Crystal and Molecular Structure of Thiocarbonohydrazide Hemihydrochloride

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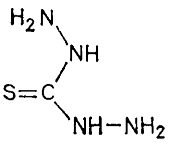
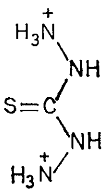
Crystals of the title compound are monoclinic, space group *C*2/*c*, *Z* = 8, unit cell dimensions: *a* = 18·397(12), *b* = 9·039(6), *c* = 13·847(11) Å, and β = 113·4(1)°. Intensities were measured by counter methods and the structure solved by direct methods and refined by least squares to *R* 0·028 for 2111 observed reflections. The basic units of the structure are dimers, $H_2N{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH_2 \ldots H_3\overset{+}{N}{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH_2$, and chloride anions. Both component monomers are in the *cis,trans*-conformation, *i.e.* with one group $\cdot NH\cdot NH_2$ bent toward C–S and the other toward the opposite side. Distances and angles in both thiocarbonohydrazide molecules are as expected, except for some C–S bonds and the angles around the carbon atom. The groups N–CS–N are planar. Internal rotation angles of $-NH_2$ and $-\overset{+}{N}H_3$ groups are discussed.

In connection with studies on compounds of thiocarbonohydrazide (tcaz) in solution [1,2] and in the solid state,[3-5] we have undertaken the study of the crystal structure of the hemihydrochloride, $[SC(NH{\cdot}NH_2)_2]_2,HCl$. The molecule of tcaz can assume the *cis,trans*- (I) or the *cis,cis*-conformation (II). The *cis,trans*-conformation has been found in the neutral molecule [3] and in complexes with metals; [4] the *cis,cis*-conformation has been found in the dihydrochloride, $[SC(NH{\cdot}NH_2)_2],2HCl,\text{-}2H_2O$.[5] The present structural determination has shown that the monoprotonated species also has the *cis,trans*-conformation.



(I)



(II)

EXPERIMENTAL

Hydrochloric acid was added to an aqueous solution of tcaz to pH *ca.* 2·5. On evaporation good transparent crystals of the compound were formed.

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

Crystal Data.—$C_2H_{12}N_8S_2,HCl$, Monoclinic. *M* = 248·766, *a* = 18·397(12), *b* = 9·039(6), *c* = 13·847(11) Å, β = 113·4(1)°, *U* = 2113·2 Å^3, D_c = 1·563, *Z* = 8, D_m = 1·575, *F*(000) = 1040. Space group: *C*2/*c* [$C_{2h}(6)$,N° 15] or *Cc* [$C_s(4)$,N° 9] from systematic absences, the former determined from the structure analysis. Mo-K_α radiation λ = 0·71069 Å; μ(Mo-K_α) = 7·157 cm^{-1}.

Intensity Data.—Intensity data were collected on a single-crystal automated Siemens diffractometer, on line with a Siemens 304 P computer, by using Zr-filtered Mo-K_α radiation and the ω—2θ scan technique. A rather irregular prism of dimensions *ca.* 0·18 × 0·18 × 0·26 mm was aligned with its [010] axis along the φ axis of the diffractometer and all the reflections with 2θ ⩽ 58° were collected. 2810 Independent reflections were measured of which 2111 were used in the crystal analysis, reflections whose intensities were less than twice their standard deviations $\{\sigma^2(I) = [\text{total counts} + (0{\cdot}005\,I)^2]\}$ being considered unobserved. Corrections for Lorentz and polarization factors were made in the usual way. No correction was made for absorption. An absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's [6] method. The normalized structure factors, E_h values were then computed.

