

Crystal and Molecular Structure of Thiocarbohydrazide

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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, $\beta=122.4(1)^\circ$, $Z=4$. 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 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 & Pellinelli, 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 ($p\text{H} \sim 8-9$). The product was recrystallized from water. The crystals are colourless prisms, m.p. 168°.

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]; ($\text{Cu } K\alpha$, $\lambda=1.5418$ Å):

$a=4.74(1)$, $b=15.53(2)$, $c=7.19(1)$ Å, $\beta=122.4(1)^\circ$.
 $V=446.9$ Å 3 , $Z=4$.

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

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-

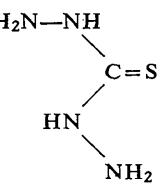
gen atoms were located by difference syntheses and not refined. The hydrogen atoms were introduced before the last cycle of refinement and the R index dropped from 9.2% to 8.2%, their ratio being 1.122 while the \mathcal{R} factor at the 0.005 level according to Hamilton (1965) is $\mathcal{R}_{24, 1000, 0.005}=1.023$; therefore we can suppose the hydrogen atoms to have been properly located. This is confirmed also by the agreement between ϱ_o and ϱ_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 $\times 10^4$)

	x	y	z
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 ($\text{N}-\text{N}=$

1.414(9) Å in the hydrazinedithiocarboxylato anion (Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969) and in thiosemicarbazide ($N-N=1.411(2)$ Å, Andreetti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969). The nitrogen–nitrogen stretching band in the infrared spectrum appears at 1018 cm^{-1} ; this means that the band is shifted with respect to that in coordinated hydrazine, in which $\nu(N-N)=931-936\text{ cm}^{-1}$ 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 $\nu(N-N)$ 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, Andreetti, 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 $(\cdots)C=N^{(+)}-$ 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^{-1} which can be assigned to the $(\cdots)C=N^{(+)}$ 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 (\AA^2)

	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: $|\Delta B_{ij}|_{\text{av}}=0.028$, $|\Delta B_{ij}|_{\text{max}}=0.097$.

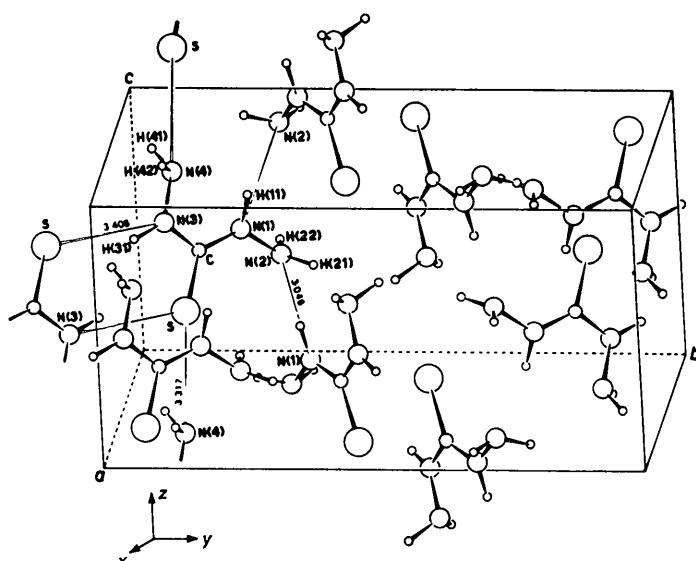


Fig. 1. Clinographic view of the structure of thiocarbohydrazide. The empty bonds indicate the shortest intermolecular contacts; $N(1)\cdots N(2)$ and $S\cdots N(3)$ are hydrogen bonds.

(C-S=1.724(10) Å) distance is equal to that found in thiourea (1.71 Å, Kunchur, & Truter, 1958) and in thiosemicarbazide (1.708(2) Å, Andreotti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1969). The thioureide group -N-CS-N is planar, again in accordance with

thiourea and thiosemicarbazide. The best plane through N(1), C, S, N(3) is $0.75334X + 0.57023Y + 0.32756Z = 1.24004$ where X, Y, Z are coordinates in Å referred to a system with $X=x$, $Y=y$, $Z \perp (X, Y)$. The atoms N(2) and N(4) are out of this plane by -0.062 Å and

