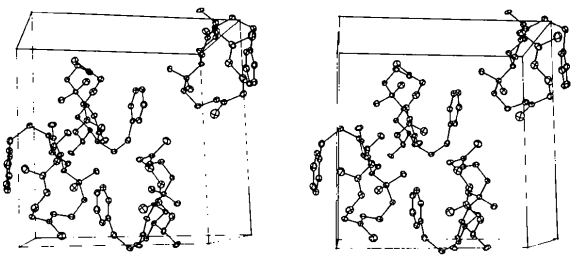

Fig. 2. The molecular packing viewed approximately along the *a* axis.

The Cremer–Pople (1975) puckering parameters for the pyran ring are: $q_2 = 0{\cdot}427$, $q_3 = 0{\cdot}316$ Å, $\varphi_2 = 239°$, $Q = 0{\cdot}531$ Å, $\theta = 53{\cdot}5°$. The torsion angles around the single bonds 6–7, 8–9, 10–11 and 12–13 flanking the double bonds in the 14-membered ring, which are of interest in relation to unsaturated-fatty-acid conformations, are 108·7 (6), 117·7 (6), −114·5 (7) and −117·7 (7)°, respectively.

The packing diagram is shown in Fig. 2. Intermolecular contacts are normal. Both hydroxyls form hydrogen bonds to the neighboring molecule related by a twofold screw axis along **a**.

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Structure of 3-Hydroxyimino-2-butanone Thiosemicarbazone, a Tridentate N–S Ligand, $C_5H_{10}N_4OS$

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(*Received* 22 *September* 1983; *accepted* 22 *December* 1983)

Abstract. $M_r = 174{\cdot}23$, monoclinic, $P2_1/c$, $a = 11{\cdot}090$ (3), $b = 12{\cdot}691$ (4), $c = 6{\cdot}112$ (2) Å, $\beta = 104{\cdot}51$ (2)°, $V = 832{\cdot}8$ (5) Å^3, $Z = 4$, $D_m = 1{\cdot}370$, $D_x = 1{\cdot}389$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}335$ mm^{-1}, $F(000) = 368$, $T = 297$ K. Final $R = 0{\cdot}035$ for 1169 observed reflections. The molecule is in the fully extended form. Electron delocalization in the thiosemicarbazide and oxime moieties is observed. In packing, pairs of intermolecular N–H···S hydrogen bonds across centres of symmetry result in dimerization of the molecules. Intramolecular N–H···N hydrogen bonds lend conformational stability to the molecules.

Introduction. Antibacterial, antiviral and even anti-tumour activities have been observed in some N,S donor ligands such as substituted thiosemicarbazides and thiosemicarbazones (Johnson, Joyner & Perry, 1952; French & Blanz, 1965, 1966; Bauer, 1972; William, 1972). These activities are, in general, attributed to their ability to form metal chelates (Sorkin, Roth & Erlenmeyer, 1952; Cymerman, Willis, Rubbo & Edgar, 1955; Kirschner, Wei, Francis & Bergman, 1966) and their reductive capacities (Palenik, Rendle & Carter, 1974).

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0108-2701/84/071193-04$01.50

The crystal-structure analysis of the tridentate ligand, 3-hydroxyimino-2-butanone thiosemicarbazone, an antibacterial and antiviral agent (Ray, 1981), has been carried out to study the molecular geometry, the forces stabilizing the molecules and also to examine the conformational differences between the ligand and its Co^{III} complex (Gerasimov, Biyushkin, Belichuk & Belov, 1979) with the ultimate aim of understanding its biological activity.

