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2-Hydroxyacetophenone 4-phenylthiosemicarbazone

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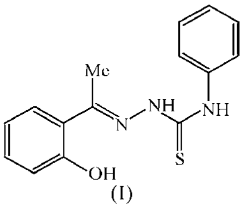
The title compound, $C_{15}H_{15}N_3OS$, exists in the thione form and adopts an *E* configuration about the hydrazine bond, which is in the *Z* form with respect to the thiocarbonyl bond. An O—H···N intramolecular hydrogen bond promotes planarity in part of the molecule.

Comment

Thiosemicarbazones of 2-hydroxyacetophenone and its derivatives are a class of versatile *O*,*N*,*S*-tridentate donor ligands capable of stabilizing both higher and lower oxidation states of transition metal ions. The biological activities of these ligands are related to their chelating ability with transition metal ions through phenol O, azomethine N and thiolate S atoms (John *et al.*, 2004, and references therein). The coordination chemistry of these compounds has been of considerable interest as they can act as dianionic chelating ligands (John *et al.*, 2002). The presence of bulky groups at the terminal 4-position increases the biological activity (Durham *et al.*, 1974). de Sousa *et al.* (2001) have reported the title compound, (I), and its tin(IV) complexes but without a crystal structure study of (I).



(I)

Compound (I) (Fig. 1 and Table 1) adopts an alternative configuration to the recently reported 2-hydroxyacetophenone *N*(4)-cyclohexylthiosemicarbazone (Seena *et al.*, 2006; hereafter hapct). Atom S1 is in the *Z* form with azomethine atom N1 with respect to the N2—C8 bond [S1—C8—N2—N1 = 10.5 (2)°], unlike the *E* configuration seen in hapct. Furthermore, the *E* conformation of atom S1 and atom C9 of the phenyl ring about the C8—N3 bond in (I) [S1—C8—N3—C9 = −179.80 (14)°] is different from the *Z* conformation seen for those atoms in hapct. The N—H···S dimer ring involving intermolecular hydrogen bonds in compound (I) (Table 2), which utilizes atom N3 rather than the N2 atom used in hapct, may promote this conformation change.

The C8═S1 and C8—N2 and C8—N3 bond distances (Table 1) are close to C═S double bonds and C—N single bonds in thiosemicarbazones (Usman *et al.*, 2002; Chattopadhyay *et al.*, 1988; Latheef *et al.*, 2006) and confirm the thione form for (I). The C8═S1 bond length of (I) is in agreement with its di-2-pyridyl (Suni *et al.*, 2006), 2-acetylpyridine (Bermejo *et al.*, 1999) and acetophenone (Jian *et al.*, 2005) counterparts, but is less than the 1.688 (2) Å value in

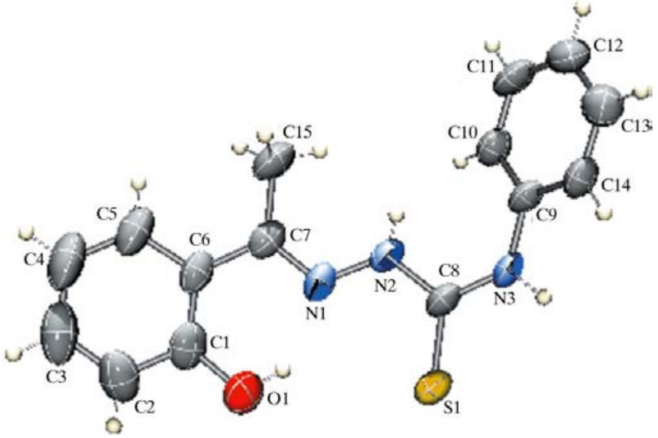


Figure 1
Compound (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

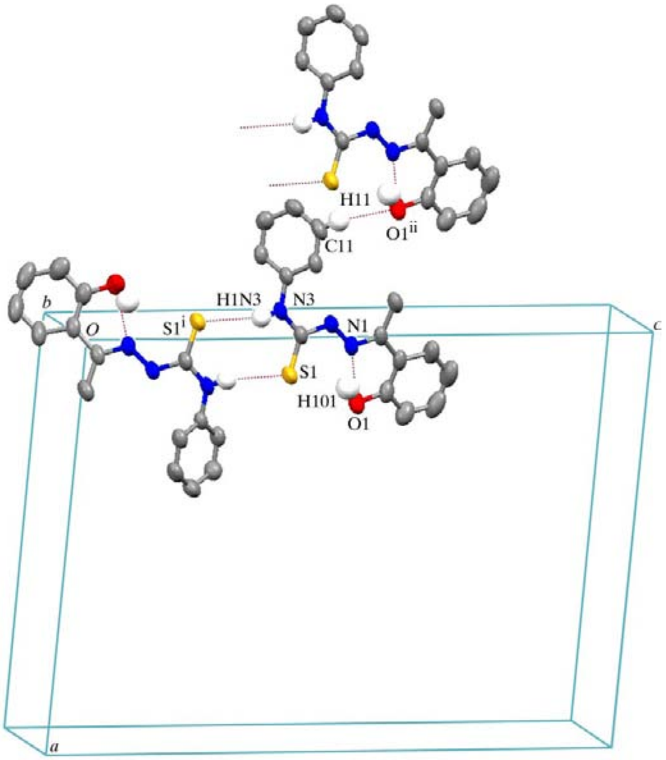


Figure 2
A view of the unit cell of (I) along the *b* axis. The intermolecular and main intramolecular hydrogen bonds (Table 2) are shown as dashed lines. The symmetry codes are as in Table 2.