Table 3. Observed and calculated structure factors

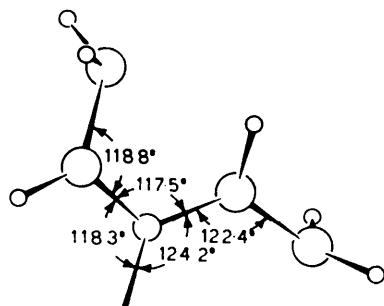
= after F_0 values indicates unobserved reflexions.

h	k	l	$10F_{\bar{2}}$	$10F_{\bar{3}}$	h	k	l	$10F_{\bar{2}}$	$10F_{\bar{3}}$	h	k	l	$10F_{\bar{2}}$	$10F_{\bar{3}}$	h	k	l	$10F_{\bar{2}}$	$10F_{\bar{3}}$	h	k	l	$10F_{\bar{2}}$	$10F_{\bar{3}}$											
1	0	0	460	471	3	2	-1	-278	-280	2	13	1	42	38	2	6	2	105	-105	2	1	-3	65	-75	1	2	7	-4	164	166					
2	0	0	326	-328	4	2	1	45	49	2	13	-1	81	73	2	6	-2	216	-241	3	1	-3	58	49	1	13	3	41	111	113					
3	0	0	163	-162	4	2	-1	101	-93	3	13	1	48	-37	3	6	2	92	-100	3	1	-3	101	100	1	13	-3	47	37	2	7	-4	154	163	
4	0	0	36	-28	5	2	-1	39	38	3	13	-1	39	31	3	6	-2	145	-160	4	1	-3	102	95	2	13	3	17	-3	3	7	-4	129	124	
5	0	0	57	48	0	3	1	218	259	0	14	1	89	-94	4	6	2	11	-29	5	1	-3	57	44	2	13	-3	21	0	4	7	-4	195	-203	
1	1	0	292	-317	1	3	-1	297	315	1	14	1	141	-133	4	6	-2	21	-9	0	2	3	207	215	3	13	-3	17	9	5	7	-4	64	-64	
2	1	0	76	-74	1	3	-1	144	161	1	14	-1	32	18	5	6	-2	62	87	1	2	3	161	169	0	14	3	183	188	0	8	4	97	97	103
3	1	0	18	-11	2	3	-1	162	155	2	14	-1	32	-10	0	7	2	25	-16	1	2	3	189	195	1	14	3	136	126	1	8	4	54	56	
4	1	0	24	24	2	3	-1	22	7	2	14	-1	110	-100	1	7	2	79	-78	2	2	3	27	2	1	14	-3	70	-63	1	8	-4	124	-117	
5	1	0	65	62	3	3	-1	27	20	3	14	-1	100	101	1	7	-2	197	-231	2	2	3	335	347	2	14	3	13	-17	2	8	-4	28	-15	
0	2	0	26	-18	3	3	-1	22	17	3	14	-1	131	-117	2	7	2	26	-24	3	2	3	98	-100	2	14	-3	76	67	2	8	-4	265	-257	
1	2	0	220	-221	4	3	-1	23	23	0	15	1	69	-122	2	7	-2	145	-151	3	2	3	131	156	1	14	3	91	83	3	8	-4	52	-73	
2	2	0	129	-120	4	3	-1	62	56	1	15	1	47	46	3	7	2	19	0	4	2	2	22	0	15	3	47	48	4	8	-4	38	27		
3	2	0	27	-30	5	3	-1	53	49	1	15	1	162	-157	3	7	2	21	6	5	2	3	70	-74	1	15	3	120	-102	5	8	-4	22	22	
4	2	0	66	-64	0	4	1	42	51	2	15	1	117	102	4	7	2	55	19	0	3	2	211	209	1	15	3	88	81	0	9	4	90	-99	
5	2	0	39	-36	1	4	1	159	-166	1	15	1	116	-109	4	7	2	66	71	1	3	3	84	67	1	15	3	67	60	7	1	9	4	26	6
1	3	0	909	-1069	1	4	-1	221	254	3	15	1	7	-13	5	7	-2	42	42	1	3	3	125	133	3	15	3	15	7	1	9	4	180	179	
2	3	0	244	-256	2	4	-1	60	-37	3	15	-1	21	-22	0	8	2	147	-146	2	3	3	25	-10	0	16	3	56	-53	2	10	4	80	72	
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4	3	0	95	97	3	4	-1	173	173	1	16	1	41	36	1	8	-2	172	-170	3	3	3	19	6	1	16	3	21	-16	3	9	-4	41	-45	
5	3	0	59	73	3	4	-1	195	-204	1	16	-1	29	28	2	8	2	30	-27	3	3	3	19	18	2	16	3	20	-14	4	9	-4	110	-111	
0	4	0	508	-519	4	4	-1	71	76	2	16	1	81	-66	2	8	-2	20	22	3	4	3	26	-3	2	16	3	26	-26	3	9	-4	21	19	
1	4	0	114	-115	4	4	-1	61	-62	2	16	1	64	54	3	8	2	16	-15	5	3	3	24	16	0	17	3	27	-27	3	10	-4	142	151	
2	4	0	151	158	5	4	-1	38	63	3	16	-1	21	21	3	8	-2	40	-39	0	4	3	269	286	3	16	3	27	-27	3	10	-4	90	91	
3	4	0	118	118	0	5	1	123	-150	0	17	1	36	-60	4	8	-2	105	-102	1	4	3	163	162	1	17	3	109	-109	5	1	10	4	110	117
4	4	0	71	83	1	5	1	33	26	1	17	1	37	32	4	8	-2	38	-33	0	4	3	17	32	2	17	-3	64	55	2	10	4	30	32	
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3	5	5	73	-63	3	5	-1	111	111	0	18	1	11	91	2	9	-2	114	115	4	4	3	21	7	1	19	3	7	-41	0	11	4	94	99	
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5	6	6	692	-782	5	5	-1	86	-104	2	18	-1	55	56	4	9	-2	137	140	1	5	3	168	-167	1	16	3	123	106	2	11	4	43	-46	
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3	7	6	132	-132	4	8	-1	50	-55	2	2	2	22	-165	1	13	2	226	223	1	8	3	30	-23	0	3	3	152	147	2	16	4	86	76	
4	7	6	32	-33	4	8	-1	45	49	3	2	2	20	-60	2	12	2	100	91	2	8	3	31	26	1	3	4	87	-86	3	16	4	111	105	
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1	8	6	65	-64	0	9	-1	34	35	3	2	2	27	-37	0	15	2	81	-80	2	9	3	19	-24	1	16	3	105	-108	1	15	3	111	-107	
2	8	6	27	-14	4	9	-1	51	54	3	2	2	26	-27	1	12	2	16	-23	2	9	3	22	25	0	15	3	105	-97	1	15	3	56	-63	
3	8	6	13	-12	0	10	-1	78	-85	3	2	2	25	-21	1	18	2	16	-21	2	9	3													

