

Piperidinothiosemicarbazide의 結晶 및 分子構造

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The Crystal and Molecular Structure of Piperidinothiosemicarbazide

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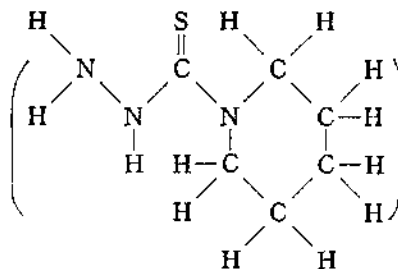
요 약. 피페리디노티오세미카르바지드의 결정구조가 X-선을 이용한 단결정 해석에 의하여 해명되었다. 공간군은 $P2_1/c$ 이며 단위세포는 4 분자를 포함하고 있고, 세포상수는 $a=14.68\pm 0.04$, $b=4.59\pm 0.02$, $c=12.92\pm 0.04$ Å, $\beta=109.4\pm 0.2^\circ$ 이다. 3차원적인 회절반점의 강도는 목록에 의하여 얻었다. 결정구조는 패터슨 함수의 해석으로 밝혔고, 원자좌표치는 최소자승법으로 정밀화하였으며 378개의 독립적인 회절반점에 대한 최종 R 값은 0.14이었다. 수소결합에는 N—H...S 형과 N—H...N 형의 두종류가 있다. N—H...S 형의 길이는 3.28 및 3.39 Å 이고, N—H...N 형의 길이는 3.03 Å 이다. 수소결합외의 분자들을 연결하는 힘은 van der Waals 힘이다.

Abstract. The crystal structure of piperidinothiosemicarbazide, $C_6H_{13}N_3S$, has been determined by single crystal X-ray analysis. The space group is $P2_1/c$ with four molecules in the unit cell of dimensions $a=14.68\pm 0.04$, $b=4.59\pm 0.02$, $c=12.92\pm 0.04$ Å and $\beta=109.4\pm 0.2^\circ$. Three-dimensional photographic intensities were estimated visually. The structure has been solved by an interpretation of a Patterson synthesis and refined by block-diagonal least-squares methods to give a final R value of 0.14 for 378 observed independent reflections. There are two independent hydrogen bonds in the structure. One of them is of the type N—H...S with the length 3.28 and 3.39 Å, and another is of the type N—H...N with the length 3.03 Å. Apart from the hydrogen bonding system the molecules are held together in the crystal by van der Waals forces.

Introduction

Some thiosemicarbazide derivatives have pharmacological activities. Although no detailed knowledge of the steric configuration of these molecules was available, attempts were made to interpret the relationship of structure and pharmacological activities as in Koo *et al.*¹ The present work gives the molecular structure of

one of these compounds, piperidinothiosemicarbazide



the aim being to get a basis for further studies on the interrelation between molecular configuration and pharmacological activities.

Experimental

Suitably grown needle-shaped transparent single crystals elongated in the b direction were obtained by slow evaporation of a benzene solution at room temperature.

The unit cell dimensions were determined from higher-order reflections recorded on Weissenberg photographs taken with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Aluminium foil diffraction ($a=4.0492 \text{ \AA}$ at 20°C) lines were superposed on the films for calibration purposes. The density of single crystals was measured by flotation method in a mixture of hexane and carbon tetrachloride and agrees well with calculated value.

Crystal data are:

Piperidinothiosemicarbazide, $\text{C}_6\text{H}_{13}\text{N}_3\text{S}$

Mw=159.25, monoclinic

$a=14.68\pm 0.04 \text{ \AA}$

$b=4.59\pm 0.02$

$c=12.92\pm 0.04$

$\beta=109.4\pm 0.2^\circ$

$Z=4$, $V=821.1 \text{ \AA}^3$

$D_m=1.28_1 \text{ g cm}^{-3}$, $D_x=1.28_8 \text{ g cm}^{-3}$

Space group: $P2_1/c$ from systematic

absences $h0l$: $l=2n+1$

$0k0$: $k=2n+1$

Intensities of reflections were recorded on multiple-film equi-inclination Weissenberg photographs with $\text{CuK}\alpha$ radiation. Four layers from $h0l$ to $h3l$ were collected around the b axis and two layers from $hk0$ to $hk1$ were collected around the c axis. The approximate dimensions of diameters of the cylindrical crystals were 0.3 mm and the lengths were 1.0 mm . Intensities were estimated visually by comparison with a standard scale. The number of observed reflections was

378 and the intensities covered a range of about 2090:1.

