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1-(1-Benzoylpropen-2-yl)-3-methylisothiosemicarbazide

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The structure of the title *S*-alkylated isothiosemicarbazide, $C_{12}H_{15}N_3OS$, was determined by single-crystal diffractometry and compared with the structures of other compounds containing the *S*-alkylthiosemicarbazide moiety. Such structures cluster into two groups, according to the different orientation of the –S*R* group with respect to the hydrazine N atom of the thiosemicarbazide. The *cis* arrangement is preferred by most molecules in the solid state, in spite of the possibility of intramolecular N—H···N interactions in the opposite orientation.

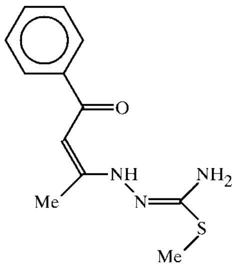
Comment

Thiosemicarbazones represent an important class of potential ligands for complexing metal cations to obtain coordination compounds of biomedical relevance (Campbell, 1975; Padhyé & Kauffman, 1985; West *et al.*, 1993; Casas *et al.*, 2000). Thiosemicarbazide itself, $N^1H_2-N^2H-C(=S)-N^4H_2$ (thsc), behaves as both a monodentate and a bidentate ligand. In the first case, coordination occurs through the S atom, while in the second case, it occurs through the S and N^1 atoms. Thsc derivatives having additional coordinating functionalities can further act as tridentate ligands, and bis(thiosemicarbazones) can be used as tetra- and pentadentate ligands.

When the S atom is alkylated, such as in *S*-alkylisothiosemicarbazide, $N^1H_2-N^2=C(-SR)-N^4H_2$ (S*R*-thsc), and its derivatives $R^1N^1H-N^2=C(-SR)-N^4H_2$ or $R^1N^1H-N^2=C(-SR)-N^4HR^2$, coordination systematically occurs through the two terminal N atoms, due to a decrease in the donor ability of S after alkylation (Gerbeleu *et al.*, 1999).

In the solid state, the thiosemicarbazide backbone is usually almost planar, allowing, in some cases, extended π-charge delocalization. In thsc (Andreetti *et al.*, 1970) and its derivatives, the S atom is *trans* to the hydrazine N^1 atom, thus placing the N^1 and N^4 atoms in suitable positions for intramolecular hydrogen bonding (Chattopadhyay *et al.*, 1989; Casas *et al.*, 2000). On the other hand, S*R*-thsc compounds prefer the *Z* form (Shova *et al.*, 1985; Gerbeleu *et al.*, 1999; Casas *et al.*, 2000), and are then subjected to reorientation into the *E* form on complexation to a central atom, allowing N^1,N^4-chelation.

In this work, we report on the structure of the tridentate ligand 1-(1-benzoylpropen-2-yl)-3-methylisothiosemicarbazide, (I). This ligand has been used to prepare square-planar Ni^{II} complexes, the synthesis, structure and physicochemical characterization of which have been reported elsewhere (Gradinaru *et al.*, 2002).



(I)

A perspective view of (I) is shown in Fig. 1. The crystal structure consists of near-planar molecules with a strong intramolecular N1—H1···O interaction (Table 1).

The phenyl ring is tilted by 9.97 (6)° with respect to the least-squares plane of atoms O, C5, C6, C7 and N1. A similar rotation was observed in the above-mentioned Ni^{II} complexes (Gradinaru *et al.*, 2002) and in the complex $[Ni(HL^2)py]$ (where HL^2 is 1-phenylbutane-1,3-dione mono-*S*-methylisothiosemicarbazone and py is pyridine; Bogdanović *et al.*, 1999), where it was ascribed to the balancing of two opposite effects, firstly, H···H repulsion (H6···H3 = 2.04 Å) and, secondly, the formation of an intramolecular C11—H11···O hydrogen bond (Table 1). A significantly greater value of this angle, equal to 23.41°, was obtained from RHF/6-31G** geometry optimization of the gas-phase isolated molecule (*GAUSSIAN*98; Frisch *et al.*, 1998), indicating that packing forces besides intramolecular effects contribute to determine the orientation of the phenyl ring in the solid state.

The planarity of the molecular backbone of (I) allows an extended conjugation along the benzoylacetoniminate arm, with shortened C5—C6 and C7—N1 single bonds and lengthened C5=O and C6=C7 double bonds [1.400 (3), 1.327 (3), 1.267 (3) and 1.370 (3) Å, respectively]. In order to characterize the S*R*-thsc moiety, the geometry of (I) was compared with that of molecules having the N—N=C(SC)N fragment, the structures of which were retrieved from the Cambridge Structural Database (CSD, April 2001 release; Allen *et al.*, 1983). The search was performed using the criteria of an agreement index $R < 0.1$ and no disorder, and only considered organic compounds. Structures where C, N or S atoms of the requested fragment were constrained by formation of a ring were obviously excluded from this search. Since only a restricted number of structures were retrieved (17), comprising both protonated [DITRAZ (Shova *et al.*, 1985) and MITCHZ (Bigoli *et al.*, 1978)] and neutral molecules (all the other compounds), the relevant bond lengths and torsion angles are presented in Table 2 for comparison, together with the corresponding values for (I). A study of the corresponding

