

## Crystal and Molecular Structure of Thiocarbohydrazide

BY A. BRAIBANTI, A. TIRIPICCHIO AND M. TIRIPICCHIO CAMELLINI  
*Istituto di Chimica Generale, Università di Parma, Parma, Italy*

(Received 27 January 1969)

The crystals of thiocarbohydrazide,  $\text{SC}(\text{NH}-\text{NH}_2)_2$ , are monoclinic, space group  $P2_1/c$  with  $a=4.74$  (1),  $b=15.53$  (2),  $c=7.19$  (1) Å,  $\beta=122.4$  (1)°,  $Z=4$ . The structure has been determined from three-dimensional data. One of the two hydrazinic radicals  $\text{H}_2\text{N}-\text{NH}-$  of the molecule is turned toward the sulphur atom. The distances and angles agree very well with those in thiourea and thiosemicarbazide. The thioureide group  $\text{N}-\text{CS}-\text{N}$  is planar; the two  $\text{NH}_2$  groups are out of the plane of the thioureide group and both on the same side. The molecules are held together by weak hydrogen bonds of type  $\text{NH}\cdots\text{N}$  and  $\text{NH}\cdots\text{S}$ .

### Introduction

The study of the structure of thiocarbohydrazide has been undertaken in connection with studies on hydrazine compounds and derivatives and particularly with determinations of the protonation equilibria in aqueous solutions (Braibanti, Leporati, Dallavalle & Pellinghelli, 1968). Thiocarbohydrazide is also capable of forming complexes with bivalent metals (Burns, 1968).

### Experimental

Crystals of the compound were obtained by heating aqueous solutions of hydrazinium hydrazinedithiocarboxylate ( $\text{pH}\sim 8-9$ ). The product was recrystallized from water. The crystals are colourless prisms, m.p.  $168^\circ$ .

#### Crystal data

Compound: thiocarbohydrazide  $(\text{H}_2\text{N}-\text{NH})_2\text{CS}$ ,  
 F.W. 106.1.

Crystal habit: prisms.

Crystal class: monoclinic prismatic.

Unit cell: from rotation and Weissenberg photographs around [100] and [010]; (Cu  $K\alpha$ ,  $\lambda=1.5418$  Å):

$a=4.74$ (1),  $b=15.53$ (2),  $c=7.19$ (1) Å;  $\beta=122.4$ (1)°.  
 $V=446.9$  Å<sup>3</sup>,  $Z=4$ .

$D_m=1.585$ ,  $D_x=1.577$  g.cm<sup>-3</sup>;  $\mu(\text{Cu } K\alpha)=49.8$  cm<sup>-1</sup>.

Space group:  $P2_1/c$  ( $C_{2h}^{(5)}$ , No. 14) from systematic absences.

#### Intensity measurement

Integrated reflexions  $0kl$ ,  $1kl$ , ...  $3kl$  and  $h0l$ ,  $h1l$ , ...  $h11l$  obtained by a Weissenberg camera were measured by a microdensitometer. Absorption corrections were applied as for cylindrical specimens ( $\mu_R[100]=0.75$ ,  $\mu_R[010]=0.80$ ). Structure factors and refinement calculations were performed on the computer Olivetti Elea 6001/S of Centro di Calcolo Elettronico of the University of Parma.

#### Determination and refinement of the structure

The structure was solved by Patterson and Fourier methods and refined by differential syntheses. The hydro-

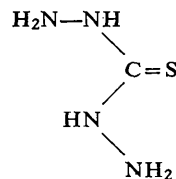
gen atoms were located by difference syntheses and not refined. The hydrogen atoms were introduced before the last cycle of refinement and the  $R$  index dropped from 9.2% to 8.2%, their ratio being 1.122 while the  $R$  factor at the 0.005 level according to Hamilton (1965) is  $R_{24, 1000, 0.005}=1.023$ ; therefore we can suppose the hydrogen atoms to have been properly located. This is confirmed also by the agreement between  $\rho_0$  and  $\rho_c$  at the hydrogen atom positions. The final conventional reliability index was  $R=7.9\%$ . The final results are given in Tables 1-4.