Structure Determination and Refinement.—The structure was solved by means of the Σ_2 Sayre relationship in the symbolic addition procedure.[7] The reflections 732 ($|E|$ = 3·06) and $24\bar{1}$ ($|E|$ = 2·72) were chosen to define the origin. Reflections 222 ($|E|$ = 3·73), $62\bar{6}$ ($|E|$ = 3·03), 954 ($|E|$ = 2·82), and $11,11,\bar{2}$ ($|E|$ = 3·36) were assigned the symbols, *a*, *b*, *c*, and *d* respectively. By applying the Σ_2 formula the solution for the symbols came out to be —,—,—,—. The signs of 328 reflections with $|E| \geqslant 1{\cdot}60$ were determined and used to compute an *E* map that revealed the whole structure except for the hydrogen atoms. A structure-factor calculation using atomic parameters obtained from the *E* map gave *R* 0·137, which decreased to 0·085 after seven cycles of block-diagonal least-squares refinement with isotropic temperature factors. Anisotropic temperature factors were introduced and *R* decreased to 0·045 after six cycles. At this stage, a difference-Fourier synthesis made it possible to determine the positions of the hydrogen atoms, which were then included, with isotropic temperature factors, in subsequent refinement. The final *R* was 0·028 (observed reflections only). Unit weights were used for all the reflections in the complete refinement.

The final atomic co-ordinates and thermal parameters are listed in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary publication No. SUP 20482 (15 pp., 1 microfiche).†

Atomic scattering factors for sulphur, chlorine, nitrogen,

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[1] A. Braibanti, E. Leporati, F. Dallavalle, and M. A. Pellinghelli, *Inorg. Chim. Acta*, 1968, **2**, 449.

[2] A. Braibanti, F. Dallavalle, and E. Leporati, *Inorg. Chim. Acta*, 1969, **3**, 459.

[3] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1969, *B*, **25**, 2286.

[4] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 392.

[5] A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 523.

[6] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[7] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, *B*, **26**, 274.

and carbon were taken from ref. 8, and for hydrogen from ref. 9.

All calculations were performed on a CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord–Orientale (Bologna), with the programs written by Immirzi.[10]

TABLE 1

Final fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
Cl(1)	5000	5827(1)	2500
Cl(2)	5000	0540(1)	2500
S(1)	3025(1)	10141(1)	9195(1)
S(2)	3564(1)	4883(1)	4333(1)
N(1)	2684(1)	7921(2)	7816(1)
N(2)	3265(1)	8458(2)	7473(2)
N(3)	1959(1)	8023(2)	8822(1)
N(4)	1564(1)	6707(2)	8336(1)
N(5)	4125(1)	7139(2)	5688(1)
N(6)	3720(1)	6515(2)	6272(1)
N(7)	4566(1)	6987(2)	4377(1)
N(8)	5065(1)	8207(2)	4838(1)
C(1)	2525(1)	8603(2)	8563(1)
C(2)	4123(1)	6406(2)	4838(1)
H(1)	2418(13)	7078(23)	7488(17)
H(2)	3082(14)	9322(27)	7153(18)
H(3)	3764(15)	8670(29)	8107(19)
H(4)	1842(12)	8482(24)	9330(16)
H(5)	1630(14)	5993(27)	8889(18)
H(6)	1025(12)	6896(24)	7964(16)
H(7)	4476(12)	7877(23)	6025(16)
H(8)	4009(12)	5754(23)	6691(15)
H(9)	3589(14)	7276(27)	6655(18)
H(10)	3224(12)	6058(23)	5774(16)
H(11)	4596(13)	6496(26)	3812(17)
H(12)	4962(15)	8925(29)	4389(19)
H(13)	5612(14)	7876(28)	5003(19)

TABLE 2

Thermal parameters (Å^2) * with estimated standard deviations (× 10^2) in parentheses