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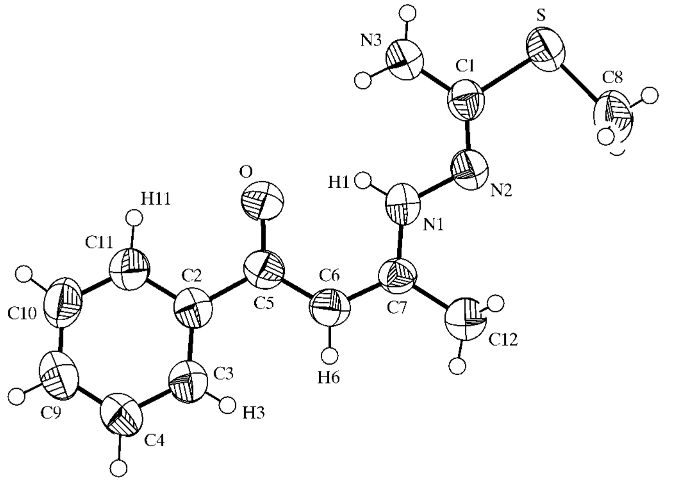

Figure 1
A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

bond lengths across all 18 compounds indicates a large variation in the geometry of the S*R*-thsc fragment, due to the differing extent of the degree of conjugation. In the case of (I), the long N1—N2 bond and the short N2═C1 distance, corresponding to the minimum value observed for this bond within the S*R*-thsc series, denote scarce conjugation.

On examining the N1—N2═C1—S torsion angles reported in Table 2, the above-mentioned preference of S*R*-thsc derivatives for a *cis* orientation of the –S*R* group with respect to atom N1 (*Z* configuration) is evident.

It is noteworthy that in S*R*-thsc derivatives, atom C8 is preferentially coplanar with the molecular backbone, as indicated by the N3—C1—S—C8 torsion angles in Table 2, but significant deviation from planarity is observed for some derivatives.

An inspection of the structures reported in Table 2 indicates that, in all cases, the *E* configuration should allow the formation of one or more intramolecular N—H···N bonds, with the sole exception of DISKIZ (Simonov *et al.*, 1985), where no potential N—H donor is present. In compound (I), which is one of the few *trans* derivatives, atom N3 acts as both donor and acceptor (Table 1).

These considerations suggest that, as a rule, other intra- and/or intermolecular effects do prevail over a possible N—H···N interaction in fixing the orientation of the –S*R* group in S*R*-thsc derivatives. A theoretical investigation of some representative structures, aimed at discerning the relative importance of intra- and intermolecular forces in determining the relative stability of the two conformations, is in progress.

Experimental

All reagents were commercially available. The CHN analyses were carried out by standard micromethods. The IR spectrum was recorded as a KBr disc (4000–400 cm^{-1}) using a Perkin–Elmer FT–IR 1720X spectrometer. The electronic spectra were recorded on a UVIKON 930 spectrophotometer (190–900 nm). The mass spectrometric analysis was performed with a Finnigan LCQ mass spectrometer using electrospray ionization and a Finnigan MAT 958 double-focusing mass spectrometer using electron ionization (70 eV) and standard resolution conditions, $m/\Delta m$ = 2300. Melting points were determined with a Buchi 510 apparatus.

The synthesis of (I) was carried out according to the procedure reported by Leovac *et al.* (1994). Crystals were obtained by dissolving a mixture of benzoylacetone (3.25 g, 20 mmol) and *S*-methylisothiosemicarbazide hydrogen iodide (4.60 g, 20 mmol) in ethanol (15 ml) with heating. An NaOH solution (1.2 g in 15 ml H_2O) was added to the reaction mixture at room temperature. The next day, yellow crystals of (I) were filtered off, washed with water and ethanol, and dried in air (yield 2.3 g, 46.12%; m.p. 363–365 K). Analysis found: C 57.56, H 5.83, N 17.07%; calculated for $C_{12}H_{15}N_3OS$: C 57.81, H 6.06, N 16.85%. ESI mass spectrum: m/z = 249 (I, 100%), $[M]^+$. EI mass spectra, m/z: 249 (I, 36.4%), $[M]^+$; 202 (I, 9.5%), $[M - SCH_3]^+$; 234 (I, 4.3%), $[M - CH_3]^+$; 216 (I, 2.5%), $[M - SH]$. IR data: 1535–1600 cm^{-1} (C═O, C═N and C═C), 3313 and 3189 cm^{-1} (NH_2), 1637 cm^{-1} (NH_2). Compound (I) gave two bands in the near ultraviolet region at 371–385 and 244–248 nm, in agreement with what has been reported for a series of vinylogous amides, *i.e.* β-amino α,β-unsaturated ketones, –N—*R*C═C*R*′—C(O)– (Ostercamp, 1970) [λ_{max}, nm (ε, dm^3 cm^{-1} mol^{-1}): 376 (13 892) and 245 (16 844) in *n*-hexane, 385 (10 275) and 248 (17 200) in chloroform, 382 (16 400) and 244 (11 504) in acetonitrile, 384 (10 892) and 247 (11 032) in methanol, and 371 (4159) and 248 (13 710) in water].