Table 1. Fractional atomic coordinates  
 (with e.d.s.'s  $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
S	0.1657 (6)	0.0970 (1)	0.2296 (3)
N(1)	-0.0098 (18)	0.1922 (2)	0.4648 (11)
N(2)	-0.2064 (19)	0.2455 (2)	0.2816 (12)
N(3)	0.3212 (21)	0.0766 (2)	0.6376 (12)
N(4)	0.2896 (22)	0.0944 (3)	0.8174 (13)
C	0.1537 (19)	0.1253 (3)	0.4570 (12)
H(11)	0.0000	0.2084	0.6000
H(21)	-0.1833	0.3069	0.3167
H(22)	-0.4500	0.2250	0.2291
H(31)	0.4666	0.0325	0.6385
H(41)	0.1463	0.0471	0.8378
H(42)	0.5166	0.0959	0.9411

### Discussion

The main intramolecular and intermolecular distances are quoted in Table 5; the whole structure of the compound is shown in Fig. 1 and the bond distances and angles in Fig. 2. The molecules have the structure



with the two hydrazinic radicals *trans* to each other. The nitrogen-nitrogen bonds in the two hydrazinic radicals are equal ( $\text{N}-\text{N}=1.405$ (8) Å). This value agrees well with the value found for the same bond ( $\text{N}-\text{N}=\text{$

1.414(9) Å) in the hydrazinedithiocarboxylato anion (Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969) and in thiosemicarbazide (N–N = 1.411(2) Å, Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969). The nitrogen–nitrogen stretching band in the infrared spectrum appears at 1018 cm<sup>-1</sup>; this means that the band is shifted with respect to that in coordinated hydrazine, in which  $\nu(\text{N–N}) = 931 - 936 \text{ cm}^{-1}$  corresponding to N–N = 1.46 Å. The shift is in accordance with the shortening of the bond N–N and with the diminution of the repulsion between the lone pairs of the nitrogen atoms. In fact, an increase in  $\nu(\text{N–N})$  in hydrazine compounds or derivatives corresponds to a shortening of the N–N distance and to the existence of bonds implying interactions, by conjugation or field effects, of one lone pair or both with the residual of the molecule (Braibanti, Dallavalle, Pellinghelli & Leporati, 1968).

The two nitrogen–carbon bonds are also equal (C–N = 1.325(6) Å); this value agrees very well with the

same bond in the hydrazinedithiocarboxylato group (C–N = 1.330(8) Å, Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969), in thiosemicarbazide (C–N = 1.321(4) Å, Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969), in thiourea (C–N = 1.33 Å, Kunchur & Truter, 1958) and in general with values obtained for dithiocarbamates. The rather short distance between the carbon and nitrogen atoms implies that canonical forms with a double bond  $(^-)\text{C}=\text{N}^+(\text{^-})$  contribute to the form of the molecule (Chatt, Duncanson & Venanzi, 1956). The infrared spectrum of the compound shows two bands at 1515 and 1450 cm<sup>-1</sup> which can be assigned to the  $(^-)\text{C}=\text{N}^+(\text{^-})$  stretching vibration; the splitting of the band could be a result of the fact that the two C–N bonds are joined to hydrazinic radicals which are not stereochemically equivalent and therefore they are subject to different constraints. It was not possible to check the assignment of these bands made by Burns (1968) who assumed  $C_{2v}$  symmetry for the molecule of thiocarbohydrazide. The carbon–sulphur

Table 2. Anisotropic thermal parameters (Å<sup>2</sup>)

	$B_{11}$ or $B$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S	3.094	1.920	1.951	0.349	1.416	0.070
N(1)	3.023	2.012	1.732	0.275	1.233	0.041
N(2)	3.073	1.824	2.396	0.701	1.345	0.179
N(3)	3.833	2.276	2.080	0.519	1.579	0.264
N(4)	3.643	2.553	2.197	0.343	1.460	0.490
C	2.562	1.456	1.928	-0.238	1.220	-0.080
H(11)	2.000					
H(21)	2.000					
H(22)	2.000					
H(31)	2.000					
H(41)	2.000					
H(42)	2.000					

Shifts of the last cycle:  $|\Delta B_{ij}|_{\text{av}} = 0.028$ ,  $|\Delta B_{ij}|_{\text{max}} = 0.097$ .

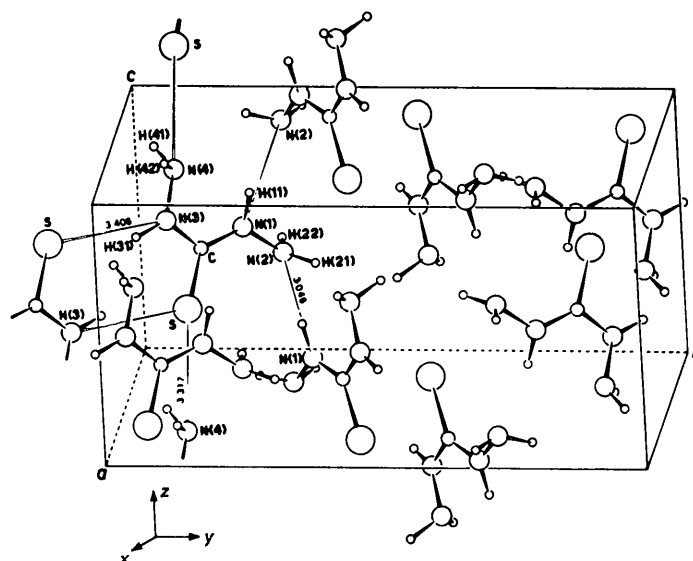


Fig. 1. Clinographic view of the structure of thiocarbohydrazide. The empty bonds indicate the shortest intermolecular contacts; N(1)···N(2) and S···N(3) are hydrogen bonds.