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	2·66(2)	2·71(2)	2·25(2)	0·00(0)	1·27(2)	0·00(0)
Cl(2)	2·36(2)	2·53(2)	3·03(2)	0·00(0)	0·97(2)	0·00(0)
S(1)	2·46(2)	2·49(2)	3·14(2)	−0·38(1)	1·40(1)	−0·49(2)
S(2)	3·24(2)	2·61(2)	2·52(2)	−0·75(2)	1·20(2)	−0·57(2)
N(1)	3·05(6)	1·88(5)	3·18(6)	−0·12(5)	2·15(5)	−0·05(5)
N(2)	4·64(8)	2·48(6)	5·31(9)	−0·36(6)	4·08(8)	−0·42(6)
N(3)	2·53(6)	2·44(6)	2·81(6)	−0·35(5)	1·58(5)	−0·40(5)
N(4)	2·78(6)	2·29(6)	3·20(6)	−0·47(5)	1·55(5)	−0·30(5)
N(5)	3·29(6)	2·27(6)	2·84(6)	−0·60(5)	2·06(5)	−0·47(5)
N(6)	2·70(6)	2·18(5)	2·72(6)	−0·10(5)	1·69(5)	−0·08(5)
N(7)	3·61(7)	2·69(6)	2·94(6)	−0·58(6)	2·13(6)	−0·48(5)
N(8)	4·54(8)	3·00(7)	4·11(8)	−1·36(7)	2·77(7)	−0·75(6)
C(1)	1·87(5)	1·92(6)	2·24(6)	0·44(5)	0·92(5)	0·31(5)
C(2)	2·22(6)	1·93(6)	2·26(6)	0·27(5)	0·95(5)	0·05(5)
H(1)	3·62(45)					
H(2)	5·53(61)					
H(3)	6·16(65)					
H(4)	4·00(49)					
H(5)	5·17(58)					
H(6)	3·93(48)					
H(7)	3·70(47)					
H(8)	3·46(45)					
H(9)	5·22(59)					
H(10)	3·56(46)					
H(11)	4·56(53)					
H(12)	6·13(65)					
H(13)	5·67(61)					

* $B_{ij} = 8\pi^2 U_{ij}$ referred to *a**, *b**, *c**.

DISCUSSION

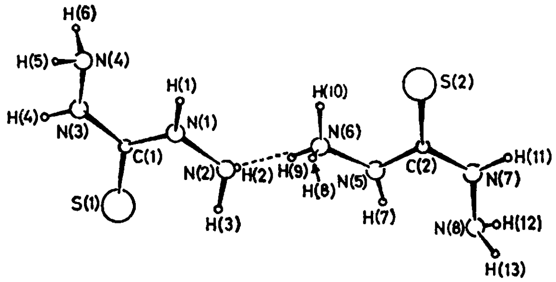

FIGURE 1 The dimer showing the atomic numbering system

TABLE 3

Main interatomic bond distances and angles [a]

(*a*) Distances (Å)

C(1)–S(1)	1·705(2)	C(2)–S(2)	1·694(2)
C(1)–N(1)	1·333(3)	C(2)–N(5)	1·349(2)
C(1)–N(3)	1·336(3)	C(2)–N(7)	1·327(3)
N(1)–N(2)	1·417(3)	N(5)–N(6)	1·416(3)
N(3)–N(4)	1·417(3)	N(7)–N(8)	1·415(3)
N(1)–H(1)	0·92(2)	N(5)–H(7)	0·92(2)
N(2)–H(2)	0·90(2)	N(6)–H(8)	0·92(2)
N(2)–H(3)	1·00(3)	N(6)–H(9)	0·96(2)
N(3)–H(4)	0·91(2)	N(6)–H(10)	0·99(2)
N(4)–H(5)	0·97(2)	N(7)–H(11)	0·92(2)
N(4)–H(6)	0·93(2)	N(8)–H(12)	0·87(3)
		N(8)–H(13)	0·99(3)

(*b*) Angles (deg.)

S(1)–C(1)–N(3)	120·1(1)	S(2)–C(2)–N(7)	120·7(1)
S(1)–C(1)–N(1)	122·4(2)	S(2)–C(2)–N(5)	123·4(2)
N(3)–C(1)–N(1)	117·5(2)	N(7)–C(2)–N(5)	115·8(2)
C(1)–N(1)–N(2)	121·9(2)	C(2)–N(5)–N(6)	118·9(2)
C(1)–N(3)–N(4)	120·6(2)	C(2)–N(7)–N(8)	120·3(1)
C(1)–N(3)–H(4)	118·4(14)	C(2)–N(7)–H(11)	118·3(15)
H(4)–N(3)–N(4)	120·9(14)	H(11)–N(7)–N(8)	120·8(16)
N(3)–N(4)–H(5)	107·7(14)	N(7)–N(8)–H(12)	110·0(17)
H(5)–N(4)–H(6)	109·2(21)	H(12)–N(8)–H(13)	111·2(16)
N(3)–N(4)–H(6)	109·9(13)	N(7)–N(8)–H(13)	106·7(15)
C(1)–N(1)–H(1)	121·8(15)	C(2)–N(5)–H(7)	124·0(14)
H(1)–N(1)–N(2)	116·2(15)	N(6)–N(5)–H(7)	115·0(14)
H(3)–N(2)–N(1)	108·8(16)	N(5)–N(6)–H(10)	108·5(13)
H(3)–N(2)–H(2)	107·4(22)	H(10)–N(6)–H(9)	108·7(20)
H(2)–N(2)–N(1)	106·2(18)	H(8)–N(6)–N(5)	110·8(14)
		H(9)–N(6)–H(8)	113·4(19)
		N(5)–N(6)–H(9)	109·6(15)
		H(8)–N(6)–H(10)	105·6(18)

[a] The estimated standard deviations in parentheses in this and the following Tables are in units of the last digit.