Experimental. Colourless transparent crystals (from ethanol), symmetry from oscillation and Weissenberg photographs, $P2_1/c$ ($0k0$, k odd and $h0l$, l odd), crystal size: 0·40 × 0·20 × 0·12 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$; accurate cell parameters from 25 high-angle ($15 \le \theta \le 20°$) reflections; 1544 unique reflections measured in the range $2 \le \theta \le 25°$ ($-13 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 7$), 1169 reflections with $I \ge 3\sigma(I)$, corrected for variation in intensity (<3%) of the standard reflections (631, 09$\bar{1}$, 0,10,0) monitored every hour of X-ray exposure, intensity corrected for Lp, absorption ignored; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); a scale factor, atomic coordinates for all atoms, isotropic thermal parameters for H atoms and anisotropic thermal parameters of non-H atoms refined by full-matrix least squares based on F (*ORFLS*, Busing, Martin & Levy, 1962), H (from ΔF synthesis) isotropic, $R = 0{\cdot}035$, $R_w = 0{\cdot}049$, $S = 1{\cdot}861$, $w = 1/\sigma^2(|F_o|)$ based on counting statistics, shift/error <0·01, peak heights from −0·189 to 0·221 e Å^{-3} in final ΔF synthesis, scattering factors: non-H from Cromer & Waber (1965), H from Stewart, Davidson & Simpson (1965), anomalous-dispersion correction for all non-H atoms from *International Tables for X-ray Crystallography* (1974).

Discussion. The atom numbering is shown in Fig. 1. The final atomic coordinates are listed in Table 1.* The intramolecular bond distances and angles are listed in Table 2. Fig. 2 shows the packing of the molecules projected on the *ab* plane together with the hydrogen-bonding scheme.

The C—S distance of 1·683 (2) Å is in the lower extreme of the range 1·687 to 1·706 Å found for this bond in most of the thiosemicarbazides and thiosemicarbazones reported (Palenik *et al.*, 1974). The significant shortening from the normal S—C(sp^2) single-bond distance, 1·747 (7) Å (Uechi & Oniki, 1982), as well as the presence of a strong band around 730 cm^{-1} in the

* Lists of structure factors, anisotropic thermal parameters, details of least-squares planes and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39225 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and thermal parameters with e.s.d.'s in parentheses [the equivalent isotropic temperature factors B_{eq} (Hamilton, 1959) for non-H atoms and isotropic temperature factors B for H atoms]*

	x	y	z	B_{eq}/B(Å^2)
S	0·05750 (5)	0·65650 (5)	0·17347 (8)	4·12
O	0·4540 (2)	0·3860 (1)	1·4044 (2)	4·91
N(1)	0·0973 (2)	0·4605 (1)	0·3251 (3)	3·98
N(2)	0·1888 (1)	0·5894 (1)	0·5693 (2)	3·40
N(3)	0·2329 (1)	0·5115 (1)	0·7248 (3)	3·13
N(4)	0·4180 (2)	0·4749 (1)	1·2645 (3)	3·48
C(1)	0·1156 (2)	0·5617 (2)	0·3633 (3)	3·15
C(2)	0·3050 (2)	0·5391 (1)	0·9157 (3)	2·82
C(3)	0·3460 (2)	0·4504 (2)	1·0728 (3)	2·93
C(4)	0·3478 (2)	0·6490 (2)	0·9807 (4)	3·93
C(5)	0·3032 (2)	0·3412 (2)	1·0049 (4)	4·70
H(N1)1	0·051 (2)	0·434 (2)	0·203 (3)	4·6 (5)
H(N1)2	0·119 (2)	0·420 (2)	0·417 (4)	5·3 (5)
H(N2)	0·191 (2)	0·655 (2)	0·614 (4)	4·9 (5)
H(C4)1	0·290 (3)	0·690 (2)	0·995 (5)	8·6 (8)
H(C4)2	0·395 (3)	0·681 (3)	0·874 (5)	9·8 (9)
H(C4)3	0·409 (3)	0·651 (2)	1·127 (5)	8·6 (8)
H(C5)1	0·356 (2)	0·299 (2)	1·007 (5)	7·7 (7)
H(C5)2	0·230 (3)	0·338 (3)	0·876 (5)	9·6 (9)
H(C5)3	0·259 (4)	0·315 (4)	1·101 (6)	13·9 (13)
H(O)	0·498 (3)	0·422 (3)	1·540 (5)	9·2 (8)

