$; $C_9H_{10}N_2S$ requires $M = 178.0565$).

Crystal data

$C_9H_{10}N_2S$
 $M_r = 178.25$
Triclinic, $P\bar{1}$
 $a = 6.8504$ (8) Å
 $b = 7.3247$ (9) Å
 $c = 9.5740$ (11) Å
 $\alpha = 87.965$ (2°)
 $\beta = 85.299$ (2°)
 $\gamma = 64.705$ (2°)
 $V = 432.87$ (9) Å 3

$Z = 2$
 $D_x = 1.368$ Mg m $^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 735 reflections
 $\theta = 3.1$ – 28.1°
 $\mu = 0.32$ mm $^{-1}$
 $T = 293$ (2) K
Lath, pale yellow
 $0.38 \times 0.18 \times 0.09$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1863 independent reflections
ω scans	1463 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.014$
$T_{min} = 0.890, T_{max} = 0.972$	$\theta_{max} = 27.0^\circ$
2796 measured reflections	$h = -6 \rightarrow 8$
	$k = -9 \rightarrow 9$
	$l = -9 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.129$
 $S = 1.10$
1863 reflections
109 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.0786P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.28$ e Å $^{-3}$
 $\Delta\rho_{min} = -0.28$ e Å $^{-3}$

H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C–H bond lengths of 0.93 (aromatic) or 0.97 Å (CH_2), and isotropic displacement parameters equal to $1.2U_{eq}(C)$ times that of the parent atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999a); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003) and *SCHAKAL97* (Keller, 1997); software used to prepare material for publication: *SHELXTL* and *PLATON*.

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