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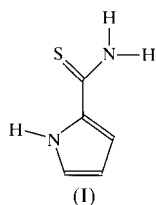
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The reaction of ethoxycarbonylpyrrole-2-thiocarboxamide with sodium hydroxide affords the known title compound, $C_5H_6N_2S$, whose structure shows a three-dimensional hydrogen-bonded lattice.

Comment

The title compound, (I), also known as pyrrole-2-thiocarboxamide, has been reported as a bidentate ligand to nickel(II) by Singh *et al.* (1992). It has now been synthesized with the aim of producing novel nickel complexes for use as synthons in the preparation of analogues of the active sites of Ni-Fe enzymes.



The molecule of (I) (Fig. 1) is essentially planar (r.m.s. deviation of the eight non-H atoms is 0.009 Å), with a rotation about the C2–C21 bond of 0.7 (1)° (calculated from the angles normal to the mean planes of the N1/C2/C3/C21 and C2/C21/N23/S22 groups). The coplanarity of the thiocarboxamide group with the ring may be assisted by the formation of an intramolecular hydrogen bond, *viz.* N1–H1···S22. Because the positions of the H and S atoms are determined principally by the geometry of the rigid pyrrole ring, the H···S distance of 2.79 (2) Å is not as short as those in the five-membered hydrogen-bonded C–C–N–H···S rings generally found in dithiocarboxamides [*e.g.* *N,N'*-bis(1-carboxyethyl)dithiooxamide; Vidal *et al.*, 1999], where the range is 2.4–2.7 Å. Similarly, our N–H···S angle of 101 (2)° is at the acute end of the range of values found in such groups, *viz.* 103–124°, the lower values being found in bifurcated hydrogen-bond cases (see below).

Molecules of (I) are linked by paired N–H···S hydrogen bonds into ribbons parallel to the *c* axis (Fig. 2). The pairs are arranged alternately about centres of symmetry (with shallow chair-shaped eight-membered rings involving the N23–

H23*B*···S22ⁱⁱⁱ bonds) and twofold symmetry axes (with ten-membered rings in a saddle shape using the N1–H1···S22ⁱ bonds); the rings share the C21–S22 bonds. The ribbons are

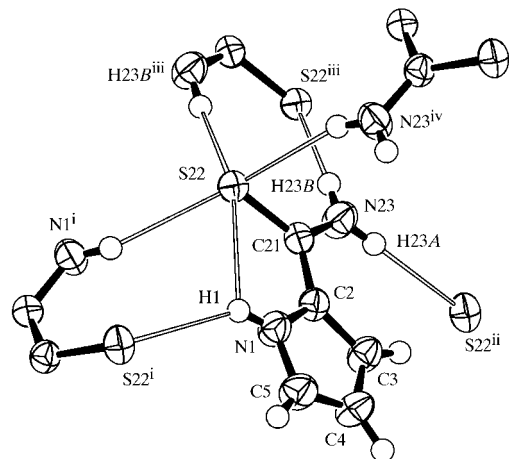


Figure 1

A molecular view of (I) showing the proposed intra- and intermolecular hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i)–(iii) are as defined in Table 1; (iv) $-x, y - \frac{1}{2}, \frac{1}{2} - z$].

crosslinked by single N23–H23A···S22ⁱⁱ hydrogen bonds, (Fig. 1), which spiral along the twofold screw axes and complete a three-dimensional lattice of hydrogen bonds [symmetry codes: (i) $\frac{1}{2} - x, y, 1 - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$].