Crystal data

$C_{12}H_{15}N_3OS$
M_r = 249.33
Monoclinic, $P2_1/n$
a = 8.932 (1) Å
b = 5.324 (1) Å
c = 26.316 (2) Å
β = 92.80 (1)°
V = 1249.9 (3) Å^3
Z = 4
D_x = 1.325 Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 1875 reflections
θ = 2.4–23.1°
μ = 0.25 mm^{-1}
T = 288 (2) K
Prism, yellow
0.32 × 0.13 × 0.08 mm

Data collection

Bruker SMART APEX area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT*; Bruker, 1997)
T_{min} = 0.858, T_{max} = 1.000
11 930 measured reflections
2858 independent reflections
1566 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = -6 \rightarrow 6$
$l = -33 \rightarrow 34$

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O	0.86	1.91	2.581 (3)	134
N1—H1···N3	0.86	2.32	2.667 (3)	104
N3—H3*A*···N1	0.86	2.40	2.667 (3)	98
C11—H11···O	0.93	2.45	2.757 (4)	99
N3—H3*B*···O^{i}	0.86	2.08	2.898 (3)	157
N3—H3*A*···N3^{i}	0.86	2.52	3.228 (4)	140
C9—H9···S^{ii}	0.93	2.89	3.751 (3)	155

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

Table 2
Selected bond lengths (Å) and torsion angles (°) for (I) and for structures retrieved from the CSD.

REFCODE	N1−N2	N2=C1	C1−N3	C1−S	S−C8	N1−N2=C1−S	N3−C1−S−C8	Reference
(I)	1.381 (3)	1.274 (3)	1.361 (3)	1.739 (2)	1.775 (3)	−179.5 (2)	174.4 (2)	This work
CIWWAG	1.385	1.309	1.344	1.748	1.795	4.5	3.3	Argay *et al.* (1983)
CMTFAZ10	1.352	1.313	1.408	1.757	1.801	−178.4	−175.3	Hutton *et al.* (1979)
DISKIZ	1.404	1.287	1.398	1.752	1.800	0.8	1.4	Simonov *et al.* (1985)
DITRAZ	1.404	1.315	1.324	1.734	1.795	−1.9	−1.9	Shova *et al.* (1985)
FEMDEG†	1.397	1.318	1.346	1.807	1.840	3.3	14.4	Bourosh *et al.* (1986)
GAZVOS	1.398	1.279	1.345	1.778	1.809	6.2	13.7	Bourosh *et al.* (1987)
JINTAB	1.394	1.283	1.389	1.744	1.790	−0.5	−0.9	Simonov *et al.* (1990)
LAJCEE	1.407	1.294	1.374	1.755	1.809	−179.1	177.1	Krapivin *et al.* (1992)
MITCHZ	1.429	1.305	1.337	1.748	1.817	176.4	178.0	Bigoli *et al.* (1978)
MTOFMZ10	1.326	1.296	1.391	1.769	1.809	−5.5	−63.6	Hutton *et al.* (1980)
SIPDTZ†	1.329	1.310	1.407	1.748	1.822	0.6	66.6	Guillerez *et al.* (1978)
SMDTHZ10	1.344	1.300	1.391	1.758	1.790	177.8	173.0	Preuss & Gieren (1975)
TADLEP	1.407	1.299	1.388	1.742	1.824	−2.0	6.3	Bourosh *et al.* (1989)
YORLOG†	1.388	1.301	1.332	1.752	1.811	0.9	9.2	Ilyukhin *et al.* (1994)
YORLUM	1.388	1.302	1.331	1.759	1.810	1.1	5.9	Ilyukhin *et al.* (1994)
YORMAT†	1.386	1.320	1.316	1.769	1.811	2.4	0.8	Ilyukhin *et al.* (1994)
YORMEX†	1.374	1.315	1.323	1.748	1.820	3.6	11.9	Ilyukhin *et al.* (1994)

† Average values for the independent molecules of the asymmetric unit. Absolute values were used for torsion-angle averaging.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.151$
$S = 0.88$
2858 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0866P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

H atoms were treated as riding, with N—H = 0.86 Å and C—H = 0.93–0.96 Å, and with $U_{\rm iso}$(H) = 1.2 or 1.5$U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1569). Services for accessing these data are described at the back of the journal.

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