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hapct. The decrease of 0.017 (3) Å for the C8—N3 bond distance compared with C8—N2 suggests greater double-bond character to the former and increased electron localization at this substituted end. This is confirmed by the typical double-bond length for N1═C7 and the considerable decrease [0.048 (2) Å] from the single-bond length for N3—C9 (Huheey *et al.*, 1993). On complexation, the coordination occurs through the thiolate form, and the C—S bond length increases to 1.734 (3) and 1.754 (8) Å in the Sn^{IV} complexes [SnMe$_2$(L)] and [SnBu$_2$(L)], respectively (de Sousa *et al.*, 2001), where L is the doubly deprotonated form of (I). The enolization on coordination leads to changes in the N2—C8, N1—N2 and N3—C8 bond lengths, although the overall conformation of (I) is retained.

The 2-hydroxyacetophenone thiosemicarbazone group excluding atoms S1 and N3 is approximately planar, with a maximum deviation of 0.074 (2) Å for atom C3. This planarity is associated with the six-membered ring (O1/H1O1/N1/C7/C6/C1) formed *via* the intramolecular O1—H1O1···N1 hydrogen bond (Table 2), as in salicylaldehyde 3-hexamethyleneiminylthiosemicarbazone (Latheef *et al.*, 2006). As a result, the exocyclic angles around atom C1 and the angles subtended at C7 show considerable asymmetry (Table 1). The core thiosemicarbazone group (C7/N1/N2/C8/S1/N3/C9) is also approximately planar, with a maximum deviation from the mean plane of 0.0813 (14) Å for atom N1; this plane makes a dihedral angle of 15.88 (6)° with the plane comprising atoms O1 and C1–C6. The phenyl substituent is twisted away from this thiosemicarbazone plane, forming an interplanar angle of 48.46 (7)°.

Two kinds of intermolecular hydrogen bonds (Fig. 2) are seen in the packing. The molecules are paired through N3—H1N3···S1 interactions, and a three-dimensional motif is formed using a second weak intermolecular hydrogen bond, *viz*. C11—H11···O1, and the C10—H10···π interaction (Table 2).

Experimental

2-Hydroxyacetophenone 4-phenylthiosemicarbazone was prepared according to the method of de Sousa *et al.* (2001). To a hot methanol (40 ml) solution of 4-phenylthiosemicarbazide (0.84 g, 5 mmol), a methanol (10 ml) solution of 2-hydroxyacetophenone (0.6 ml, 5 mmol) was added with constant stirring. The mixture was refluxed for 4 h. After cooling, the resulting pale-yellow compound was filtered off, washed with methanol and diethyl ether, and finally dried over P_4O_{10} *in vacuo*. Yellow block-shaped crystals suitable for X-ray analysis were obtained by slow evaporation from a solution in a mixture of methanol–diethyl ether (1:1) after one week. Elemental analysis found: C 62.61, H 5.35, N 14.57%; calculated: C 63.13, H 5.30, N 14.73%.

Crystal data

$C_{15}H_{15}N_3OS$
$M_r = 285.36$
Monoclinic, $C2/c$
$a = 16.858$ (2) Å
$b = 7.449$ (2) Å
$c = 23.312$ (7) Å
$\beta = 94.390$ (15)°
$V = 2918.7$ (12) Å^3
$Z = 8$
$D_x = 1.299$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.22$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur-S diffractometer
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.867$, $T_{max} = 0.959$
12882 measured reflections
2552 independent reflections
1947 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.095$
$S = 1.06$
2552 reflections
194 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.928P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.6659 (16)	N2—C8	1.3631 (19)
N1—C7	1.2905 (19)	N3—C8	1.346 (2)
N1—N2	1.3736 (19)	N3—C9	1.422 (2)
C7—N1—N2	118.85 (14)	O1—C1—C6	123.24 (16)
C8—N2—N1	118.64 (14)	N1—C7—C6	114.88 (15)
C8—N3—C9	128.99 (13)	N1—C7—C15	124.18 (15)
O1—C1—C2	116.49 (19)		
C8—N3—C9—C10	−48.5 (3)		

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

$Cg1$ is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1N3···S1^{i}	0.829 (19)	2.604 (19)	3.4148 (18)	166.0 (17)
O1—H1O1···N1	0.82 (2)	1.81 (2)	2.534 (2)	146 (2)
C11—H11···O1^{ii}	0.93	2.55	3.471 (3)	168
C10—H10···$Cg1^{iii}$	0.93	2.83	3.681 (2)	152

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

Atoms H1O1, H1N2 and H1N3 were located from difference maps and refined with isotropic displacement parameters. All other H atoms were positioned geometrically and treated as riding on their parent C atoms, with C—H distances of 0.93 and 0.96 Å, and with U_{iso}(H) values of 1.2U_{eq}(C) for aromatic and 1.5U_{eq}(C) for methyl H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3010). Services for accessing these data are described at the back of the journal.

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