

N'-(2-Methoxythiobenzoyl)pyridine-2-carbohydrazide**N. K. Singh,^{a‡} Ray J Butcher^{b*}
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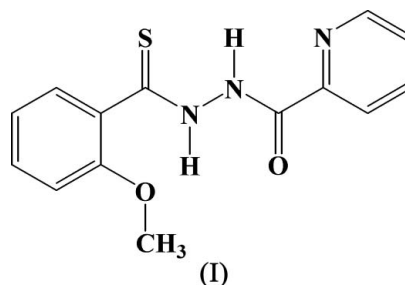
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Key indicatorsSingle-crystal X-ray study
 $T = 93$ K
Mean $\sigma(\text{N}-\text{C}) = 0.002$ Å
Disorder in main residue
 R factor = 0.034
 wR factor = 0.095
Data-to-parameter ratio = 14.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$, intermolecular $\text{N}-\text{H}\cdots\text{O}$ ($\text{H}\cdots\text{O} = 2.03$ Å) and $\text{C}-\text{H}\cdots\text{S}$ ($\text{H}\cdots\text{S} = 2.77$ Å) hydrogen bonds link molecules into a two-dimensional framework.

Comment

In recent years, there has been considerable interest in metal complexes of nitrogen-sulfur donor ligands, such as thiohydrazides, whose properties can be altered by introducing different organic substituents. These ligands can coordinate to metal ions to give structures with different geometries and properties (Singh *et al.*, 1988; Shrivastav *et al.*, 2002; Liu *et al.*, 1992). As part of our ongoing research on these ligands, we report here the crystal structure of the title compound, (I), a new thiohydrazide.



The molecular structure of (I), together with the atom-labeling scheme, is shown in Fig. 1. The molecule is not exactly planar, but can be divided into three planar fragments, *viz.* an *o*-methoxyphenyl ring, a carbonothioyl carbohydrazide unit and a pyridine ring. The peripheral rings are disordered over two orientations, with occupancies of 0.556 (6) and 0.444 (6) for the pyridine ring and 0.519 (3) and 0.481 (3) for the *o*-methoxyphenyl ring (Fig. 2). The carbohydrazide unit is almost coplanar with the pyridine ring [dihedral angles = 3.26 (3) and 4.44 (6)° for the major and minor components, respectively]. The *o*-methoxyphenyl ring plane is twisted away from the carbonothioyl carbohydrazide plane [60.2 (2) and 55.9 (2)° for the major and minor components, respectively]. This twisting may be attributed to an intermolecular $\text{C}2-\text{H}2\text{A}\cdots\text{O}2$ hydrogen bond. The dihedral angles between the *o*-methoxyphenyl ring and the pyridine ring are 61.3 (3) and 60.0 (3)° for the major and minor components, respectively. Hydrazinic atoms H2B and H3B are *trans* to each other, as are the C7-S and C6-O1 groups [torsion angles $\text{N}3-\text{N}2-\text{C}6-\text{O}1$ and $\text{N}2-\text{N}3-\text{C}7-\text{S} = -1.8$ (2) and 1.2 (2)°, respectively]. In addition, the C-S bond distance of 1.669 (1) Å agrees well with equivalent bonds in similar structures, being intermediate between 1.82 Å for a C-S single bond and 1.56 Å for a C=S

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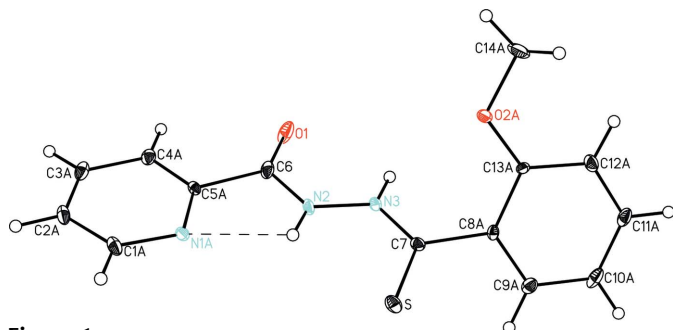


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are shown as small spheres of arbitrary radii. Only one disorder component is shown. The dashed line indicates a hydrogen bond.

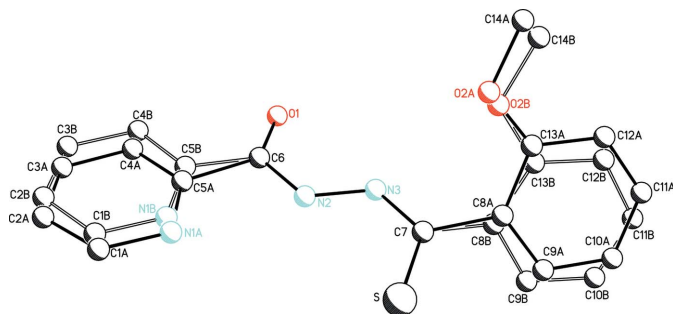


Figure 2
The molecular structure of (I), showing the disordered rings. H atoms have been omitted for clarity.

double bond (Wu *et al.*, 2000). The corresponding C7–N3 bond distance of 1.3279 (16) Å is also intermediate between 1.47 Å for a C–N single bond and 1.29 Å for a double bond (Boga *et al.*, 1999). The N2–N3 distance of 1.3767 (13) Å also shows partial double-bond character, suggesting extensive delocalization in the compound. The zigzag conformation of (I) makes atoms S, N2 and N1 potential donor sites for coordination with metals. Intermolecular N–H...O, C–H...O and C–H...S hydrogen bonds link the molecules together in the solid state (Table 2 and Fig. 2).