Table 2. *Bond lengths* (Å) *and angles* (°) *in 3-hydroxyimino-2-butanone thiosemicarbazone*

N(1)–C(1)	1·312 (3)	N(1)–H(N1)1	0·86 (2)
C(1)–S	1·683 (2)	N(1)–H(N1)2	0·75 (2)
C(1)–N(2)	1·362 (2)	N(2)–H(N2)	0·87 (3)
N(2)–N(3)	1·374 (2)	C(4)–H(C4)1	0·85 (3)
N(3)–C(2)	1·287 (2)	C(4)–H(C4)2	1·02 (3)
C(2)–C(4)	1·495 (3)	C(4)–H(C4)3	0·98 (3)
C(2)–C(3)	1·476 (3)	C(5)–H(C5)1	0·79 (2)
C(3)–C(5)	1·490 (3)	C(5)–H(C5)2	0·98 (3)
C(3)–N(4)	1·280 (3)	C(5)–H(C5)3	0·92 (4)
N(4)–O	1·411 (2)	O–H(O)	0·96 (3)

N(1)–C(1)–S	124·2 (2)	N(3)–N(2)–H(N2)	119 (2)
N(1)–C(1)–N(2)	116·5 (2)	N(4)–O–H(O)	98 (2)
N(2)–C(1)–S	119·3 (2)	C(2)–C(4)–H(C4)1	114 (2)
C(1)–N(2)–N(3)	118·7 (1)	C(2)–C(4)–H(C4)2	112 (2)
N(2)–N(3)–C(2)	117·6 (1)	C(2)–C(4)–H(C4)3	112 (2)
N(3)–C(2)–C(4)	125·4 (2)	H(C4)1–C(4)–H(C4)2	110 (3)
N(3)–C(2)–C(3)	113·7 (2)	H(C4)1–C(4)–H(C4)3	105 (3)
C(2)–C(3)–C(5)	120·2 (2)	H(C4)2–C(4)–H(C4)3	103 (3)
C(2)–C(3)–N(4)	115·5 (2)	C(3)–C(5)–H(C5)1	116 (2)
C(3)–N(4)–O	112·2 (2)	C(3)–C(5)–H(C5)2	114 (3)
C(1)–N(1)–H(N1)1	125 (1)	C(3)–C(5)–H(C5)3	110 (3)
C(1)–N(1)–H(N1)2	122 (1)	H(C5)1–C(5)–H(C5)2	116 (3)
H(N1)1–N(1)–H(N1)2	113 (2)	H(C5)1–C(5)–H(C5)3	105 (3)
C(1)–N(2)–H(N2)	120 (2)	H(C5)2–C(5)–H(C5)3	92 (4)

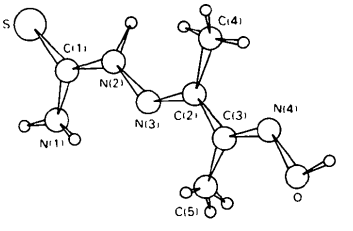
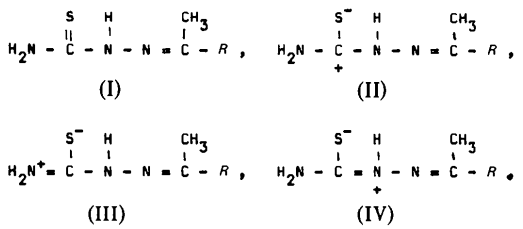


Fig. 1. Atomic-numbering scheme with perspective view of the molecule down the *a* axis.

IR spectrum confirms the existence of the thiocarbonyl (keto) form of the ligand (Bellamy, 1975). The C–S distance is, however, longer than the normal S–C(sp^2) double-bond distance of 1·59 Å (Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969). The C–S bond, therefore, possesses partial double-bond character in agreement with the following canonical structures [where $R = -C(CH_3)=N-OH$], similar to the earlier reported canonical forms (Restivo & Palenik, 1970).