Table 3 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$10F_2$	$10F_E$	<i>h</i>	<i>k</i>	<i>l</i>	$10F_2$	$10F_E$	<i>h</i>	<i>k</i>	<i>l</i>	$10F_2$	$10F_E$	<i>h</i>	<i>k</i>	<i>l</i>	$10F_2$	$10F_E$	<i>h</i>	<i>k</i>	<i>l</i>	$10F_2$	$10F_E$						
1	16	-6	60	-61	2	7	-7	20 ^a	13	5	2	-8	36	31	2	4	-5	221	-229	5	9	-5	43	-44	6	0	-6	16 ^a	-1	
2	14	-6	88	-83	4	7	-7	16 ^a	-14	2	3	-8	101	-100	3	4	-5	77	-77	0	10	5	44	32	0	1	6	85	83	
3	14	-6	36	-40	4	7	-7	86	-72	2	3	-8	75	62	4	4	-5	74	-69	1	10	5	32	29	5	6	-6	52	35	
2	15	-6	40	-42	5	7	-7	51	-43	5	4	-8	190	178	5	4	-5	20 ^a	21	1	10	-5	54	55	1	1	-6	25	-15	
3	15	-6	4 ^a	-52	0	8	-7	79	-86	4	3	-8	128	110	6	4	-5	7 ^a	48	2	10	-5	21 ^a	21	0	7	6	48	47	
0	1	7	126	-113	2	8	-7	97	-97	3	3	-8	15 ^a	15 ^a	0	5	-5	197	-201	3	10	-5	69	-70	3	1	-6	69	84	
1	1	7	121	-106	2	8	-7	177	-167	1	4	-8	41	45	1	3	-5	136	130	4	10	-5	20 ^a	0	4	1	-6	151	-140	
2	1	7	32	35	3	8	-7	74	-70	3	4	-8	157	98	1	3	-5	354	-361	5	10	-5	13 ^a	-7	5	1	-6	55	-59	
3	1	7	99	87	4	8	-7	37	-30	3	4	-8	72	66	2	3	-5	109	113	0	11	5	108	118	6	1	-6	11 ^a	-3	
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5	1	7	21 ^a	7	0	9	-7	9	-36	5	4	-8	73	-101	3	3	-5	66	11	1	11	-5	164	157	1	2	6	21	24	
0	2	7	52	47	1	9	-7	87	-85	1	5	-8	10 ^a	10 ^a	9	4	-5	54	54	59	1	2	-6	93	-91	1	8	6	58	-49
1	2	7	148	164	2	9	-7	18	6	2	5	-8	38	-34	5	5	-5	61	73	3	11	-5	107	-112	2	2	-6	35	18	
2	2	7	184	173	3	9	-7	105	98	3	5	-8	23 ^a	-13	0	6	-5	64	76	1	11	-5	10 ^a	11 ^a	2	8	-6	92	2	
3	2	7	73	63	4	9	-7	51	49	4	5	-8	37 ^a	13	1	6	-5	55	52	9	1	-5	28	-28	4	2	-6	96	92	
4	2	7	31	-28	5	9	-7	3 ^a	-10	5	5	-8	31	42	1	6	-5	34	22	0	12	-5	119	-122	5	2	-6	22	-7	
5	2	7	70	-65	1	10	-7	41	-41	1	6	-8	56	63	2	6	-5	39	-36	1	12	-5	107	-110	6	2	-6	50	-50	
0	3	7	45	12	2	10	-7	43	-34	2	6	-8	139	132	2	6	-5	151	155	1	12	-5	22 ^a	-20 ^a	0	3	6	76	-52	
1	3	7	25	25	3	10	-7	76	-67	3	6	-8	43	38	3	6	-5	141	153	2	12	-5	83	-82	1	3	6	32	-24	
2	3	7	30	-13	4	10	-7	62	-54	4	6	-8	56	-54	4	6	-5	53	59	3	12	-5	70	-71	1	3	6	20 ^a	19 ^a	