Experimental

Compound (I) was synthesized by the reaction of 2-methoxyphenylcarbonothioylthioacetic acid and picolinic acid hydrazide in an alkaline medium. The phenylcarbonothioylthioacetic acid was prepared according to the literature method of Jensen & Pedersen (1961). Solutions of 2-methoxyphenylcarbonothioylthioacetic acid (2.42 g, 10 mmol) and picolinic acid hydrazide (1.36 g, 10 mmol) in 1 N NaOH were mixed together and allowed to stand for 2 h. The resulting filtered solution was acidified with acetic acid (20% *v/v*). The precipitated product was filtered off, washed twice with portions of cold water and dried *in vacuo*. White single crystals of (I) (m.p. 431 K) suitable for X-ray analysis were obtained by slow evaporation of a methanol–diethyl ether (50:50) solution over a period of 4 d (yield 1.4 g, 68%). IR (ν , cm^{-1}): 3248 and 3184 (–NH), 1666 (–C=O), 912 (–C=S); ^1H NMR (DMSO- d_6 , TMS): 3.88 (*s*, 3H, –OCH₃), 7.03–7.46 (*m*, 4H, aromatic), 7.98–8.75 (*m*, 4H, pyridine), 11.79 and 13.20 (*s*, 1H from –NH, D₂O exchangeable); ^{13}C NMR (DMSO- d_6 , TMS): 149.08 (C1), 127.53 (C2), 138.23 (C3), 120.33 (C4), 147.77 (C5), 159.33

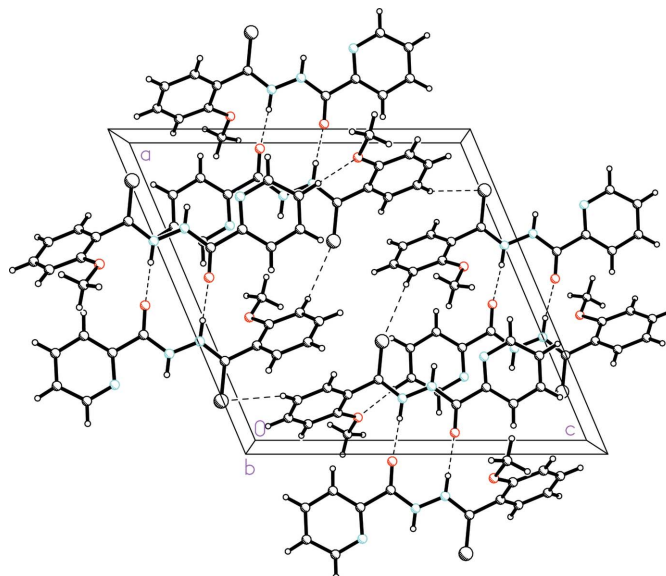


Figure 3
A projection of the crystal packing of (I) along the *b* axis. Only one disorder component is shown. The dashed lines indicate hydrogen bonds.

(C6), 184.91 (C7), 122.32 (C8), 131.65 (C9), 127.05 (C10), 111.96 (C11), 131.32 (C12), 155.13 (C13), 56.00 (C14).

Crystal data

C₁₄H₁₃N₃O₂S
M_r = 287.33
 Monoclinic, *P*2₁/*n*
a = 14.608 (2) Å
b = 6.7090 (11) Å
c = 14.975 (3) Å
 β = 112.946 (3)°
V = 1351.5 (4) Å³
Z = 4

D_x = 1.412 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 5777 reflections
 θ = 3.0–28.3°
 μ = 0.24 mm^{−1}
T = 93 (2) K
 Chunk, colorless
 0.80 × 0.55 × 0.45 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.710, *T_{max}* = 0.896
 10072 measured reflections

3221 independent reflections
 2639 reflections with *I* > 2 σ (*I*)
R_{int} = 0.031
 θ_{max} = 28.3°
h = −19 → 18
k = −8 → 8
l = −19 → 17

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.034
wR(*F*²) = 0.095
S = 1.05
 3221 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.3326P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S–C7	1.6690 (12)	N3–C7	1.3279 (16)
O1–C6	1.2299 (17)	C5A–C6	1.587 (10)
N2–C6	1.3357 (17)	C5B–C6	1.446 (8)
N2–N3	1.3767 (13)		
C6–N2–N3	121.41 (10)	C7–N3–N2	119.80 (10)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2A···N1A	0.88	2.17	2.639 (11)	113
N3–H3A···O1 ⁱ	0.88	2.03	2.8524 (14)	155
C2A–H2AA···O2A ⁱⁱ	0.95	2.35	3.152 (13)	141
C2B–H2BA···O2A ⁱⁱ	0.95	2.45	3.268 (13)	145
C12A–H12A···S ⁱⁱⁱ	0.95	2.77	3.584 (6)	144

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$

The peripheral rings of (I) are disordered over two orientations, as described in the *Comment*. The two components were restrained to have similar geometric and displacement parameters. All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with $C-H = 0.98$ Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C–C bond. The amine H atoms, as well as those attached to C atoms, were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $N-H = 0.88$ Å, $C-H = 0.95-1.00$ Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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