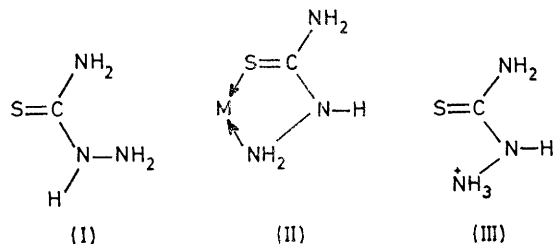


## Crystal and Molecular Structure of Thiosemicarbazide Hydrochloride

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Crystals of the title compound are orthorhombic with  $a = 11.116(11)$ ,  $b = 12.043(9)$ ,  $c = 7.646(5)$  Å, space group  $Pbca$ ,  $Z = 8$ . The structure was solved from three-dimensional diffractometer data by Patterson and Fourier methods and refined by block-diagonal least-squares to  $R$  0.029 for 1029 observed reflections. The structure consists of protonated cations in the *cis*-conformation, *i.e.* with the  $-\text{NH}-\text{NH}_2$  group bent towards the  $\text{C}=\text{S}$  bond, and of chloride anions. Packing is determined by hydrogen-bonds formed by the  $-\text{NH}_2^+$ ,  $-\text{NH}_2$ , and  $>\text{NH}$  groups with  $\text{Cl}^-$  and  $\text{S}$ .

THE crystal structure analysis of thiosemicarbazide hydrochloride has been carried out as part of a study of effects responsible for the different conformations the molecules of this class of organic derivatives can assume in different chemical situations. In fact it is found that thiosemicarbazide in the crystalline state, when the molecule is in the unprotonated free state, assumes the *trans*-conformation (I), while when it acts as a chelating



ligand it takes on the *cis*-conformation (II). The present study shows that the same *cis*-conformation (III) is assumed when the molecule is protonated on the terminal hydrazine  $-\text{NH}_2$  group. An acceptable explanation of this behaviour cannot be given in terms of pure steric effects alone, since in all these cases the terminal hydrazine group is tetrahedral (taking into account the lone pair in the case of the free molecule) so there would be no intermolecular hindrance in the case of the free thiosemicarbazide crystals even if a *cis*-conformation were present. The *trans*-conformation found for it was justified<sup>1</sup> by the existence of hydrogen bonds formed by the  $-\text{NH}_2$  groups of two molecules related by a centre of symmetry. The chelating effect can justify the existence of the *cis*-structure (II), while the *cis*-structure (III) is probably a consequence of interactions between anions and neighbouring sulphur atoms on the  $-\text{NH}_3^+$  group.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

<sup>1</sup> G. D. Andreotti, P. Domiano, G. Fava Gasparri, M. Nardelli, and P. Sgarabotto, *Acta Cryst.*, 1970, **B26**, 1005.

<sup>2</sup> D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

### EXPERIMENTAL

**Preparation.**—The compound was obtained as colourless crystals by evaporation of a hydrochloric acid solution of thiosemicarbazide.

**Crystal Data.**— $\text{CH}_6\text{ClN}_3\text{S}$ ,  $M = 127.60$ . Orthorhombic,  $a = 11.116(11)$ ,  $b = 12.043(9)$ ,  $c = 7.646(5)$  Å,  $U = 1023.5$  Å<sup>3</sup>,  $D_c = 1.66$  g cm<sup>-3</sup>,  $Z = 8$ ,  $F(000) = 528$ . Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-}K_\alpha) = 9.84$  cm<sup>-1</sup>. Space group  $Pbca$  from systematic absences.

Unit-cell parameters were determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer.

**Intensity Data.**—Intensity data were collected on a single-crystal automated Siemens diffractometer, on-line with a Siemens 304/P computer, by use of Zr-filtered Mo- $K_\alpha$  radiation and the  $\omega$ - $2\theta$  scan technique. A prism of dimensions *ca.* 0.130, 0.110, 0.300 mm was aligned with its [001] axis along the  $\phi$  axis of the diffractometer and all reflections with  $2\theta \leq 58^\circ$  were collected. Of 1373 independent reflections, 1029 having  $I \geq 2\sigma(I)$  were considered observed and were used in the analysis. Corrections for Lorentz and polarization factors were made in the usual way. No correction was applied for absorption. The absolute scale-factor and the mean isotropic temperature factor were obtained by Wilson's method.