Lorentz and polarization correction and spot-shape corrections were made. Relative intensities were placed on an approximately absolute scale by Wilson's statistical method².

Structure Determination

A three-dimensional Patterson synthesis was carried out. The position of the sulfur atom was deduced from a study of the Harker section ($U, 1/2, W$) and line ($O, V, 1/2$) and confirmed by the general peak at (U, V, W).

The coordinates of the sulfur atom were used to calculate structure factors. A three-dimensional electron density map was then plotted with all the terms using the signs of which were calculated on the basis of the sulfur atom. The resulting map showed all the ten atoms except hydrogen atoms in the molecule. Positional and thermal parameters were refined by the block-diagonal least-squares methods. At the first cycle the reliability index, $R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ were 0.29. Three further cycles of least-squares refinement were carried out with isotropic temperature factors. The R index then dropped to 0.14. The function minimized was $w(|F_0|-|F_c|)^2$ and the weighting scheme $w=(a+b|F_0|+c|F_0|^2)^{-1}$ suggested by Cruickshank³, where $a=3.38$, $b=1$ and $c=0.119$, was employed and atomic scattering factors were taken from the International Table for X-ray Crystallography⁴. No effort to locate hydrogen atoms was made. All these calculation was performed with the programs by Shiono^{5,6} on IBM 1130 electronic computer.

The final positional and thermal parameters together with their estimated standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 2.

Table 1. Final atomic coordinates and isotropic thermal parameters in piperidinothiosemicarbazide. The estimated standard deviation given in parentheses refer to the last decimal positions.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
S	0.140(1)	0.185(2)	0.026(1)	2.7(2)
N(1)	0.214(2)	-0.104(7)	0.214(3)	1.3(7)
N(2)	0.076(2)	0.164(8)	0.201(3)	1.6(7)
N(3)	-0.002(2)	0.334(8)	0.141(3)	2.2(7)
C(1)	0.148(3)	0.060(9)	0.151(3)	2.1(8)
C(2)	0.226(4)	-0.174(13)	0.323(4)	2.4(12)
C(3)	0.331(4)	-0.046(11)	0.396(4)	3.8(12)
C(4)	0.414(4)	-0.181(13)	0.359(4)	4.8(14)
C(5)	0.386(4)	-0.096(12)	0.230(4)	3.6(13)
C(6)	0.286(4)	-0.228(11)	0.167(4)	3.2(12)

Results and Discussion

In Fig. 1 and Table 3, the bond lengths and angles are given. These values are in good agreement within the experimental error comparing with the values of some other similar compounds.

The structure of piperidinothiosemicarbazide is not isomorphous with that of morphorinothiosemicarbazide. But the configuration of the molecule, the hydrogen bonding scheme and molecular packing system of both compound are similar.

Bond lengths of C(1)—S and C(1)—N(1) suggest that the partial double-bond character for C—N and C—S bond appear to be retained. And these features could be explained by the contribution of ionic canonical forms in the conformation of the molecule as in Restivo and Palenik⁷, in Gabe *et al.*⁸ and in Domiano *et al.*⁹

Some least-squares planes are listed in Table 4. The atoms N(1) and C(4) deviate from plane B by 0.64 and -0.78Å respectively and thus the piperidine ring forms a normal chair configuration.

A least-squares plane was fitted to the atoms of N(1), C(1), C(2) and C(6) and this plane is flat within experimental error as in Wagner *et al.*¹⁰

Some intermolecular contacts less than 3.5 Å

are given in Table 3.

