Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N-(Pyridin-2-yl)hydrazinecarbothioamide

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Received 16 May 2005
Accepted 15 June 2005
Online 24 June 2005

Key indicators

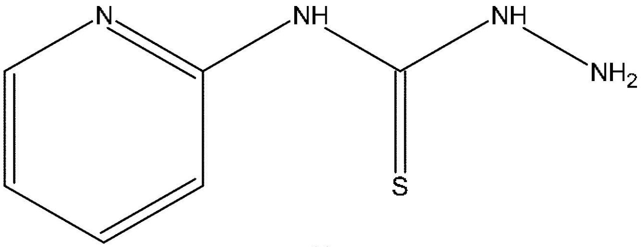
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.107
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_6H_8N_4S$, crystallizes as the thione tautomer, with intramolecular N···H—N and S···H—N hydrogen bonds, and π–π stacking along the *b* axis. Intermolecular N···H—N hydrogen bonds link the molecules into one-dimensional sheets stacked along the *c* axis.

Comment

The biological activity of thiosemicarbazones is due to their ability to form chelates with biologically important metal ions, bonding through an S and two N atoms, *NNS* (Klayman *et al.*, 1984). The biological activities of thiosemicarbazones and their metal complexes include antitumour, fungicidal, bactericidal, anti-inflammatory and antiviral (Sreekanth & Kurup, 2003). This prompted us to carry out the crystal structure determination of the title N4-substituted thiosemicarbazide, (I), a potential *NNS*-donor ligand. The presence of a pyridine ring and the absence of an azomethine bond are expected to be useful in the structure–activity correlation study of this type of compound.



(I)

The C—S bond distance of 1.6897 (13) Å in (I) is intermediate between the values of 1.82 Å for a C—S single bond and 1.56 Å for a C═S double bond (He *et al.*, 2000). Similarly, the C6—N2 and C6—N3 bond distances (Table 1) indicate some double-bond character and the existence of extensive delocalization of the thiosemicarbazide moiety. This thiosemicarbazide moiety is planar, with a maximum deviation of 0.0127 (1) Å for atom C6. The N4—N3—C6—N2 torsion angle of 177.77 (16)° indicates that the hydrazine atom N4 is positioned *trans* to the thioamide atom N2, while the S1—C6—N3—N4 torsion angle of −0.42 (24)° indicates that atom N4 is *cis* to the thionyl atom S1 about the C6—N3 bond. These are in agreement with values in thiosemicarbazones (Fun *et al.*, 2005). This is due to the presence of the pyridine ring N atom, which forms an intramolecular hydrogen bond and facilitates the geometry. This observation was confirmed by the geometry of 4-phenyl-1-(propan-2-ylidene)thiosemicarbazide (Jian *et al.*, 2005), where the hydrazine N atom is *cis* to the thioamide N atom and *trans* to the thionyl S atom.

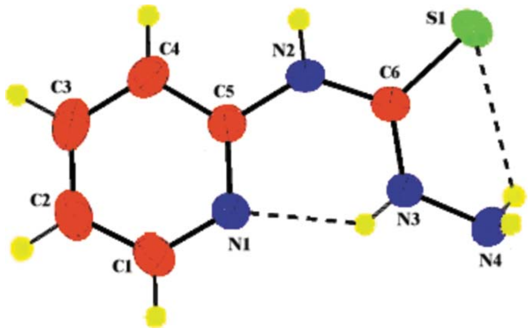


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of fixed radii. Dashed lines denote the intramolecular N···H—N and S···H—N interactions.

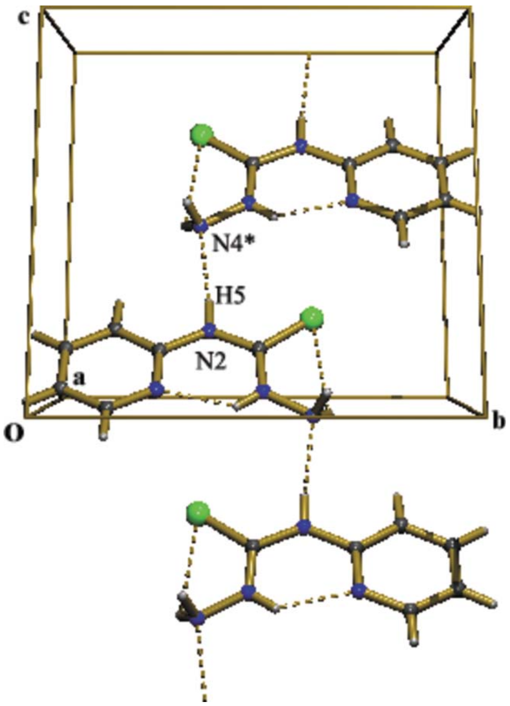


Figure 2
A view of (I) along the *a* axis. Inter- and intramolecular hydrogen bonds are indicated by dashed lines. The molecules are stacked along the *b* direction. [Symmetry code: (*) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{1}{2}$.]

