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Pyridine-2-carbaldehyde N^4-phenethylthiosemicarbazone

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Key indicators

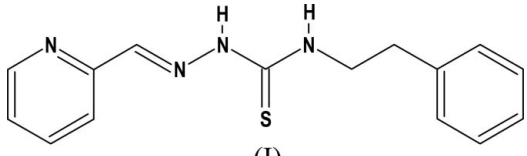
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.077
Data-to-parameter ratio = 17.3

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

In the molecule of the title compound, $C_{15}H_{16}N_4S$, the thiosemicarbazone group adopts an *EE* configuration, *i.e.* *trans* configurations are observed about both the azomethine and hydrazinic bonds. The phenylethyl group is disordered over two sites. In addition to an intramolecular N—H···N bond, intermolecular N—H···N hydrogen bonds [H···N = 2.063 (16) Å] link the molecules into one-dimensional chains in the *a*-axis direction. In the crystal structure, further stabilization is provided by weak C—H···π(arene) interactions.

Comment

N-Heterocyclic thiosemicarbazones have been widely studied due to their antimicrobial activities. For example, N^4-substituted thiosemicarbazones have been shown to possess antitumour properties in mammalian cells with the inhibition of DNA synthesis through the coordination of iron (Borges *et al.*, 1997). 4-Morpholino-2-formylpyridine thiosemicarbazone is reported to be an active antineoplastic agent in mice bearing Sarcoma 180 ascites cells (Agrawal *et al.*, 1976). Similarly, the cytotoxicity of copper and iron complexes of 5-substituted 2-formylpyridine thiosemicarbazones against Ehrlich ascites tumour cells has been measured (Antholine *et al.*, 1976). In the light of these reports, we have synthesized the title compound, (I), with the aim of investigating its antimicrobial behaviour and related metal complexes.



(I)

The title compound is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The C15═S1 and C15—N2 bond distances are typical for these types of bonds, as are the remaining bond lengths and angles in (I) (Allen *et al.*, 1987), and are similar to those in the structures of previously reported thiosemicarbazones (*e.g.* John *et al.*, 2003; Joseph *et al.*, 2004; Philip *et al.*, 2004; Sreekanth *et al.*, 2004; Usman *et al.*, 2002). The thiosemicarbazone reveals an *EE* configuration, since *trans* configurations are observed about both the C14═N3 and C15—N2 bonds.

The phenylethyl group (atoms C1–C8) is disordered over two sites, with relative occupancies 0.433 (11) and 0.567 (11) for the *A* and *B* components; the H atom attached to N1 is also disordered, with these same occupancies. The pyridyl ring is

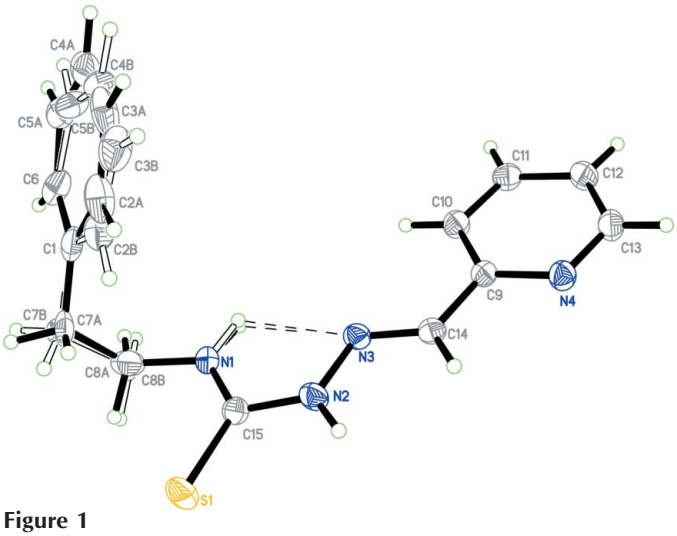


Figure 1
The molecular structure of (I), with ellipsoids drawn at the 60% probability level. Dashed lines denote hydrogen bonds. Both disorder components are shown.

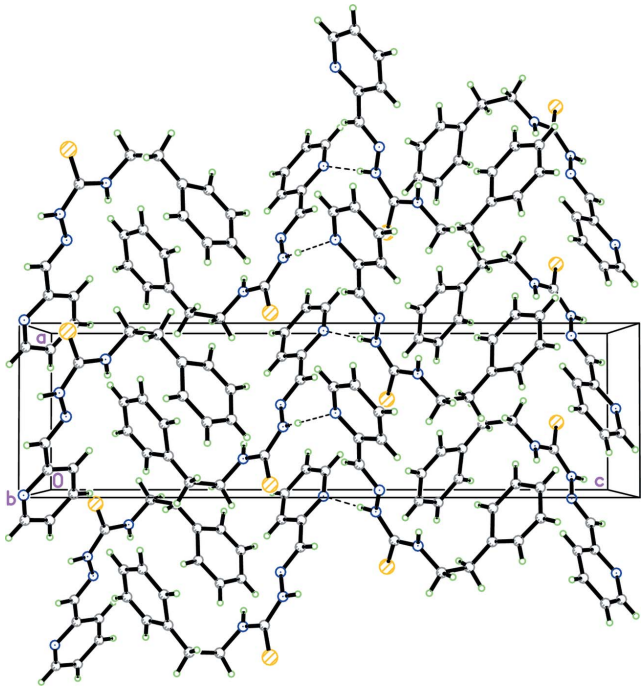


Figure 2
The crystal packing of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines. For clarity, only one disorder component of the phenylethyl group is shown.