The structure viewed down the *b* and *c* axes

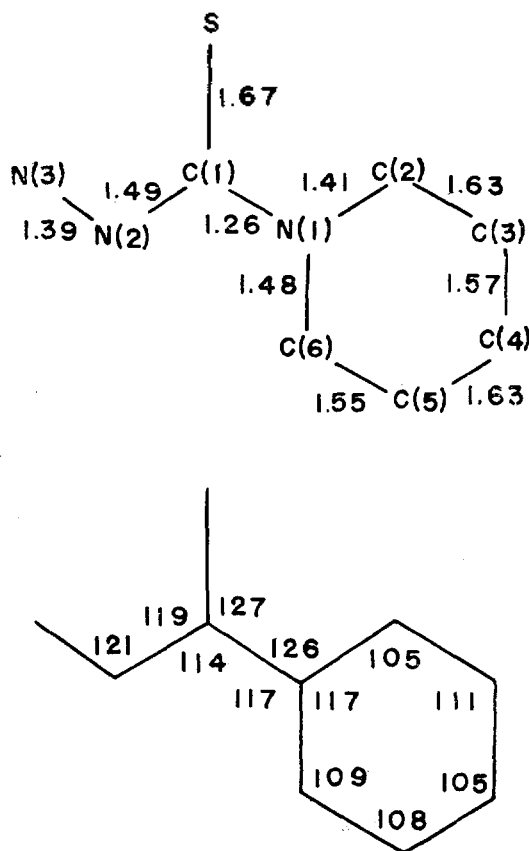


Fig. 1. Bond lengths(Å) and angles(°) in piperidinothiosemicarbazide.

Table 2. Observed and calculated structure factors. Columns are: Index, $|F_{\text{obs}}|$, $|F_{\text{cal}}|$.