3	3	7	41	-34	1	11	-7	130	-139	5	6	-8	63	-68	5	6	-5	20 ^a	-30	0	13	5	29	20	2	3	-6	174	169	
4	3	7	25 ^a	3	2	11	-7	17 ^a	-17	-1	7	-8	30	39	0	7	5	78	-81	1	13	5	8 ^a	20	2	3	-6	148	163	
5	3	7	33	26	3	11	-7	94	84	2	7	-8	21	-17	1	7	5	46	47	1	13	-5	21 ^a	1	4	3	-6	160	-156	
0	4	7	104	100	4	11	-7	80	81	2	7	-8	106	-111	1	7	5	90	-89	2	13	-5	34	-32	5	3	-6	38	33	
1	4	7	31	31	1	12	-7	4 ^a	49	6	7	-8	127	-133	2	7	5	19	25	3	13	-5	57	44	6	3	-6	7 ^a	51	
2	4	7	48	41	2	12	-7	146	156	2	8	-8	21	-23	2	7	5	93	95	0	14	5	50	-47	0	4	6	53	46	
3	4	7	19 ^a	7	3	12	-7	75	81	3	8	-8	16	9	3	7	5	47	54	1	14	-5	120	-113	1	4	6	29	26	
4	4	7	47	-41	2	13	-7	9	-5	4	8	-8	42	48	4	7	-5	23	24	2	14	-5	146	-135	1	4	-6	96	93	
5	4	7	90	-95	3	13	-7	6 ^a	-33	2	9	-8	31	33	5	7	-5	57	47	3	14	-5	32	-34	2	4	-6	54	-49	
0	5	7	120	122	1	0	-8	141	-118	3	9	-8	33	-38	0	8	5	186	211	1	15	5	65	-76	3	4	-6	164	-163	
1	5	7	152	135	2	0	-8	211	-189	4	9	-8	7 ^a	-18	1	8	5	149	160	1	15	-5	104	-105	4	4	-6	29	-20	
2	5	7	42	-45	3	0	-8	40	-36	3	10	-8	67	-7 ^a	1	8	5	98	95	2	15	-5	43	-37	5	4	-6	59	61	
3	5	7	131	-128	4	0	-8	128	106	2	1	-9	9 ^a	-26	2	8	5	10 ^a	-16	3	15	-5	47	52	0	5	6	33	19	
4	5	7	93	-99	5	0	-8	130	114	3	1	-9	120	-112	2	8	-5	204	202	1	16	-5	13 ^a	6	1	5	6	60	-44	
5	5	7	32 ^a	-61	1	1	-8	101	-88	4	1	-9	107	-106	3	8	-5	48	51	2	16	-5	55	54	1	5	6	30 ^a	13	
0	6	7	52	-61	2	1	-8	56	-50	2	2	-9	107	-121	4	8	-5	20 ^a	21	1	13	-5	41	46	2	5	-6	90	80	
1	6	7	21 ^a	3	1	-8	35	30	3	2	-9	69	-69	5	8	-5	82	-73	0	6	6	80	-72	3	5	-6	26	18		
2	6	7	46	-38	4	1	-8	65	49	4	2	-9	98	103	0	9	5	60	67	1	0	6	106	-93	4	5	-6	45	-42	
3	6	7	44	5	1	-8	15	-6	3	3	-9	36	-37	1	9	5	62	-58	1	0	6	46	-32	5	5	-6	30 ^a	-9		
4	6	7	82	84	2	4	-8	17 ^a	14	4	3	-9	11 ^a	-32	1	9	5	149	153	2	0	6	225	229	6	6	-6	88	71	
5	6	7	39	50	2	2	-8	47	-47	3	4	-9	74	-68	2	9	-5	85	91	3	0	6	220	228	6	6	-6	101	101	
0	7	7	70	76	3	2	-8	48	-43	4	4	-9	6 ^a	-29	3	9	-5	47	-46	4	0	6	78	-69	1	6	-6	22	17	
1	7	7	77	73	4	2	-8	20 ^a	-7	3	5	-9	115	138	4	9	-5	100	-101	5	0	6	110	-90	2	6	-6	194	-190	