**Structure Determination and Refinement.**—The structure was solved by three-dimensional Patterson and Fourier methods and refined by block-matrix least-squares, first with isotropic then with anisotropic thermal parameters to  $R$  0.042. At this stage a  $\Delta F$  map showed all the hydrogen atom positions, and when all the atoms were refined,  $R$  was reduced to 0.029. Unit weights for all observed reflections were used in all stages of the refinement. Atomic scattering factors for chlorine, sulphur, nitrogen, and carbon were taken from ref. 2 and for hydrogen from ref. 3. Final atomic co-ordinates are given in Table 1. Thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21784 (8 pp., 1 microfiche).† All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), with programs written by Immirzi.<sup>4</sup>

<sup>3</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

<sup>4</sup> A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

TABLE 1

Fractional atomic co-ordinates ( $\times 10^3$  for H, others  $\times 10^4$ ), with estimated standard deviations in parentheses

	$x/a$	$y/b$	$z/c$
Cl	357(1)	67(1)	7 493(1)
S	1 955(1)	3 050(1)	-495(1)
N(1)	3 036(2)	1 077(2)	-567(3)
N(2)	2 086(2)	692(2)	512(3)
N(3)	4 114(2)	2 481(2)	-1 719(3)
C	3 108(2)	2 180(2)	-950(3)
H(1)	374(3)	69(2)	-50(4)
H(21)	201(3)	113(2)	162(4)
H(22)	235(3)	0(3)	98(4)
H(23)	139(3)	66(2)	-6(4)
H(31)	416(3)	318(2)	-193(4)
H(32)	460(3)	196(2)	-182(4)

## DISCUSSION

Figure 1 shows the relevant part of the structure which consists of  $\text{H}_2\text{N}-\text{CS}-\text{NH}-\text{NH}_3^+$  cations and  $\text{Cl}^-$  anions.

Table 2 gives bond distances and angles in the cation. Comparison of the conformation of the protonated and unprotonated molecules shows that protonation causes a rotation around the C-N (imine) bond giving rise to a *cis*-conformation. This alteration can be accounted for

as a consequence of steric effects: protonation of the terminal hydrazinic nitrogen prevents that peculiar

TABLE 2

Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

(a) Distances			
C-S	1.692(3)	N(2)-H(21)	1.00(3)
C-N(1)	1.363(4)	N(2)-H(22)	0.95(4)
C-N(3)	1.314(3)	N(2)-H(23)	0.89(3)
N(1)-N(2)	1.418(3)	N(3)-H(31)	0.86(2)
N(1)-H(1)	0.91(3)	N(3)-H(32)	0.83(3)
(b) Angles			
S-C-N(1)	121.0(2)	N(1)-N(2)-H(23)	112(2)
S-C-N(3)	124.5(2)	H(21)-N(2)-H(22)	100(2)
N(1)-C-N(3)	114.5(2)	H(21)-N(2)-H(23)	111(3)
C-N(1)-N(2)	119.2(2)	H(22)-N(2)-H(23)	114(3)
C-N(1)-H(1)	117(2)	C-N(3)-H(31)	114(2)
N(2)-N(1)-H(1)	116(2)	C-N(3)-H(32)	113(2)
N(1)-N(2)-H(21)	113(2)	H(31)-N(3)-H(32)	133(3)
N(1)-N(2)-H(22)	106(2)		

intra-intermolecular bifurcated hydrogen bonding observed in the crystals of unprotonated thiosemicarbazide, so there is no longer room for the  $-\text{NH}_3^+$  group: the whole hydrazine part of the molecule therefore must rotate

TABLE 3

Distances and angles of the thiosemicarbazide (tsem) and thiocarbonohydrazide (tcaz) in different crystals