$k=0\ l=0$	2 16.9 14.1	1 20.3 24.2	2 10.3 13.0	-8 19.0 16.8	-11 15.7 16.4	-7 11.1 13.0
2 37.3 38.7	3 54.0 50.6	3 8.0 9.7	6 20.3 24.0	-11 14.5 13.1	-12 29.5 31.2	-8 21.7 22.6
3 17.4 20.6	4 13.5 11.5	7 20.3 22.7	$k=3\ l=3$	-12 16.1 19.8	-13 20.3 29.2	-9 12.9 16.0
4 37.2 40.3	6 13.5 13.9	$k=2\ l=1$	0 22.2 26.8	-14 14.7 18.8	$k=1\ l=3$	$k=1\ l=10$
5 22.9 22.7	7 19.9 16.0	0 29.1 32.6	1 14.5 14.7	$k=0\ l=8$	-4 19.1 14.9	-3 19.5 16.7
7 32.4 30.1	8 9.7 12.2	1 39.7 49.8	2 6.1 6.4	-2 33.4 37.3	-5 19.4 18.1	-4 22.2 24.9
8 26.4 23.9	9 6.8 8.3	2 37.8 41.4	3 17.4 20.0	-3 13.6 11.7	-6 15.9 13.6	-5 17.6 22.3
11 22.1 26.5	10 10.6 15.0	4 28.6 30.1	5 16.4 20.6	-5 31.9 33.5	-7 34.7 31.0	-7 33.1 36.8
13 22.2 27.3	$k=1\ l=2$	5 48.8 58.3	6 22.2 25.3	-6 27.1 28.9	-8 18.5 19.8	-14 9.9 11.4
14 27.1 33.5	0 56.7 59.2	5 16.1 16.6	7 20.3 25.2	-7 34.8 39.9	-9 17.7 21.5	$k=1\ l=11$
$k=0\ l=2$	1 91.3 89.4	$k=2\ l=2$	$k=3\ l=4$	-8 38.8 46.4	-11 13.5 15.7	-2 12.1 15.7
0 48.1 43.2	2 50.5 47.4	0 11.3 13.1	1 17.4 21.9	-9 31.2 34.7	$k=1\ l=4$	-4 12.4 7.9
2 59.0 54.7	3 11.4 11.7	3 20.8 23.0	2 9.4 9.9	-11 15.6 17.3	-1 41.5 37.1	-10 11.9 14.8
3 40.4 40.6	4 46.6 43.2	4 38.8 44.9	4 9.8 15.4	-13 12.5 12.4	-2 45.5 47.3	-11 14.4 17.1
4 46.2 44.4	6 8.5 6.5	6 20.3 24.1	5 12.0 15.4	-15 11.5 12.1	-3 31.8 34.8	-12 10.7 13.1
5 18.6 15.9	8 27.1 26.0	8 10.7 13.3	$k=3\ l=5$	$k=0\ l=10$	-4 17.5 17.9	$k=1\ l=14$
6 59.4 58.8	9 23.5 31.1	$k=2\ l=3$	0 17.1 21.8	-1 19.3 23.1	-6 53.4 48.8	-4 13.5 13.6
7 66.7 45.5	$k=1\ l=3$	0 14.5 13.6	2 10.1 11.8	-2 15.0 18.1	-7 28.1 27.8	-8 12.2 12.7
10 12.0 13.0	0 6.3 3.7	2 9.1 10.2	3 13.7 17.2	-4 13.9 18.4	-8 13.7 7.5	$k=2\ l=1$
$k=0\ l=4$	5 25.9 21.1	3 25.7 28.2	$k=3\ l=6$	-5 26.6 26.8	-9 17.2 17.9	-1 10.6 12.5
1 31.4 28.7	6 26.8 28.9	4 18.2 19.3	0 13.7 19.5	-7 35.9 40.3	-10 17.6 17.0	-2 9.0 11.2
2 26.4 27.4	$k=1\ l=4$	8 11.9 17.7	$k=3\ l=7$	-9 25.1 26.4	$k=1\ l=5$	-3 30.3 36.1
3 36.4 43.7	0 11.0 9.3	$k=2\ l=4$	1 20.3 25.2	-10 14.2 15.2	-1 10.4 8.4	-4 14.3 16.2
9 22.2 28.0	1 25.6 19.8	0 12.1 10.0	2 21.3 24.2	-12 17.5 23.2	-2 7.6 7.0	-5 11.7 17.7
10 21.8 24.9	4 15.7 14.0	2 17.2 18.3	3 9.7 12.1	-13 14.2 17.5	-4 15.9 16.5	-6 13.0 17.5
$k=0\ l=6$	5 18.6 19.0	3 21.0 21.7	$k=4\ l=0$	$k=0\ l=12$	-6 15.4 11.1	-8 16.4 21.8
0 43.8 47.4	7 14.5 17.8	6 11.0 13.5	0 8.0 13.5	-3 17.4 19.1	-7 10.5 11.4	-10 18.0 27.8