(I) (II)

(III) (IV)

The C(2)–N(3) bond should therefore be a double bond; this is in agreement with the value of 1·287 (2) Å found in this study. The C(1)–N(2) and C(1)–N(1) bond distances of 1·362 (2) and 1·312 (3) Å respectively are indicative of some double-bond character for these bonds and are in agreement with the above resonance forms, among which the minimum contribution is from (II). The C(3)–N(4) distance of 1·280 (3) Å indicates a double-bond character. Although shortening of N(2)–N(3) to 1·374 (2) Å is similar to 1·372 Å (Gabe, Taylor, Glusker, Menken & Patterson, 1969), 1·374 Å (Mathew & Palenik, 1971) and 1·365 (3) Å (Restivo & Palenik, 1970), an N–N distance of 1·411 (2) Å in the thiosemicarbazide indicates the possibilities of other canonical forms also. Shortening of the N–N distances in thiosemicarbazones may be attributed to the effect of implantation of additional conjugated double bonds which promotes electron delocalization throughout the new and extended conjugated system. In the present case condensation of thiosemicarbazide with 2,3-butanedione monoxime results in two conjugated double bonds, C(2)=N(3) and C(3)=N(4). Thus in this system the introduction of two additional conjugated double bonds renders the molecule a much more effective donor than thiosemicarbazide as is evident from the greater stability of the metal complexes of this ligand compared to the stability of the corresponding metal complexes of thiosemicarbazide (Ray, 1981).

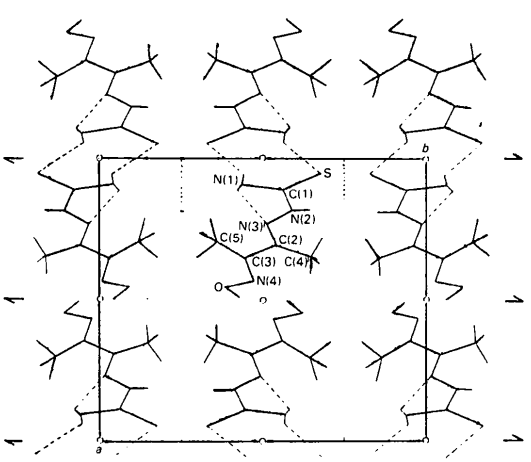


Fig. 2. Molecular packing of 3-hydroxyimino-2-butanone thiosemicarbazone; hydrogen bondings are shown by dotted lines.

The S–C(1)–N(2)–N(3) torsion angle of 178·3 (1)° and the N(3)–C(2)–C(3)–N(4) torsion angle of 179·9 (2)° indicate the *trans* conformation of the free ligand. The torsion angles C(1)–N(2)–N(3)–C(2) = 177·9 (2), N(2)–N(3)–C(2)–C(3) = 179·1 (1) and C(2)–C(3)–N(4)–O = −179·5 (2)° show that the molecular conformation is fully extended.

Of the four available H atoms the hydrogen attached to N(2) is involved in an intermolecular hydrogen-bond-like contact [N(2)–H(N2) = 0·87 (3), N(2)···S = 3·659 (1), H(N2)···S = 2·88 (2) Å] with a glide-related sulphur. An N(1)–H···N(3) intramolecular hydrogen bond appears to stabilize the molecular conformation of the thiosemicarbazide moiety. Similar intramolecular hydrogen bonds have been observed in some thiosemicarbazides and thiosemicarbazones (Andreetti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970; Restivo & Palenik, 1970). Pairs of N(1)–H(N1)···S hydrogen bonds across centres of inversion result in hydrogen-bonded dimers of the 3-hydroxyimino-2-butanone thiosemicarbazone molecule. Such dimerization has also been observed in other similar compounds (Palenik *et al.*, 1974; Restivo & Palenik, 1970; Mathew & Palenik, 1971; Naik & Palenik, 1974; Brown & Agrawal, 1978). The details of the hydrogen-bond geometries (Å and deg) are as follows:

A–H···B	d_{A-H}	$d_{A\cdots B}$	$d_{H\cdots B}$	∠A–H···B
N(1)–H(N1)1···S^{i}	0·86 (2)	3·437 (2)	2·58 (2)	171 (2)
N(1)–H(N1)2···N(3)	0·75 (2)	2·609 (2)	2·30 (2)	106 (2)

Symmetry code: (i) $-x, 1-y, -z$.