(a) Distances ( $\text{\AA}$ )	C-S	C-N(1)	C-N(3)	N(1)-N(2)	N(3)-N(4)
tsem, HCl <sup>a</sup>	1.692(3)	(c) 1.363(3) <sup>b</sup>	1.314(3)	(c) 1.418(3) <sup>o</sup>	
(tcaz)H <sub>2</sub> Cl <sub>2</sub> , 2H <sub>2</sub> O <sup>d</sup>	1.645(3)	(c) 1.363(5)	(c) 1.363(5)	(c) 1.418(6)	(c) 1.418(6)
tcaz, H <sub>2</sub> SO <sub>4</sub> <sup>e</sup>	1.663(4)	(c) 1.349(4)	(c) 1.338(4)	(c) 1.411(4)	(c) 1.412(4)
(tcaz) <sub>2</sub> HCl <sup>f</sup>	1.694(2)	(c) 1.349(3)	(f) 1.327(3)	(c) 1.416(3)	(f) 1.415(3)
{tcaz	1.705(2)	(f) 1.335(9)	(c) 1.315(11)	(f) 1.407(14)	(c) 1.404(9)
tcaz <sup>g</sup>	1.724(10) <sup>h</sup>	(f) 1.326(2)	1.316(3)	(f) 1.411(2)	
tsem <sup>i</sup>	1.707(2)	(f) 1.326(2)	1.320(6)	(f) 1.412(6)	
tsem <sup>j</sup>	1.701(5)	(f) 1.325(5)	1.320(2)	(f) 1.395(2)	
Phtsem <sup>k</sup>	1.696(2)	(f) 1.330(2)			
(b) Angles ( $^\circ$ )	S-C-N(3)	S-C-N(1)	N(1)-C-N(3)	C-N(1)-N(2)	C-N(3)-N(4)
tsem, HCl <sup>a</sup>	124.5(2)	(c) 121.0(2)	114.5(2)	(c) 119.2(2)	
(tcaz)H <sub>2</sub> Cl <sub>2</sub> , 2H <sub>2</sub> O <sup>d</sup>	(c) 124.4(1)	(c) 124.4(1)	111.1(2)	(c) 117.8(2)	(c) 117.8(2)
tcaz, H <sub>2</sub> SO <sub>4</sub> <sup>e</sup>	(c) 123.3(2)	(c) 123.6(2)	113.1(3)	(c) 118.5(2)	(c) 118.4(2)
(tcaz) <sub>2</sub> HCl <sup>f</sup>	(f) 120.7(1)	(c) 123.4(2)	115.8(2)	(c) 118.9(2)	(f) 120.3(1)
{tcaz	(c) 122.4(2)	(f) 120.1(1)	117.5(2)	(f) 120.6(2)	(c) 121.9(2)
tcaz <sup>g</sup>	(c) 124.2(5)	(f) 118.3(6)	117.5(7)	(f) 118.8(7) <sup>h</sup>	(c) 122.4(7)
tsem <sup>i</sup>	122.0(1)	(f) 119.2(2)	118.8(2)	(f) 121.1(2)	
tsem <sup>j</sup>	122.11(31)	(f) 118.84(33)	118.98(42)	(f) 120.81(37)	
Phtsem <sup>k</sup>	123.5(1)	(f) 120.2(1)	116.3(2)	(f) 120.3(1)	

<sup>a</sup> Present work. <sup>b</sup> (c) groups *cis*, and (t) groups *trans* with respect to S: C. <sup>o</sup> Values in italics are for protonated groups  $\text{NH}-\text{NH}_3^+$ . <sup>d</sup> Ref. 8. <sup>e</sup> Ref. 10. <sup>f</sup> Ref. 9. <sup>g</sup> Ref. 7. <sup>h</sup> Non-diffractometer data. <sup>i</sup> Ref. 1. <sup>j</sup> F. Hansen and R. Grønbaek Hazell, *Acta Chem. Scand.*, 1969, **23**, 1359. <sup>k</sup> M. Czugler, A. Kálmán, and Gy. Argay, *Cryst. Struct. Comm.*, 1973, **2**, 655.

