

Ying-Ying Liu, Jian-Fang Ma* and
Ji-Cheng MaDepartment of Chemistry, Northeast Normal
University, Changchun 130024, People's
Republic of ChinaCorrespondence e-mail:
jianfangma@yahoo.com.cn

Key indicators

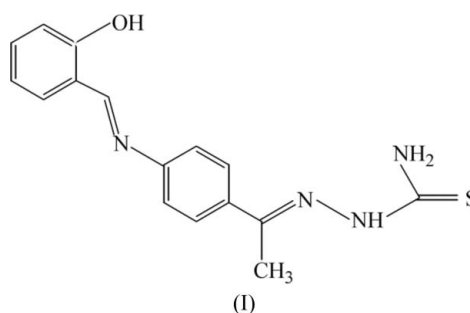
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.044
 wR factor = 0.087
Data-to-parameter ratio = 17.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-(2-Hydroxybenzylideneamino)acetophenone
thiosemicarbazone

The title compound, $\text{C}_{16}\text{H}_{16}\text{N}_4\text{OS}$, is a potential O,N,S -tridentate donor ligand. The molecule is non-planar, with the salicylaldehyde benzene ring, the 4-aminoacetophenone benzene ring, and the thiosemicarbazide group being slightly twisted with respect to each other. There is an intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond between the hydroxyl group and the adjacent imine N atom.

Received 3 August 2006
Accepted 5 August 2006

Comment

Research on the reactions of thiosemicarbazones with transition metals has increased steadily for many years due to their variety of biological activities, such as antitumor, antiviral and fungicidal (Kang *et al.*, 1997; Ackerman *et al.*, 1999). Much attention has been devoted to the synthesis of new thiosemicarbazone ligands (Liu *et al.*, 2003; Dinçer *et al.*, 2005). In this work, a new thiosemicarbazone ligand, (I), has been synthesized and its structure studied in detail.



The molecular skeleton of (I) is non-planar; the dihedral angles between the 4-aminoacetophenone benzene ring and the salicylaldehyde benzene ring, and between the 4-aminoacetophenone benzene ring and the thiosemicarbazone unit are $6.8(2)$ and $21.3(2)^\circ$, respectively. The thiosemicarbazone unit is almost planar, with a maximum deviation of $0.202(2)\text{ \AA}$ for atom S1 (Fig. 1). According to previous work, there is thione–thiol tautomerism of the thioamide $-\text{NH}-\text{C}=\text{S}$ functional group (Tian *et al.*, 1997). The distances $\text{C16}-\text{S1}$ and $\text{C14}-\text{N2}$ (Table 1) are $1.680(2)$ and $1.287(2)\text{ \AA}$ respectively, similar to those found in analogous thiosemicarbazone compounds with a thio–keto tautomeric form (Vrdoljak *et al.*, 2005). There exists an intramolecular hydrogen bond between the hydroxyl group and the adjacent imine N atom (Table 2 and Fig. 1).

Experimental

Compound (I) was obtained in two steps. Firstly, thiosemicarbazide (0.911 g, 10 mmol) dissolved in hot ethanol (20 ml) was added to a

solution of 4-aminoacetophenone (1.352 g, 10 mmol) in hot water (30 ml). Two drops of acetic acid was added to the reaction mixture. After refluxing for 2 h on an oil bath, the mixture was cooled to room temperature. The product, aminoacetophenone thiosemicarbazone, was collected by filtration and washed with ethanol, dried in air (yield 85%). A mixture of salicylaldehyde (0.611 g, 5 mmol) and aminoacetophenone thiosemicarbazone (1.042 g, 5 mmol) in absolute methanol (40 ml) was then stirred at 323 K for 2 h. The resulting orange solid (I) was filtered off and washed with ethanol. Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a DMF solution (yield 78%).

Crystal data

$C_{16}H_{16}N_4OS$	$Z = 4$
$M_r = 312.39$	$D_x = 1.325 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.582 (11) \text{ \AA}$	$\mu = 0.21 \text{ mm}^{-1}$
$b = 23.835 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 11.773 (2) \text{ \AA}$	Block, orange
$\beta = 90.93 (3)^\circ$	$0.44 \times 0.32 \times 0.19 \text{ mm}$
$V = 1566 (3) \text{ \AA}^3$	

Data collection

Bruker APEX CCD area-detector diffractometer	14927 measured reflections
ω scans	3577 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1345 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.89$, $T_{\max} = 0.95$	$R_{\text{int}} = 0.083$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.82$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3577 reflections	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
211 parameters	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—O1	1.359 (2)	C16—N3	1.366 (3)
C7—N1	1.284 (2)	C16—S1	1.680 (2)
C14—N2	1.287 (2)	N2—N3	1.380 (2)
C16—N4	1.334 (3)		
N4—C16—N3	115.9 (2)	C14—N2—N3	119.27 (19)
N4—C16—S1	122.55 (19)	C16—N3—N2	118.21 (18)
N3—C16—S1	121.51 (17)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H18 \cdots N1	0.898 (16)	1.722 (18)	2.559 (3)	154 (2)

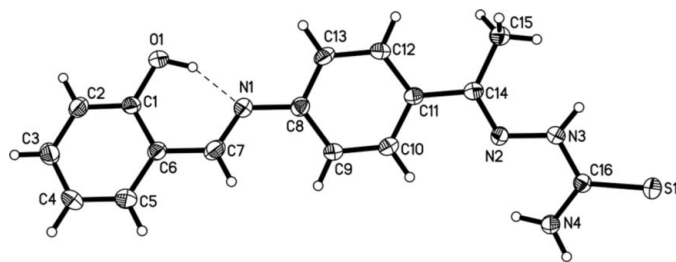


Figure 1

A view of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level. (Sheldrick, 1990).

All C-bound H atoms were positioned geometrically and refined as riding atoms, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times $U_{\text{eq}}(\text{C})$. The amino and imine H atoms were located in a difference Fourier map and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. The hydroxyl H atom was located in a difference Fourier map and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus (Sheldrick, 1990); software used to prepare material for publication: SHELXL97.

We thank the National Natural Science Foundation of China (No. 20471014), the Program for New Century Excellent Talents in Chinese Universities (NCET-05-0320), the Fok Ying Tung Education Foundation, the Science Foundation for Young Teachers of NENU (No. 20050310) and the Analysis and Testing Foundation of Northeast Normal University for support.

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