The basic units of the crystal structure are dimers, $H_2N\cdot NH\cdot CS\cdot NH\cdot NH_2 \ldots H_3\overset{+}{N}\cdot NH\cdot CS\cdot NH\cdot NH_2$ and chloride anions. The two molecules of the dimer (Figure 1) are held together by the hydrogen bond [N(6)–H(9) · · · N(2) 2·767(3) Å] which is short compared with normal values for hydrogen bonds between nitrogen atoms. Both molecules of tcaz are in the *cis,trans*-conformation. The two molecules are almost identical, although there are small differences in distances and angles (Table 3) which are statistically significant. The bond C(1)–S(1) [1·705(2) Å] in the neutral molecule is only slightly longer than C(2)–S(2) [1·694(2) Å] in the protonated species, but the former is closer to the value in neutral tcaz with C–S 1·724(1) Å,[3] and the latter to that in the biprotonated form [C–S

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A*, **24**, 321.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

1·645(3) Å].[5] The same can be said for the angles N–C–N. The angle N(1)–C(1)–N(3) 117·5(2)° can be compared with N–C–N 117·5(7)° in the neutral molecule,[3] whereas N(5)–C(2)–N(7) [115·8(2)°] in the monoprotonated species is closer to N–C–N [111·1(2)°] in the diprotonated *cis,cis*-species.[5] The small differences in the C–N bonds could also be dependent upon the changing of the single–double-bond character of the C–S bond. This means that a small redistribution of the electron cloud occurs over the conjugate system of the two thioureide groups, N–CS–N. The N–N bonds [1·417(2), 1·417(3), 1·416(3), 1·415(3) Å, mean 1·416(3) Å] of the hydrazinic groups are equal, and seem to be unaffected in tcaz by the presence of the proton; their values are comparable with those [1·418(6) Å] in the diprotonated species [5] and [1·404(9) and 1·405(14) Å] in the neutral molecule.[3]

TABLE 4

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

Plane (1):

N(1), C(1), S(1), N(3) $-0{\cdot}4396X + 0{\cdot}5747Y - 0{\cdot}6903Z = 3{\cdot}0209$

[N(1) −0·0023(16), C(1) 0·0058(16), S(1) −0·0013(13), N(3) −0·0022(16), H(1) −0·017(22), H(2) 0·008(22), N(2) 0·0247(22), N(4) −0·0575(16)]

Plane (2):

N(5), C(2), S(2), N(7) $-0{\cdot}5994X + 0{\cdot}5725Y - 0{\cdot}5801Z = -3{\cdot}0893$

[N(5) 0·0060(17), C(2) −0·0155(17), S(2) 0·0036(14), N(7) 0·0059(17), H(7) −0·127(22), H(11) −0·044(24), N(6) −0·1297(17), N(8) −0·0876(17)]

TABLE 5

Torsion angles of hydrazinic groups

(i) Group $-N(1)H-N(2)H_2$ (*cis*)

	Plane	Rotation ϕ/deg.
(*a*)	C(1), N(1), N(2)	0
(*b*)	N(1), N(2), H(3)	48·68
(*c*)	H(1), N(1), N(2)	180·64
(*d*)	N(1), N(2), H(2)	293·32
(*e*)	N(1), N(2), lone pair	171·00

Group $-N(3)H-N(4)H_2$ (*trans*)

	Plane	Rotation ϕ/deg.
(*a*)	C(1), N(3), N(4)	0
(*b*)	N(3), N(4), H(5)	123·37
(*c*)	H(4), N(3), N(4)	178·48
(*d*)	N(3), N(4), H(6)	242·23
(*e*)	N(3), N(4), lone pair	362·79

Rotation from + synclinal conformation/deg.