coplanar with the thiosemicarbazone group (S1/N2/N3/C14/C15), with an r.m.s. deviation of 0.025 Å and a maximum deviation of 0.173 (1) Å for atom S1. The C15—N1—C8*A*—C7*A* torsion angle of 73.6 (10)° [C15—N1—C8*B*—C7*B* = 81.3 (7)°], indicates a (+)-*syn*-clinal conformation in this part of the molecule. The dihedral angles between the thiosemicarbazone group and the phenyl ring disorder components are 52.3 (2) and 50.78 (16)° for the *A* and *B* disorder components, respectively.

In addition to an ntramolecular N—H···N hydrogen-bonded *S*(5) ring (Bernstein *et al.*, 1995), the molecules are linked by intermolecular N—H···N hydrogen bonds to form one-dimensional chains in the *a*-axis direction (Fig. 2 and Table 2). In the crystal structure, further stabilization is provided by weak C—H···π(arene) interactions (Table 2).

Experimental

A solution containing *N*-methyl-*N*-phenyl-3-thiosemicarbazide (1 g, 5.52 mol) (Klayman *et al.*, 1984), 2-phenylethylamine (0.725 ml, 5.52 mmol) and pyridine-2-carbaldehyde (0.525 ml, 5.52 mmol) in CH_3CN (5 ml) was heated under reflux for 1 h. The solution was chilled (overnight), and the crystals that separated were collected and washed well with CH_3CN. After recrystallization from ethanol, the sample was dried *in vacuo* over P_4O_{10}. Single crystals of X-ray diffraction quality were prepared by the slow evaporation of an ethanol solution of the title compound (m.p. 436–438 K).

Crystal data

$C_{15}H_{16}N_4S$
M_r = 284.39
Orthorhombic, $P2_12_12_1$
a = 6.7341 (9) Å
b = 8.9533 (12) Å
c = 24.003 (3) Å
V = 1447.2 (3) Å^3
Z = 4
D_x = 1.305 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4238 reflections
θ = 1.7–30.0°
μ = 0.22 mm^{-1}
T = 100.0 (1) K
Rod, colourless
0.43 × 0.19 × 0.13 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.951, T_{max} = 0.972
22005 measured reflections
4232 independent reflections
3928 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 30.0°
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.077
S = 1.03
4232 reflections
244 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.2742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Absolute structure: Flack (1983), 1790 Friedel pairs
Flack parameter: 0.02 (6)

Table 1
Selected geometric parameters (Å, °).

S1—C15	1.6849 (13)	N1—C8*A*	1.407 (13)
N3—C14	1.2837 (15)	N1—C8*B*	1.506 (8)
N3—N2	1.3783 (14)	N4—C13	1.3416 (16)
N2—C15	1.3587 (16)	N4—C9	1.3488 (16)
N1—C15	1.3401 (16)		
C14—N3—N2	114.37 (10)	C15—N1—C8*B*	126.7 (4)
C15—N2—N3	120.47 (10)	N3—C14—C9	121.90 (11)
C15—N1—C8*A*	119.9 (5)		
C2*A*—C1—C7*A*—C8*A*	−111.5 (7)	C15—N1—C8*B*—C7*B*	81.3 (7)
C15—N1—C8*A*—C7*A*	73.6 (10)	N3—N2—C15—S1	175.08 (8)

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

*Cg*1 and *Cg*2 are the centroids of rings N1/C9–C13 and C1/C2*A*–C4*A*/C6, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···N3	0.90	2.23	2.6481 (15)	108
N1—H1*A*···N3	0.90	2.29	2.6481 (15)	104
N2—H1N2···N4^{i}	0.90 (2)	2.06 (2)	2.9597 (14)	176
C10—H10*A*···*Cg*2^{ii}	0.93	2.85	3.625 (3)	142
C12—H12*A*···*Cg*1^{iii}	0.93	2.87	3.6495 (15)	142

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

H atoms bonded to N2 and C6 were located in a difference map and refined isotropically. The remaining H atoms were placed in calculated positions, with C—H distances of 0.93 and 0.97 Å, and N—H distances of 0.90; the U_{iso} values were constrained to $1.2U_{eq}$ of the carrier atom for these H atoms.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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