

Semicarbazones and Thiosemicarbazones. VIII.* Structure of 2-Hydroxyacetophenone Thiosemicarbazone†

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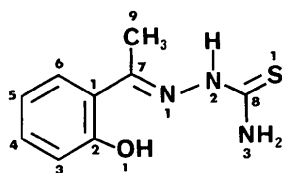
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Abstract. $C_9H_{11}N_3OS$, $M_r = 209.3$, monoclinic, $P2_1/n$, $a = 8.219$ (3), $b = 9.297$ (5), $c = 13.654$ (5) Å, $\beta = 102.83$ (2)°, $V = 1017$ (1) Å³, $Z = 4$, $D_x = 1.37$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.276$ mm⁻¹, $F(000) = 440$, $T = 293$ K, final $R = 0.042$ for 1486 observed reflections. The S atom is *trans* to the N atom of the hydrazine group. The angle between the normals to the planes of the phenyl ring of the salicylidene part of the molecule and the thiosemicarbazone fragment is 22.2 (4)°. The crystal structure is stabilized by intra- and intermolecular hydrogen bonds.

Introduction. A great number of studies have been devoted to the search for derivatives of semicarbazides and thiosemicarbazides which have been used as drugs whose action is attributed to their ability to form metal complexes (Petering & Van Giessen, 1965). Several ligands and metal complexes of semicarbazide and thiosemicarbazide have been the subject of chemical and structural studies (Ablov & Gerbeleu, 1965; Ryabova, Ponomarev, Zelentsov & Atovmyan, 1981; Biyushkin, Gerasimov & Belov, 1981; Soriano-García, Toscano, Valdés-Martínez & Fernández-G., 1985; Soriano-García, Valdés-Martínez, Toscano & Gómez-Lara, 1985; Soriano-García, Valdés-Martínez, Toscano, Gómez-Lara & Villalobos-Peñalosa, 1986).

As a part of our studies on thiosemicarbazide derivatives, we have now prepared the title compound (1) and carried out the crystal structure analysis, in order to establish its molecular structure and stereochemistry.



(1)

* Part VII: Valdés-Martínez, Toscano, Soriano-García, Caranza, Rubio, Gómez-Lara & Vázquez-M. (1988).

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Experimental. Crystals of the title compound prepared as described by Jensen, Anthoni, Kagi, Larsen & Pedersen (1968). Prismatic crystal $0.40 \times 0.40 \times 0.60$ mm mounted on a glass fibre along the needle axis. Nicolet R3 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $5.3 < 2\theta < 24.7^\circ$. 1796 reflections measured with $3 < 2\theta < 50^\circ$ for two octants, of which 1486 had $I > 2.5\sigma(I)$ and used in refinement. Index range $h \pm 9$, $k 0 \rightarrow 10$, $l 0 \rightarrow 16$, ω -scan mode, variable scan speed, scan width 1.0° (θ). Two standard reflections (11 $\bar{3}$; 211) monitored every 50 measurements; no significant variation. Lp correction, absorption ignored and $R_{int} = 0.036$. Structure solved by direct methods using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms with anisotropic thermal parameters. The H atoms of CH and CH₃ groups were allowed to ride on bonded C atoms. The H atoms attached to N and O atoms were found on a difference Fourier map at an advanced stage of refinement and their coordinates were refined; all H atoms assigned fixed isotropic temperature factor, $U = 0.66$ Å². $\sum w(\Delta F)^2$ minimized, $w = \{\sigma^2(F_o) + 0.0015 (F_o)^2\}^{-1}$. In the last cycle $(\Delta/\sigma)_{max} = 0.017$; residual electron density within -0.20 to 0.28 e Å⁻³; final $R = 0.042$ and $wR = 0.058$. Scattering factors from *International Tables for X-ray Crystallography* (1974) and $S = 1.15$.

All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

Discussion. Final positional parameters and equivalent isotropic temperature factors are given in Table 1. § The molecular structure with numbering is illustrated in Fig. 1. Bond lengths and angles for non-H atoms are listed in Table 2.

§ Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44503 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$$

	x	y	z	U_{eq}
S(1)	12349 (1)	5265 (1)	6113 (1)	48 (1)
O(1)	10092 (2)	-837 (2)	6137 (1)	52 (1)
N(1)	9545 (2)	1870 (1)	6152 (1)	37 (1)
N(2)	10074 (2)	3257 (2)	5996 (2)	41 (1)
N(3)	12579 (3)	2761 (2)	7050 (2)	47 (1)
C(1)	7420 (3)	206 (3)	6225 (2)	37 (1)
C(2)	8468 (3)	-980 (3)	6187 (2)	40 (1)
C(3)	7872 (4)	-2385 (3)	6197 (2)	52 (1)
C(4)	6254 (4)	-2626 (3)	6271 (2)	60 (1)
C(5)	5209 (4)	-1492 (3)	6323 (2)	60 (1)
C(6)	5770 (3)	-97 (3)	6295 (2)	50 (1)
C(7)	7981 (3)	1704 (2)	6162 (2)	35 (1)
C(8)	11639 (3)	3649 (2)	6406 (2)	35 (1)
C(9)	6801 (3)	2936 (3)	6119 (2)	46 (1)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

S(1)—C(8)	1.692 (2)	O(1)—C(2)	1.358 (3)
N(1)—N(2)	1.392 (3)	N(1)—C(7)	1.297 (3)
N(2)—C(8)	1.334 (3)	N(3)—C(8)	1.322 (3)
C(1)—C(2)	1.407 (3)	C(1)—C(6)	1.409 (4)
C(1)—C(7)	1.476 (3)	C(2)—C(3)	1.396 (4)
C(3)—C(4)	1.374 (4)	C(4)—C(5)	1.372 (4)
C(5)—C(6)	1.379 (4)	C(7)—C(9)	1.493 (3)
N(2)—N(1)—C(7)	117.1 (2)	N(1)—N(2)—C(8)	119.6 (2)
C(2)—C(1)—C(6)	116.9 (2)	C(2)—C(1)—C(7)	122.4 (2)
C(6)—C(1)—C(7)	120.7 (2)	O(1)—C(2)—C(1)	122.8 (2)
O(1)—C(2)—C(3)	116.3 (2)	C(1)—C(2)—C(3)	120.9 (2)
C(2)—C(3)—C(4)	120.1 (3)	C(3)—C(4)—C(5)	120.4 (3)
C(4)—C(5)—C(6)	120.3 (3)	C(1)—C(6)—C(5)	121.5 (3)
N(1)—C(7)—C(1)	115.8 (2)	N(1)—C(7)—C(9)	123.0 (2)
C(1)—C(7)—C(9)	121.2 (2)	S(1)—C(8)—N(2)	119.6 (2)
S(1)—C(8)—N(3)	122.0 (2)	N(2)—C(8)—N(3)	118.4 (2)

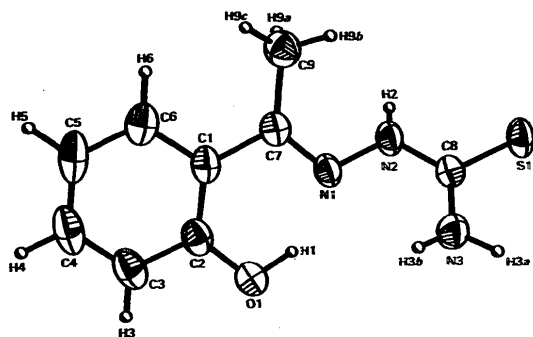


Fig. 1. The molecular conformation of 2-hydroxyacetophenone thiosemicarbazone, showing the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

The S atom and the hydrazinic N(1) atom are *trans* with respect to the C(8)—N(2) bond. A similar conformation was observed in thiosemicarbazide (Hansen & Hazell, 1969), thiosemicarbazide hydrochloride (Coghi, Manotti Lanfredi & Tiripicchio, 1976), 4-phenylthiosemicarbazide (Kálmán, Argay & Czugler, 1972), 1-phenylthiosemicarbazide (Czugler, Kálmán & Argay, 1973) and 5-methoxysalicylaldehyde 4-phenyl-

thiosemicarbazone—methanol (Soriano-García, Valdés-Martínez, Toscano, Gómez-Lara & Villalobos-Peñaloza, 1986).

The phenyl ring of the salicylidene part of the molecule deviates considerably from planarity; maximum deviation is -0.025 (4) \AA for C(3). The average phenyl C—C bond length of 1.390 (4) \AA is normal.

The bond length C(1)—C(7) [1.476 (3) \AA] shows the influence of conjugation between the C(1)—C(6) phenyl ring and the C(7)—N(1) double bond. The torsion angle C(2)—C(1)—C(7)—N(1) is -5.5 (3) $^\circ$.

The distribution of bond lengths in the thiosemicarbazone fragment indicates delocalization of the π electrons. However, it is not altogether planar; maximum deviations from the plane are 0.481 (4) and 0.438 (4) \AA for N(3) and C(9), respectively. The thiosemicarbazone fragment forms a dihedral angle of 22.2 (4) $^\circ$ with the salicylidene group.