$\phi_b - 60$	−11·32
$\phi_d - 300$	−6·68
Mean $\Delta\phi$	−9·00

$\phi_b - 300\ (+360)$	180 + 3·37
$\phi_d - 60$	180 + 2·23
Mean $\Delta\phi$	180 + 2·80

Interplanar angles/deg.

(*a*)–(*b*)	48·68
(*a*)–(*d*)	66·68
(*b*)–(*d*)	115·36

(*a*)–(*b*)	123·37
(*b*)–(*d*)	118·86
(*a*)–(*d*)	117·76

(ii) Group $-N(5)H-N(6)H_3$ (*cis*)

	Plane	Rotation ϕ/deg.
(*a*)	C(2), N(5), N(6)	0
(*b*)	N(5), N(6), H(10)	38·71
(*c*)	N(5), N(6), H(9)	157·30
(*d*)	H(7), N(5), N(6)	195·98
(*e*)	N(5), N(6), H(8)	283·22

Group $-N(7)H-N(8)H_2$ (*trans*)

	Plane	Rotation ϕ/deg.
(*a*)	C(2), N(7), N(8)	0
(*b*)	N(7), N(8), H(13)	118·04
(*c*)	H(11), N(7), N(8)	170·83
(*d*)	N(7), N(8), H(12)	234·76
(*e*)	N(7), N(8), lone pair	356·40

Rotation from + synclinal conformation/deg.

$\phi_b - 60$	−21·29
$\phi_c - 180$	−22·70
$\phi_e - 300$	−16·78
Mean $\Delta\phi$	−20·26

$\phi_b - 300\ (+360)$	180 − 1·96
$\phi_d - 60$	180 − 5·24
Mean $\Delta\phi$	180 − 3·60

Interplanar angles/deg.

(*b*)–(*e*)	115·49
(*c*)–(*e*)	125·92
(*b*)–(*c*)	118·59

(*a*)–(*b*)	118·04
(*b*)–(*d*)	116·72
(*a*)–(*d*)	125·24

The thioureide groups N–CS–N are practically planar, confirming conjugation; although the statistical analysis reveals that there are statistically significant deviations, these are actually very small (Table 4). The planarity is confirmed by the sum of the angles around carbon which is 360·0° for C(1) and 359·9° for C(2).

The positions of the hydrogen atoms as deduced from the difference-Fourier map are in accordance with sp^3 hybridization for N(2), N(4), N(6), N(8) and with sp^2 hybridization for N(1), N(3), N(5), N(7).

The torsion angles (Table 5) as calculated from the projection on the plane normal to the N–N axis show (Figure 2) that the *cis*-group $-NH_2$ formed by N(2), H(2), H(3) is in the + synclinal position with respect to and N(8) are in the — synclinal positions. The rotation of $-NH_2$ groups could also be defined by the position of the nitrogen lone-pair as deduced from the bisector of the angle H–N–H. Deviations from the perfectly + synclinal positions are 9° for the *cis*-group N(2), and from the — synclinal position 2·8 and —3·6° for the *trans*-groups N(4) and N(8). The *cis*-group $-\overset{+}{N}H_3$, corresponding to N(6), is rotated *ca.* 20° from the exact + synclinal position with respect to the C–N bond.

Some relevant implications can be inferred from these rotation angles: (i) the $-NH-NH_2$ groups as such in the *cis*- and *trans*-conformations are opposite conformers; they are in fact related to one another not only by 180° rotation around the bond C–N (*cis–trans*) but also by 180° rotation + synclinal to — synclinal around the N–N bond; (ii) in the neutral and chelated[4] species the hydrazinic groups possess equal orientations with respect to C–N but different conformations around N–N, because in complexes the lone pair of the *cis*-group, directed toward the metal atom, is in — synclinal conformation; (iii) the protonated group N(6) tends to bring one hydrogen atom [H(10)] closer to S [S(2) · · · H(10) 2·55 Å] than it would be in an exactly + synclinal conformation [*e.g.* S(1) · · · H(2) 2·96, S(1) · · · H(3) 2·74 Å]; the promixity between S(2) and H(10) could be interpreted as an intramolecular hydrogen bond, but this is not in accordance with the observed shortening of sulphur–carbon bonds in protonated species of tcaz. There may be a possible explanation of (iii) in terms of the field effect of protons on the electrons of the conjugated system $\mathrm{S{-}C}\langle^{\mathrm{NH-}}_{\mathrm{NH-}}$