The intramolecular hydrogen bonds in (I) (Fig. 1 and Table 2) facilitate almost planar geometry in the compound, with a maximum deviation of 0.1440 (1) Å for hydrazine atom N4. The N3—H6···N1 hydrogen bond forms a six-membered ring and the N4—H7···S1 hydrogen bond forms a five-membered ring. In the packing, molecules are stacked along the *b* axis and an intermolecular N2—H5···N4* hydrogen bond (Fig. 2) produces independent polymeric chains (Fig. 3). π–π interactions between the planar pyridine rings may stabilize the packing.

Experimental

The title compound was prepared by refluxing a solution of 4-methyl-4-phenyl-3-thiosemicarbazide (1 g, 5.52 mmol) and 2-aminopyridine (0.520 g, 5.52 mmol) in acetonitrile (20 ml) for 45 min. The solution was chilled and the compound separated and washed well with acetonitrile. The product was recrystallized from ethanol. X-ray quality single crystals of (I) were obtained by slow evaporation of an ethanol solution over 7 d.

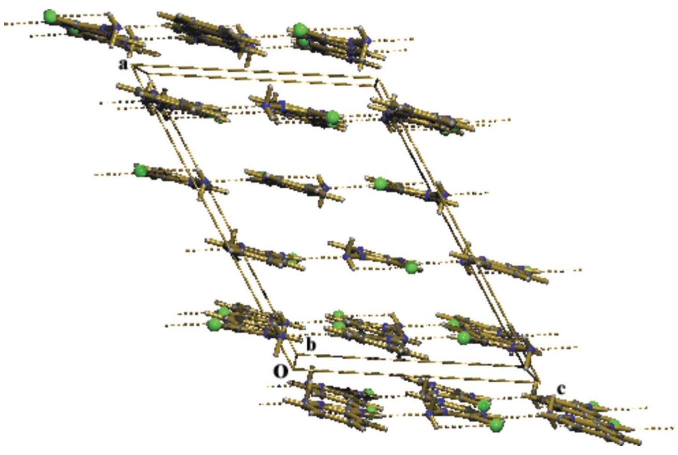


Figure 3
The packing of (I), viewed along the *b* axis, showing the independent polymeric sheets stacked as layers along the *c* axis.

Crystal data

$C_6H_8N_4S$
$M_r = 168.22$
Monoclinic, $C2/c$
$a = 15.5846\ (17)$ Å
$b = 10.1592\ (11)$ Å
$c = 11.1622\ (12)$ Å
$\beta = 121.118\ (2)^\circ$
$V = 1513.0\ (3)$ Å^3
$Z = 8$

$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4378 reflections
$\theta = 2.7$–28.2°
$\mu = 0.36$ mm^{-1}
$T = 293\ (2)$ K
Block, light yellow
$0.32 \times 0.28 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
4378 measured reflections
1748 independent reflections

1604 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\rm max} = 28.2^\circ$
$h = -20 \rightarrow 16$
$k = -13 \rightarrow 12$
$l = -11 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.107$
$S = 1.12$
1748 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.5476P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.6897 (13)	N2—C5	1.3947 (16)
N4—N3	1.4104 (16)	C6—N3	1.3283 (17)
N2—C6	1.3639 (16)		
N3—C6—N2	117.96 (11)	N2—C6—S1	118.85 (10)
N3—C6—S1	123.16 (10)	C6—N3—N4	122.79 (12)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H5···N4^{i}	0.86	2.21	3.058 (2)	169
N4—H7···S1	0.75 (3)	2.72 (3)	3.025 (2)	107 (2)
N3—H6···N1	0.79 (2)	2.06 (2)	2.6698 (16)	134 (2)

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

Atoms H6, H7 and H8 were located from difference maps and refined isotropically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

MRPK and EM thank the Kerala State Council for Science, Technology and Environment for financial assistance.

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