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Di-2-pyridyl ketone N^4,N^4-(butane-1,4-diyl)thiosemicarbazone

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The title compound, $C_{16}H_{17}N_5S$, is in the thione form and crystallizes with two independent molecules in the asymmetric unit. In both molecules, the pentamethyleneimine five-membered ring adopts an envelope conformation, and in one of the molecules this ring shows positional disorder. The thione S and hydrazine N atoms are in the *Z* configuration with respect to the C—N bond.

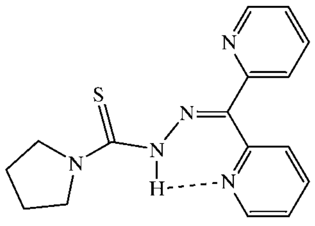
Comment

A large number of studies have been devoted to the search for derivatives of thiosemicarbazides, which have been used as drugs and have the ability to form complexes (Petering & van Giessen, 1966). Thiosemicarbazones of α-*N*-heterocyclic carbaldehydes act as tridentate ligands. The biological activity of the thiosemicarbazone depends on the parent aldehyde or ketone (Padhye & Kauffman, 1985; Liberta & West, 1992; Lukevics *et al.*, 1995). Among thousands of screened compounds (Klayman *et al.*, 1979), 2-acetylpyridine thiosemicarbazones were the first compounds reported as potent antimalarial agents. Among these, the 2-acetylpyridine thiosemicarbazones with the highest activity are those having the N^4 atom disubstituted or as part of the ring system.

As part of our studies of thiosemicarbazones and their metal complexes (Usman *et al.*, 2002), we have now prepared the title tetradentate N_3S compound, (I), and analysed its crystal structure. Compound (I) was prepared (Ali & Livingstone, 1974; Campbell, 1975; Livingstone, 1965) by adopting the procedures reported by Scovill (1991). Thiosemicarbazones are reported to exhibit thione–thiol tautomerism in solution. However, the absence of a peak at *ca* δ = 4.0 p.p.m. in the ^{1}H NMR spectrum of (I) indicates that the compound exists as a thione in solution. This fact is supported by the crystallographic data.

There are two crystallographically independent molecules, *A* and *B*, in the asymmetric unit of (I), with bond lengths and angles which agree with each other and are within normal ranges (Allen *et al.*, 1987). Molecules *A* and *B* are related by a local pseudo-twofold rotation axis (Fig. 1). Both molecules show an *E* configuration about the C6—N3 and C12—N4 bonds relative to the N3—N4 bond. The S and hydrazine N3 atoms in both molecules are in the *Z* configuration with respect to the C12—N4 bond. A similar configuration was observed in di-2-pyridyl ketone thiosemicarbazone (Duan *et al.*, 1996), where the N^4 position is unsubstituted.

The C12—S1 and C12—N4 bond distances in both molecules are typical of a C═S double bond and a C—N single bond, respectively (Table 1). Comparison of the N3—N4 bond distance [1.361 (3) Å in molecule *A* and 1.354 (4) Å in molecule *B*] with the corresponding distance in di-2-pyridyl ketone thiosemicarbazone (1.371 Å) indicates that it is a single bond and suggests the thione form for (I).



(I)

In both molecules of (I), the pentamethyleneimine five-membered ring (N5/C13–C16) is not planar and tends towards an envelope conformation. In molecule *A*, atom C14 deviates by 0.410 (5) Å from the N5/C13/C15/C16 plane. In molecule *B*, this ring shows disorder, so that in the major and minor configurations, atoms C14*B* and C14*C* deviate in opposite directions by 0.382 (2) and 0.543 (2) Å, respectively, from the N5/C13/C15/C16 plane.

In both molecules *A* and *B*, the relative conformations of the two pyridyl rings with respect to the planar thiosemicarbazone (S1/N3/N4/C6/C12) are conditioned by the sp^2-hybridized C6 atom (the average bond angle subtended at C6 is 120.0° in molecule *A* and 119.8° in molecule *B*). The dihedral angles between the thiosemicarbazone and the two pyridyl rings are relatively small [35.8 (1) and 22.7 (2)° in molecule *A*, and 21.7 (2) and 22.7 (2)° in molecule *B*], due to a resonance effect between the π systems.