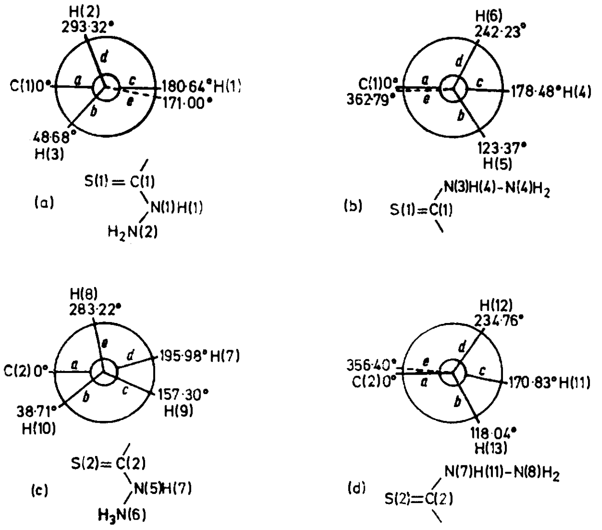

FIGURE 2 Rotation angles of hydrazinic groups $\cdot NH\cdot NH_2$ around N–N; conformations: (a) *cis*, + synclinal, (b) *trans*, — synclinal, (c) *cis*, + synclinal, (d) *trans*, — synclinal

The *trans,trans* species of tcaz are not expected to be stable because of the repulsion between lone pairs of two terminal groups $-NH_2$.

The shortest approach distances (Table 6) between chloride ions and nitrogen atoms are N(5) · · · Cl(2^{III}) 3·175(3), N(6) · · · Cl(1^{III}) 3·121(3), and N(7) · · · Cl(1^{IV}) 3·184(3) Å. These are hydrogen bonds, which are not perfectly linear as shown by the angles N(5)–H(7) · · · Cl(2^{III}) 148(2), N(6)–H(8) · · · Cl(1^{III}) 161(2), and N(7)–H(11) · · · Cl(1^{IV}) 161(2)°. One chlorine atom [Cl(1)] bridges two different dimers (Figure 3) and it appears to be the main interdimer link in the crystal, whereas the other chlorine atom [Cl(2)] is bound to one nitrogen only. Both $\overset{+}{N}H_3$ and NH groups are effective

TABLE 6

Geometry of hydrogen bonds *

(*a*) Distances (Å)	
N(6)–H(9) · · · N(2)	2·767(3)
H(9) · · · N(2)	1·82(3)
N(1)–H(1) · · · S(1^{I})	3·590(3)
H(1) · · · S(1^{I})	2·77(2)
N(3)–H(4) · · · S(2^{II})	3·497(4)
H(4) · · · S(2^{II})	2·59(2)
N(5)–H(7) · · · Cl(2^{III})	3·175(3)
H(7) · · · Cl(2^{III})	2·36(2)
N(6)–H(8) · · · Cl(1^{III})	3·121(3)
H(8) · · · Cl(1^{III})	2·24(2)
N(7)–H(11) · · · Cl(1^{IV})	3·184(3)
H(11) · · · Cl(1^{IV})	2·30(2)
N(6)–H(10) · · · S(1^{I})	3·259(6)
H(10) · · · S(1^{I})	2·46(2)
(*b*) Angles (deg.)	
N(6)–H(9) · · · N(2)	169·8(23)
H(9)–N(6) · · · N(2)	6·7(15)
N(1)–H(1) · · · S(1^{I})	149·2(19)
H(1)–N(1) · · · S(1^{I})	23·2(15)
N(3)–H(4) · · · S(2^{II})	176·1(18)
H(4)–N(3) · · · S(2^{II})	2·9(14)
N(5)–H(7) · · · Cl(2^{III})	147·5(19)
H(7)–N(5) · · · Cl(2^{III})	23·6(14)
N(6)–H(8) · · · Cl(1^{III})	161·0(20)
H(8)–N(6) · · · Cl(1^{III})	13·5(14)
N(7)–H(11) · · · Cl(1^{IV})	161·0(21)
H(11)–N(7) · · · Cl(1^{IV})	13·6(16)
N(6)–H(10) · · · S(1^{I})	137·6(16)
H(10)–N(6) · · · S(1^{I})	30·6(13)

* Roman numerals defined in footnote to Table 7.