Table 4. Atomic peak heights ( $e.\text{\AA}^{-3}$ ), curvatures ( $e.\text{\AA}^{-5}$ ) and e.s.d.'s

		$q$	$-A_{hh}$	$-A_{hk}$	$-A_{ll}$	$A_{kk}$	$A_{hl}$	$A_{kl}$
S	obs.	36.7	374	396	423	24	227	-31
	calc.	37.3	381	394	422	19	228	-29
N(1)	obs.	11.7	117	112	122	7	68	-17
	calc.	11.9	118	112	121	6	69	-17
N(2)	obs.	11.1	97	108	102	-1	52	-3
	calc.	11.5	101	107	103	-2	53	-2
N(3)	obs.	11.0	95	108	103	5	53	-6
	calc.	11.3	96	108	103	3	54	-5
N(4)	obs.	10.7	93	98	106	-1	57	0
	calc.	10.9	95	98	106	0	58	-2
C	obs.	10.3	107	95	111	-1	61	-6
	calc.	10.4	107	95	112	0	61	-7
E.s.d.		0.1	2	2	2	1	2	1
		$q_o$ $q_c$						
H(11)		0.9 0.8						
H(21)		1.2 1.0						
H(22)		0.8 0.9						
H(31)		0.6 0.6						
H(41)		1.0 0.9						
H(42)		0.9 0.9						

Table 5. Main interatomic distances and angles

Asymmetric unit transformations:

$$\begin{array}{l} ' \quad x \quad \frac{1}{2}-y \quad \frac{1}{2}+z \\ '' \quad x \quad y \quad -1+z \\ ''' \quad 1-x \quad -y \quad 1-z \end{array}$$

Intramolecular bonds and related angles

C—S	1.724 (10) Å	S—C—N(1)	124.2 (5)°
C—N(1)	1.315 (11)	S—C—N(3)	118.3 (6)
C—N(3)	1.335 (9)	N(1)—C—N(3)	117.5 (7)
N(1)—N(2)	1.404 (9)	N(2)—N(1)—C	122.4 (7)
N(3)—N(4)	1.407 (14)	N(4)—N(3)—C	118.8 (7)
N(1)—H(11)	0.98	H(11)—N(1)—C	122.0
N(2)—H(21)	0.98	H(11)—N(1)—N(2)	115.7
N(2)—H(22)	1.05	H(31)—N(3)—C	117.1
N(3)—H(31)	0.97	H(31)—N(3)—N(4)	124.0
N(4)—H(41)	1.06	N(1)—N(2)—H(21)	114.0
N(4)—H(42)	0.96	N(1)—N(2)—H(22)	101.9
		H(21)—N(2)—H(22)	109.7
		N(3)—N(4)—H(41)	112.5
		N(3)—N(4)—H(42)	103.7
		H(41)—N(4)—H(42)	111.7

Intermolecular contacts and related angles

N(1)—N(2')	3.046 (21)	N(1)—H(11)—N(2')	154.1
S—N(4')	3.317 (19)	S—H(42'')—N(4')	83.7
S—N(3''')	3.406 (14)	S—H(31''')—N(3''')	157.3
H(11)—N(2')	2.13		
H(42'')—S	3.28		
H(31''')—S	2.49		

## References

- ANDRETTI, G. D., DOMIANO, P., FAVA GASPARRI G., NARDELLI, M. & SGARABOTTO, P. (1969). To be published.
- BRAIBANTI, A., DALLAVALLE, F., PELLINGHELLI, M. A. & LEPORATI, E. (1968). *Inorg. Chem.* **7**, 1430.
- BRAIBANTI, A., LEPORATI, E., DALLAVALLE, F. & PELLINGHELLI, M. A. (1968). *Inorg. Chim. Acta*, **2**, 144.
- BRAIBANTI, A., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & LOGIUDICE, F. (1969). *Acta Cryst.* **B25**, 93.
- BURNS, G. R. (1968). *Inorg. Chem.* **7**, 277.
- CHATT, J., DUNCANSON, L. A. & VENANZI, L. (1956). *Acta chem. genu.* **B29**, 75.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
- KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* **517**, 2551.