An intramolecular N4—H4···N2 hydrogen bond forms a six-membered N2—C7—C6—N3—N4—H4 ring in both molecules of (I) (Fig. 1 and Table 2). In the packing, the molecules are stacked in to molecular columns parallel to the *b* direction.

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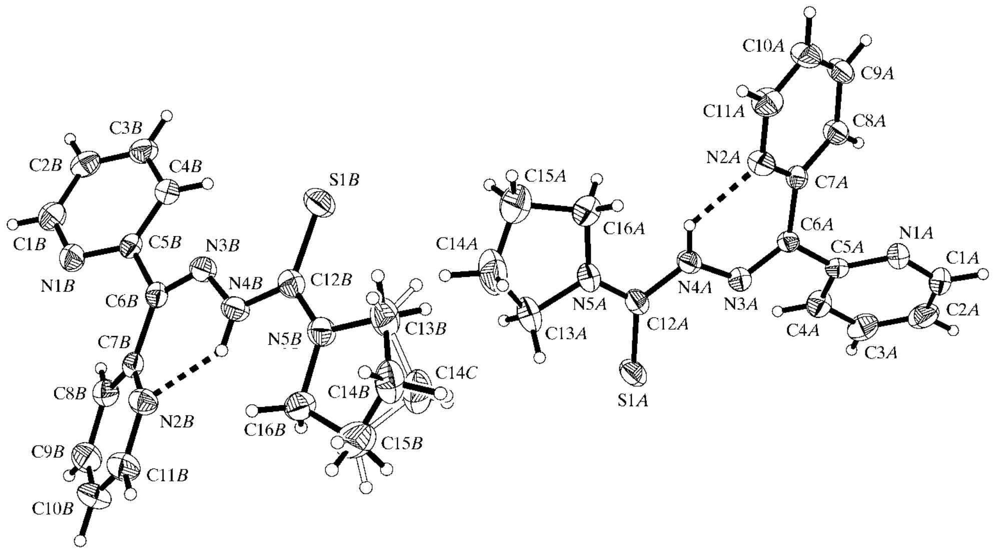

Figure 1
The two independent molecules of (I), with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii and dashed lines denote the intramolecular N—H···N interactions.

Experimental

Compound (I) was prepared by refluxing a methanol solution of di-2-pyridyl ketone (0.184 g, 1 mmol) with pyrrolidine-1-thiocarboxylic acid hydrazide (0.145 g, 1 mmol) and glacial acetic acid (3 drops) for 3 h. The needle-shaped yellow crystals which separated on cooling were filtered off and washed with ethanol. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol solution. Elemental analysis, found (calculated): C 62.10 (61.71), H 5.56 (5.50), N 22.43% (22.49%).

Crystal data

$C_{16}H_{17}N_5S$
$M_r = 311.41$
Triclinic, $P\overline{1}$
$a = 9.0068$ (7) Å
$b = 11.2034$ (8) Å
$c = 15.8750$ (12) Å
$\alpha = 103.753$ (2)°
$\beta = 90.361$ (2)°
$\gamma = 90.392$ (1)°
$V = 1555.9$ (2) Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2342 reflections
$\theta = 2.6$–28.3°
$\mu = 0.21$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.5 × 0.4 × 0.3 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.901$, $T_{\max} = 0.939$
9895 measured reflections
7299 independent reflections
4123 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 28.3°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 12$
$l = -21 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.170$
$S = 1.02$
7299 reflections
407 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 1.3792P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

S1*A*—C12*A*	1.671 (4)	S1*B*—C12*B*	1.670 (3)
N3*A*—C6*A*	1.297 (4)	N3*B*—C6*B*	1.303 (4)
N3*A*—N4*A*	1.361 (3)	N3*B*—N4*B*	1.354 (4)
N4*A*—C12*A*	1.374 (4)	N4*B*—C12*B*	1.375 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*AB*···N2*A*	0.86	1.98	2.636 (3)	132
N4*B*—H4*BB*···N2*B*	0.86	1.95	2.616 (3)	133

All H atoms were fixed geometrically and treated as riding on their parent C and N atoms, with C—H distances in the range 0.93–0.97 Å, N—H distances of 0.86 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C, N})$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1085). Services for accessing these data are described at the back of the journal.

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