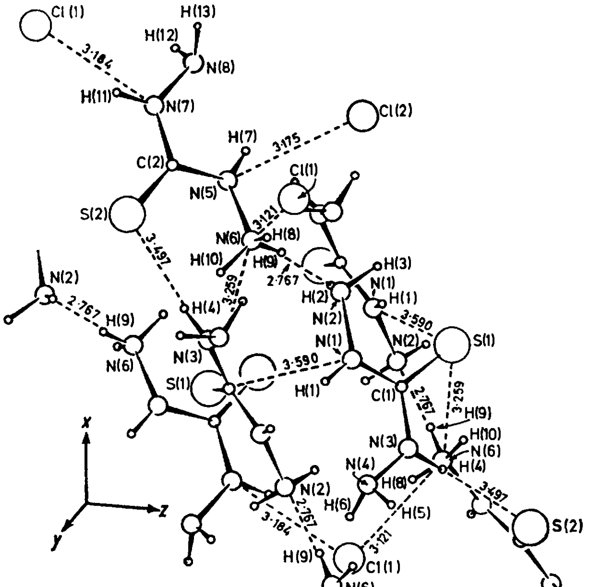

FIGURE 3 Clinographic projection of the structure with intermolecular hydrogen bonds

in these bonds. Apart from the previously mentioned N(6) $\cdots$ N(2) short hydrogen bond, there are no other hydrogen bonds between nitrogen atoms.

Donohue has said [11] that the N $\cdots$ S distance alone is not a sufficient criterion in ascertaining whether such an interaction is a hydrogen bond, the distance H $\cdots$ S and the angles N–N $\cdots$ S also requiring to be taken into account. The interaction N(3) $\cdots$ S(2$^{\text{II}}$) 3·497(4) Å, with H(4) $\cdots$ S(2$^{\text{II}}$) 2·59(2) Å and H(4)–N(3) $\cdots$ S(2$^{\text{II}}$) 3(1)° must therefore be considered a hydrogen bond. Weaker hydrogen bonds could also be considered: N(1) $\cdots$ S(1$^{\text{I}}$) 3·590(3) Å, with H(1) $\cdots$ S(1$^{\text{I}}$) 2·77(2) Å and H(1)–N(1) $\cdots$ S(1$^{\text{I}}$) 23(2)°, and N(6) $\cdots$ S(1$^{\text{I}}$) 3·259(6) Å, with H(10) $\cdots$ S(1$^{\text{I}}$) 2·46(2) Å and H(10)–N(6) $\cdots$ S(1$^{\text{I}}$) 31(1)°. Other contacts (Table 7) between nitrogen and sulphur, though shorter than these, can in no way be considered as hydrogen bonds, a result which supports Donohue's point of view.[11] Generally, each –NH is effective in at least one hydrogen bond, $-\overset{+}{\text{N}}\text{H}_3$ taking part in three, whereas only one $-\text{NH}_2$ group [N(2)] participates, as acceptor, to one hydrogen bond.

TABLE 7

Shortest intermolecular distances (Å)

		N(4) $\cdots$ N2$^{\text{I}}$)	3·203(3)
N(1) $\cdots$ S(2$^{\text{III}}$)	3·280(3)	N(6) $\cdots$ N(3$^{\text{I}}$)	3·378(3)
N(5) $\cdots$ S(1$^{\text{V}}$)	3·330(3)	N(1) $\cdots$ S(2$^{\text{X}}$)	3·555(3)
N(4) $\cdots$ S(2$^{\text{III}}$)	3·671(6)	N(2) $\cdots$ S(2$^{\text{X}}$)	3·625(4)
N(4) $\cdots$ S(1$^{\text{VI}}$)	3·605(4)	N(8) $\cdots$ S(1$^{\text{XI}}$)	3·669(6)
N(8) $\cdots$ S(2$^{\text{VII}}$)	3·631(4)	N(2) $\cdots$ Cl(2$^{\text{VII}}$)	3·304(6)
N(4) $\cdots$ Cl(2$^{\text{VIII}}$)	3·331(4)	N(8) $\cdots$ N(8$^{\text{XII}}$)	3·294(3)
N(3) $\cdots$ Cl(1$^{\text{IX}}$)	3·490(5)	N(3) $\cdots$ N(3$^{\text{VI}}$)	3·216(4)
N(4) $\cdots$ Cl(1$^{\text{IX}}$)	3·456(4)	N(6) $\cdots$ Cl(2$^{\text{III}}$)	3·513(3)