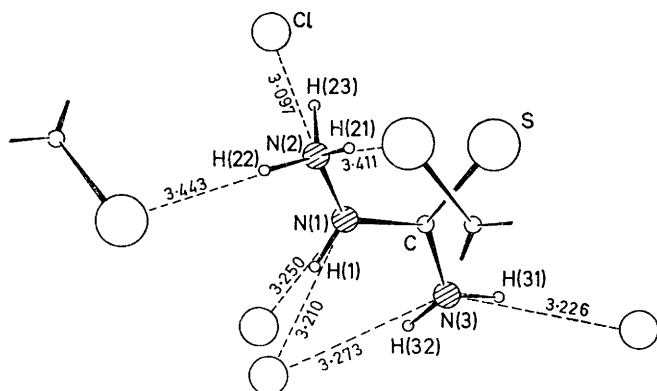


FIGURE 1 Projection of the structure on the (001) plane

around the N-C bond by  $180^\circ$ . This effect has been observed in the cases of carbono-<sup>5,6</sup> and thiocarbonohydrazide.<sup>7-11</sup> Protonation also causes small but significant effects on bond distances producing a shortening

<sup>5</sup> P. Domiano, M. A. Pellinghelli, and A. Tiripicchio, *Acta Cryst.*, 1972, **B28**, 2495.

<sup>6</sup> A. M. Manotti Lanfredi, M. A. Pellinghelli, and A. Tiripicchio, *J.C.S. Perkin II*, 1974, 308.

<sup>7</sup> A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1969, **B25**, 2286.

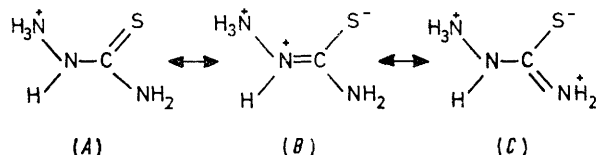
<sup>8</sup> A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 523.

<sup>9</sup> A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *J.C.S. Perkin II*, 1972, 2116.

<sup>10</sup> F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, and A. Tiripicchio, *J.C.S. Perkin II*, 1972, 2121.

<sup>11</sup> A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *J.C.S. Dalton*, 1975, 2168.

of the C-S bond and a lengthening of the C-N (imine) bond, as can be deduced from the data of Table 3. This fact can be explained, on the basis of the VB theory, considering that protonation of the terminal hydrazinic nitrogen reduces the contribution of the canonical structure (B) with respect to that of structure (A).



Comparison of this effect in different protonated molecules shows it to be more important when sulphur is not

TABLE 4

Equation of the best least-squares plane in the form  $AX + BY + CZ = D$  where  $X = x$ ,  $Y = y$  and  $Z = z$  is perpendicular to  $X$ ,  $Y$ . Distances (Å) of relevant atoms from the plane are given in square brackets

Plane: S, C, N(1), N(3)

$$-0.4008X - 0.1834Y - 0.8976Z = -1.2054$$

[S 0.000 5(8), C -0.008 8(23), N(3) 0.004 3(23), N(1) 0.004 0(23), H(31) -0.026(31), H(32) -0.028(31), H(1) -0.270(31), N(2) -0.228 2(23)]

involved in the hydrogen bonding, in agreement with the fact that hydrogen-bonding, inducing a negative charge

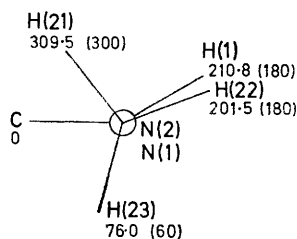


FIGURE 2 Rotation angles ( $^{\circ}$ ) around the N-N bond (calc. angles for gauche conformation in parentheses)

on the sulphur atom, favouring canonical structures (B) and (C).

Analysis of the planarity of the molecule (Table 4) shows that the non-hydrogen atoms of the thioamide part of the molecule are strictly planar, with the hydrogen atoms

attached to amidic nitrogen not significantly out of that plane, although the imine hydrogen and the protonated nitrogen are out of that plane nearly by the same distance on the same side. This indicates that while the  $sp^2$  character of N(3) is preserved, N(1) assumes a little pyramidal character: N(1) is 0.19 Å out of the plane through N(2), H(1), C. The conformation around the N(1)-N(2) bond is nearly gauche (Figure 2).