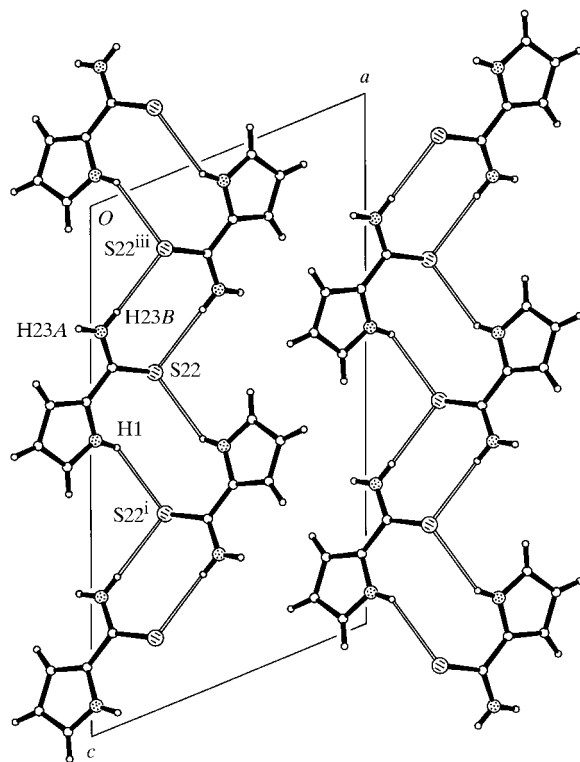


Figure 2

One layer of molecules in the unit cell of (I), showing the linking of molecules into chains parallel to the *c* axis. Symmetry codes are as in Table 1.

This hydrogen-bond scheme shows similarities with that in dithioamide (Wheatley, 1965), where eight- and ten-membered rings are also linked in chains. However, the ten-membered ring there is without symmetry and has a different conformation of two planes which are hinged sharply at the S...N vector of one dithioamide molecule. The ribbons are further linked into sheets and there are weaker hydrogen bonds between the sheets.

There are similar ten-membered intermolecular hydrogen-bonded rings in *N,N'*-diethyldithioamide (Drew *et al.*, 1982), paired about inversion centres and linking the molecules into chains. Rather weaker links are found in chains of similar shape in *N,N'*-dicyclohexyldithioamide (Perec *et al.*, 1995). The H...S distances in these crystals are 2.85 and 3.11 Å, respectively.

All the ten-membered ring systems reported here incorporate five-membered intramolecular ring bonds. The H atoms are thus involved in bifurcated systems forming both intra- and intermolecular hydrogen bonds.

Experimental

Compound (I) was synthesized according to the method described by Papadopoulos (1973). Crystals of (I) were grown by solvent evaporation from an ethanol solution.

Crystal data

C ₅ H ₆ N ₂ S	$D_x = 1.408 \text{ Mg m}^{-3}$
$M_r = 126.18$	Mo $K\alpha$ radiation
Monoclinic, $I2/a$	Cell parameters from 24 reflections
$a = 9.7411 (9) \text{ \AA}$	$\theta = 10\text{--}11^\circ$
$b = 7.5931 (7) \text{ \AA}$	$\mu = 0.43 \text{ mm}^{-1}$
$c = 17.444 (2) \text{ \AA}$	$T = 293 (1) \text{ K}$
$\beta = 112.682 (8)^\circ$	Block, pale brown
$V = 1190.5 (2) \text{ \AA}^3$	$0.48 \times 0.10 \times 0.05 \text{ mm}$
$Z = 8$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.036$
Scintillation counter; ω/θ scans	$\theta_{\text{max}} = 30^\circ$
Absorption correction: ψ scan (EMPABS; Sheldrick <i>et al.</i> , 1977)	$h = -1 \rightarrow 12$
$T_{\text{min}} = 0.044$, $T_{\text{max}} = 0.078$	$k = -1 \rightarrow 10$
2049 measured reflections	$l = -24 \rightarrow 24$
1734 independent reflections	3 standard reflections
1323 reflections with $I > 2\sigma(I)$	frequency: 167 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.2968P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{\text{max}} = -0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
1734 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
98 parameters	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
All H-atom parameters refined	Extinction coefficient: 0.0097 (18)

Table 1
Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$N1\text{--}H1\cdots S22$	0.83 (2)	2.79 (2)	3.057 (1)	101 (2)
$N1\text{--}H1\cdots S22^i$	0.83 (2)	2.71 (2)	3.394 (1)	141 (2)
$N23\text{--}H23A\cdots S22^{ii}$	0.84 (2)	2.68 (2)	3.479 (2)	161 (2)
$N23\text{--}H23B\cdots S22^{iii}$	0.85 (2)	2.70 (2)	3.504 (2)	159 (2)

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

In the structure refinement, H atoms were included in idealized positions, apart from the amide H atoms, which were located from difference Fourier maps. Initially, all H-atom parameters were set to ride on those of the parent atoms, but finally all were refined freely [$C\text{--}H = 0.92 (2)\text{--}0.95 (2) \text{ \AA}$]. In the final difference map, the highest peaks (to *ca* 0.24 e \AA^{-3}) were close to the midpoints of bonds.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4* processing program (Hursthouse, 1976); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1971); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1450). Services for accessing these data are described at the back of the journal.

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