Roman numerals as superscripts refer to the following transformations relative to the reference molecule at *x*, *y*, *z*:

I	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$	VII	$1 - x, 1 - y, 1 - z$
II	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$	VIII	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
III	$x, 1 - y, \frac{1}{2} + z$	IX	$-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$
IV	$1 - x, y, \frac{1}{2} - z$	X	$\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$
V	$x, 2 - y, -\frac{1}{2} + z$	XI	$1 - x, y, \frac{3}{2} - z$
VI	$\frac{1}{2} - x, \frac{3}{2} - y, 2 - z$	XII	$1 - x, 2 - y, 1 - z$

The i.r. spectra of thiocarbonohydrazide, thiosemicarbazide, thiocarbonohydrazide dihydrochloride dihydrate, thiocarbonohydrazide hemihydrochloride, and bis(thiocarbonohydrazide-*N*,*S*)-cadmium dichloride have been taken as KBr discs. The spectra of the pure molecule, thiocarbonohydrazide and thiosemicarbazide, are simpler and with better defined peaks than those of the protonated and complex species. The spectrum of tcaz has been interpreted by Burns,[12] and on the basis of his assignments the peaks can be subdivided into four groups (i) **3310, 3275,** and **3201** cm^{-1} are attributed to the stretching vibrations of NH_2 and NH, (ii) **1638, 1619, 1538,** and **1489** cm^{-1} are attributed to the bending vibrations of NH_2 and NH mixed with some contributions from the stretching vibration, ν(C–N); (iii) **1285** cm^{-1} is attributed to the combined stretching vibrations ν(C–N) and ν(C–S); and (iv) **1011** and **931** cm^{-1} are attributed to the stretching, ν(N–N), mixed with some bending, $\alpha(\widehat{\text{CNN}})$ and stretching, ν(C–S) + ν(C–N), respectively. Group (i) is maintained in the spectra of every compound except in the hydrated dichloride where this group of maxima is confused in broad smooth bands, in accordance with the protonation of the groups themselves and with the presence of water molecules in the structure. In the hemichloride these maxima appear at **3318, 3290,** and **3200** cm^{-1}, which are practically unchanged with respect to the simple molecule. In the group (ii), the two maxima around **1620** cm^{-1} overlap each other, thus forming a broad band at **1612—1590** cm^{-1}, and the two maxima near **1500** cm^{-1} overlap in a second broad band at **1520—1482** cm^{-1}. The whole group (ii) of bands is slightly shifted towards low frequencies. The peak (iii) for tcaz and thiosemicarbazide at **1285** cm^{-1} appears in the hemichloride to be split into three bands at **1345, 1268,** and **1225** cm^{-1}. This is consistent with the finding that the C–S and N–C bond lengths are those distances which are shown by the structure determinations to have been changed. On the basis of the variations of the bond lengths one expects that ν(C–S) is shifted toward higher and ν(C–N) toward lower frequencies than in the simple molecule. According to this interpretation the band at **1345** cm^{-1} could be attributed to ν(C–S), and those at **1268** and **1225** cm^{-1} to ν(C–N). In the group (iv), the band at **1010** cm^{-1} due mainly to ν(N–N) follows the empirical rule [13] that the stretching vibration of the hydrazinic group is shifted toward higher frequencies with respect to the band at **885** cm^{-1} in hydrazine [14] where N–N is **1·46** Å.[15] In the hemichloride there are two bands at **1050** and **978** cm^{-1} which could perhaps be attributable to the stretching vibrations of two different hydrazinic groups, *e.g.* the protonated group could be shifted to higher and the non-protonated ones to lower frequencies than in the simple molecule. They are always higher than the stretching vibration in pure hydrazine.

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