The structure is built up of a system of hydrogen bonds (Figure 1 and Table 5), three formed by the  $\text{NH}_3^+$  group

TABLE 5

Environment of the protonated thiosemicarbazide cation

(a) Hydrogen bonds

(i) Distances (Å)

N(3) $\cdots$ Cl <sup>II</sup>	3.226(3)	H(23) $\cdots$ Cl <sup>IV</sup>	2.31(3)
H(31) $\cdots$ Cl <sup>I</sup>	2.38(3)	N(2) $\cdots$ S <sup>V</sup>	3.443(4)
N(3) $\cdots$ Cl <sup>III</sup>	3.273(3)	H(22) $\cdots$ S <sup>V</sup>	2.72(4)
H(32) $\cdots$ Cl <sup>II</sup>	2.48(3)	N(1) $\cdots$ Cl <sup>III</sup>	3.210(3)
N(2) $\cdots$ S <sup>III</sup>	3.411(3)	H(1) $\cdots$ Cl <sup>II</sup>	2.47(3)
H(21) $\cdots$ S <sup>III</sup>	2.42(3)	N(1) $\cdots$ Cl <sup>VI</sup>	3.250(3)
N(2) $\cdots$ Cl <sup>IV</sup>	3.097(3)	H(1) $\cdots$ Cl <sup>VI</sup>	2.66(3)

(ii) Angles ( $^{\circ}$ )

N(3)-H(31) $\cdots$ Cl <sup>II</sup>	170(3)	H(23)-N(2) $\cdots$ Cl <sup>IV</sup>	24(2)
H(31)-N(3) $\cdots$ Cl <sup>I</sup>	7(2)	N(2)-H(22) $\cdots$ S <sup>V</sup>	133(2)
N(3)-H(32) $\cdots$ Cl <sup>III</sup>	159(3)	H(22)-N(2) $\cdots$ S <sup>V</sup>	35(2)
H(32)-N(3) $\cdots$ Cl <sup>II</sup>	16(2)	N(1)-H(1) $\cdots$ Cl <sup>II</sup>	138(2)
N(2)-H(21) $\cdots$ S <sup>III</sup>	172(2)	H(1)-N(1) $\cdots$ Cl <sup>II</sup>	31(2)
H(21)-N(2) $\cdots$ S <sup>III</sup>	6(2)	N(1)-H(1) $\cdots$ Cl <sup>VI</sup>	123(2)
N(2)-H(23) $\cdots$ Cl <sup>IV</sup>	148(3)	H(1)-N(1) $\cdots$ Cl <sup>VI</sup>	43(2)

(b) Shortest intermolecular distances (Å)

N(2) $\cdots$ Cl <sup>VI</sup>	3.348(4)	N(3) $\cdots$ S <sup>VIII</sup>	3.640(4)
N(2) $\cdots$ Cl <sup>VII</sup>	3.246(3)	N(1) $\cdots$ S <sup>IX</sup>	3.646(4)
N(1) $\cdots$ Cl <sup>IV</sup>	3.542(4)	Cl $\cdots$ S <sup>III</sup>	3.677(2)

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at  $x$ ,  $y$ ,  $z$ :

I $\frac{1}{2} - x, \frac{1}{2} + y, -1 + z$	VI $\frac{1}{2} - x, -y, -\frac{1}{2} + z$
II $\frac{1}{2} + x, y, \frac{1}{2} - z$	VII $-x, -y, 1 - z$
III $x, \frac{1}{2} - y, \frac{1}{2} + z$	VIII $\frac{1}{2} + x, \frac{1}{2} - y, -z$
IV $x, y, -1 + z$	IX $\frac{1}{2} - x, -\frac{1}{2} + y, z$
V $\frac{1}{2} - x, y - \frac{1}{2}, z$	

with a Cl<sup>-</sup> anion and two sulphur atoms, a bifurcated one formed by the imine hydrogen with two Cl<sup>-</sup> anions, and two formed by the amido-group with two Cl<sup>-</sup> anions.

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