The thioureide group exhibits a high degree of electron delocalization. The C—S distance of 1.692 (2) \AA is similar to that found in thiourea [1.72 (1) \AA ; Truter, 1967] and in most of the thiosemicarbazides and thiosemicarbazones reported (Palenik, Rendle & Carter, 1974; Nandi, Chaudhuri, Mazumdar & Ghosh, 1984; Soriano-García, Valdés-Martínez, Toscano, Gómez-Lara & Villalobos-Peñaloza, 1986).

The crystal structure contains both intra- and intermolecular hydrogen bonds which play an important role in the stabilization. Fig. 2 shows the hydrogen-bond scheme and crystal packing. The conformation of the thiosemicarbazone fragment orients the imino N atom in such a way that an intramolecular hydrogen bond is formed from N(1) to the O(1)—H hydroxyl group of the salicylidene part of the molecule, resulting in the formation of a planar six-membered ring. The O(1)---N(1) and H(1)---N(1)

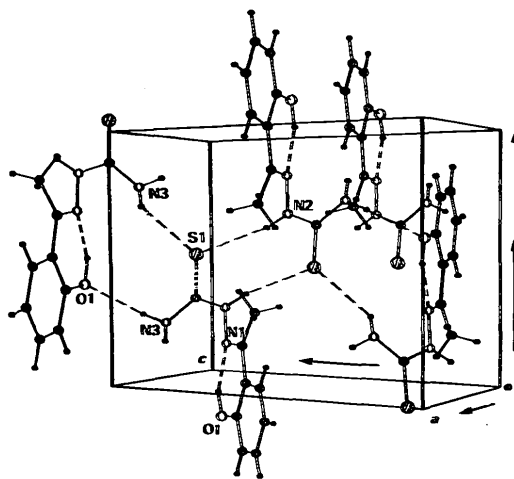


Fig. 2. A perspective drawing of the packing arrangement. The dashed lines indicate the intra- and intermolecular hydrogen bonds.

distances are 2.557 (3) and 1.75 (3) Å and the O(1)—H(1)—N(1) angle is 147 (3)°. In addition, there are three polar H atoms on the thiosemicarbazone fragment, one on N(2) and the other two on N(3) that participate in the hydrogen-bond scheme. The distances and angles are: N(2)...S(1) 3.406 (2), H(2)...S(1) 2.56 (1) Å; 167 (1)° (2-x, 1-y, 1-z); N(3)...O(1) 3.064 (3), H(3A)...O(1) 2.24 (1) Å; 151 (1)° (2.5-x, 0.5+y, 1.5-z); N(3)...S(1) 3.408 (2), H(3B)...S(1) 2.75 (1) Å; 142 (1)° (2.5-x, -0.5+y, 1.5-z). Similar intramolecular hydrogen bonds have been observed in some thiosemicarbazides and thiosemicarbazones (Andretti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970; Restivo & Palenik, 1970; Nandi, Chaudhuri, Mazumdar & Ghosh, 1984).

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Structure of *sym*-C₂F₄Br₂

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Abstract. The structure of 1,2-dibromo-1,1,2,2-tetrafluoroethane is shown to be stable down to low temperatures. $M_r = 259.84$, monoclinic, $P2_1/c$, $Z = 2$. At $T = 100$ K, $a = 5.963$ (5), $b = 6.252$ (5), $c = 8.656$ (8) Å, $\beta = 114.64$ (5)°, $V = 293.3$ (4) Å³, $D_x = 2.94$ Mg m⁻³. At $T = 4.2$ K, $a = 5.934$ (5), $b = 6.190$ (5), $c = 8.460$ (8) Å, $\beta = 114.36$ (5)°, $V = 283.1$ (4) Å³, $D_x = 3.05$ Mg m⁻³. The technique of powder neutron diffraction ($\lambda = 2.2018$ Å) followed by constrained refinement was used, achieving R factors

for the two temperatures of 15.4% and 13.4%. Refinements result in a structure close to that obtained by packing calculations. The structure is not that of a plastic crystal but has features very similar to the disordered structure of 1,2-dichloroethane.

Introduction. Some substituted ethanes have interesting phase transitions, and we undertook the present study to investigate the phase structure of 1,2-dibromo-1,1,2,2-tetrafluoroethane (*sym*-C₂F₄Br₂). Spectroscopic and acoustic studies on the internal rotation in the liquid material (Crook, Park & Wyn-Jones, 1969) have shown that, owing to the repulsion of the large Br

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