Thus the typical dimerization through intermolecular hydrogen bonding lends extra stability to the *trans* configuration of the molecule.

The S atom assumes the *trans* configuration with respect to the hydrazinic $-NH_2$ group, N(3), in 3-hydroxyimino-2-butanone thiosemicarbazone (Fig. 1) while on chelation with Co^{III} (Gerasimov *et al.*, 1979) it assumes the *cis* configuration. The *trans* configuration of S is the only configuration observed in uncomplexed thiosemicarbazones (Palenik *et al.*, 1974). This happens because of the flexibility of the thiosemicarbazide and its derivatives in assuming a *cis* or *trans* configuration for sulphur and hydrazinic $-NH_2$ with respect to the C–NH bond, and this has been put in evidence as a general rule (Fava Gasparri, Mangia, Musatti & Nardelli, 1968). The conformation, S *trans* to N(3), places N(1) *cis* to N(3) and in the favourable

orientation for intramolecular hydrogen bonding to N(3). Similar conformations are observed in 4-phenylthiosemicarbazide (Kálmán, Argay & Czugler, 1972) and in thiosemicarbazide (Andreetti *et al.*, 1970; Domiano *et al.*, 1969).

The overall conformation of the molecule is such that for it to act as a tridentate ligand, two major changes must occur before the ligand will be in the proper orientation; first, there must be a 180° rotation about the C(2)–C(3) bond to make N(4) *cis* to N(3) to facilitate the formation of a five-membered chelate ring with a metal ion and, secondly, there must be a 180° rotation about the C(1)–N(2) bond to switch the position of S so that it participates in a second five-membered chelate ring with the metal ion and N(3). The rotations around C(1)–N(2) and C(2)–C(3), in the presence of a metal ion, are caused at the expense of chelation or packing and hydrogen-bonding energy, orienting S and N(4) in the *cis* configuration; this is an ideal geometry for tridentate ligands favouring metal chelation.

It is now established that the biological activity of thiosemicarbazides and thiosemicarbazones is centred around the S atom and that the activity of the thiosemicarbazones is also dependent on the parent carbonyl compound (Libermann, Rist, Grumbach, Moyeux, Gauthier, Rouaix, Maillard, Himbert & Cals, 1954). In the present case the parent carbonyl compound, 2,3-butanedione monoxime, contains an oxime moiety ($\geq$C=N–OH) and it has been shown recently that the introduction of an oxime moiety into an active molecule results in significant enhancement of its antibacterial activity (Ghosh, Bandyopadhyay, Ray & Mitra, 1983). The presence of this oxime moiety in a strategic position along with the hydrazinic nitrogen, N(3), and the S atom makes the ligand a much more powerful metal-chelating agent, compared to either thiosemicarbazide or 2,3-butanedione monoxime (Ablóv & Bleichuk, 1962, 1963*a*,*b*,*c*; Ray, 1981), towards metal ions and thereby enhances its biological activity. Of the two five-membered chelate rings that the ligand makes when chelated to a metal ion (Gerasimov *et al.*, 1979), the ring containing the larger S atom has comparatively less angle strain and this lends some extra stability to the metal-complex molecule as a whole. In addition to this, the presence of the soft donor S atom increases the versatility of the ligand by inducing in it a capacity for complexing soft acceptor metal ions. All these factors reinforce each other and render the ligand an efficient scavenger of metal ions present in the bacteria.

The authors thank Dr P. K. Ray of the Indian Association for the Cultivation of Science, Inorganic Chemistry Division, for preparing the compound.

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