Fig. 2. Distances and angles in the molecule of thiocarbonylhydrazide.



-0.120 Å respectively; therefore they are both on the same side of the plane. The angle N(1)-C-N(3)=117.5(7)° is not significantly different from those in thiourea [116.0(1.0)°] and thiosemicarbazide [118.8(1)°]. The two angles S-C-N(1)=124.2(5)° and S-C-N(3)=118.3(6)° are significantly different from one another probably as a result of the different steric constraints. The sum of the angles around C is exactly 360° however and therefore the hybridization of the carbon atom is purely planar. A small difference has also been found between N(2)-N(1)-C=122.4(7)° and N(4)-N(3)-C=118.8(7)°. The angles between bonds to hydrogen atoms are reasonable; the sums of the angles around N(1) and N(3) are very close to 360°, which means that these two nitrogen atoms are very probably in the sp^2 configuration. On the other hand the angles formed by N(2) and N(4) with the hydrogen atoms attached to them show that they are very likely in the sp^3 configuration.

Short intermolecular distances are N(1)...N(2)=3.046 Å and S...N(3)=3.406 Å. These can be classified as weak hydrogen bonds. The corresponding angles at the hydrogen atoms are: N(1)-H(11)...N(2)=154.1°, S...H(31)-N(3)=157.3°, which are acceptable deviations from linear hydrogen bonds (Hamilton & Ibers, 1968).

The short distance S...N(4)=3.317 Å with angle S...H(42)-N(2)=83.7° probably does not correspond to a hydrogen bond because the angle is much less than 180° and the distance H(42)...S=3.28 Å is rather long. The Consiglio Nazionale delle Ricerche, Rome, is thanked for financial help.

Table 4. *Atomic peak heights (e.Å⁻³), curvatures (e.Å⁻⁵) and e.s.d.'s*

	ρ	$-A_{hh}$	$-A_{hk}$	$-A_{ll}$	A_{kk}	A_{hl}	A_{kl}
S	obs.	36.7	374	396	423	24	227
	calc.	37.3	381	394	422	19	228
N(1)	obs.	11.7	117	112	122	7	68
	calc.	11.9	118	112	121	6	69
N(2)	obs.	11.1	97	108	102	-1	52
	calc.	11.5	101	107	103	-2	53
N(3)	obs.	11.0	95	108	103	5	53
	calc.	11.3	96	108	103	3	54
N(4)	obs.	10.7	93	98	106	-1	57
	calc.	10.9	95	98	106	0	58
C	obs.	10.3	107	95	111	-1	61
	calc.	10.4	107	95	112	0	61
E.s.d.		0.1	2	2	1	2	1
	ρ_o	ρ_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:

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

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		

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