1 19.2 16.0	8 17.4 21.0	10 23.2 26.8	$k=0\ l=2$	-6 14.3 15.9	$k=1\ l=6$	-11 10.3 14.0
2 21.4 23.9	$k=1\ l=5$	$k=2\ l=5$	-1 42.3 44.3	$k=0\ l=14$	-1 19.3 20.1	-12 16.4 20.5
3 34.3 41.9	0 46.7 43.9	0 19.7 20.1	-2 77.4 78.8	-6 16.7 13.6	-2 29.8 27.8	$k=2\ l=2$
7 21.9 26.6	4 10.0 9.5	1 18.3 16.4	-3 32.4 32.6	-8 13.7 12.2	-3 52.3 52.3	-1 16.0 17.6
$k=0\ l=8$	$k=1\ l=6$	2 27.0 31.7	-4 32.8 42.1	-9 17.7 15.6	-4 27.2 23.8	-2 7.7 7.1
1 12.8 15.7	1 27.3 23.6	3 15.3 14.0	-5 52.9 53.3	-10 16.5 16.3	-9 28.0 26.0	-3 29.1 30.8
2 13.7 9.9	2 18.8 14.8	$k=2\ l=6$	-6 26.5 22.2	$k=0\ l=16$	-10 24.2 25.2	-7 15.7 23.8
5 28.3 38.2	4 22.2 25.8	0 21.4 27.0	-7 43.5 49.4	-6 8.6 6.8	$k=1\ l=7$	-10 13.6 16.7
6 38.8 46.5	5 38.8 42.7	2 23.5 26.7	-8 38.1 38.2	-8 8.8 12.1	-2 24.0 21.0	$k=2\ l=3$
$k=0\ l=10$	$k=1\ l=7$	3 10.1 11.2	-10 41.0 49.1	$k=1\ l=1$	-3 8.4 11.5	-1 7.1 8.9
1 17.4 21.8	0 13.0 13.5	$k=2\ l=7$	-13 23.2 23.5	-1 102.9 94.1	-4 25.2 23.1	-2 29.1 31.7
2 24.2 26.6	2 23.3 26.6	0 20.8 21.4	$k=0\ l=4$	-3 27.7 31.2	-5 23.9 19.3	-3 18.4 19.2
$k=0\ l=12$	3 12.1 11.4	1 24.7 27.5	-3 52.4 53.5	-4 34.4 35.6	-7 14.2 12.8	-5 29.1 33.7
2 10.4 15.9	6 11.6 15.1	4 28.4 38.3	-4 34.9 76.7	-5 14.1 12.9	$k=1\ l=8$	-9 12.3 17.4
$k=1\ l=0$	$k=1\ l=8$	$k=3\ l=0$	-5 26.7 27.9	-6 14.5 16.7	-2 10.9 10.1	-11 17.2 21.6
2 79.1 92.4	0 34.4 32.8	1 9.7 10.8	-6 26.8 28.6	-9 13.7 14.1	-3 10.8 8.0	$k=2\ l=4$
3 46.0 53.2	1 19.3 21.6	4 5.1 7.4	-7 26.3 21.6	-12 17.6 21.1	-4 11.6 8.7	-1 25.3 30.4
4 10.6 10.4	3 29.1 33.9	$k=3\ l=1$	-8 29.1 25.0	$k=1\ l=2$	-5 23.9 26.5	-3 16.5 17.1
5 47.5 45.9	4 16.9 19.1	0 16.4 18.0	-9 14.8 14.0	-1 24.1 29.6	-6 26.0 22.3	-4 48.4 49.2
6 36.7 38.4	8 13.5 16.2	2 14.5 18.4	-11 19.3 19.6	-2 12.0 8.9	-7 25.7 21.2	-5 27.7 38.3
8 9.7 14.2	$k=l\ 2=9$	3 20.3 23.6	-12 25.0 27.7	-4 27.7 25.5	-8 22.8 23.5	-6 10.7 16.6
9 21.1 25.0	5 16.4 20.5	4 21.3 23.5	$k=0\ l=6$	-5 51.0 50.6	-10 20.8 17.8	-9 12.7 14.0
11 16.4 20.6	$k=1\ l=10$	5 25.2 30.0	-1 31.5 32.4	-6 24.6 21.3	-11 23.9 27.4	-11 13.9 16.3
$k=1\ l=1$	0 15.5 15.9	7 16.4 17.4	-2 11.4 12.3	-7 24.1 21.6	-13 15.6 19.7	$k=2\ l=5$
0 9.7 12.1	$k=2\ l=0$	$k=3\ l=2$	-5 19.6 16.9	-9 9.5 11.0	$k=1\ l=9$	-1 9.1 12.2
1 40.3 43.2	0 38.8 39.2	0 4.2 5.5	-7 30.7 29.0	-10 22.8 24.4	-6 22.4 25.3	-2 19.9 21.4

-3 15.6 15.4	-7 15.7 17.6	-10 12.3 11.1	-3 10.6 13.8	-2 5.8 5.3	$k=3 l=5$	-5 15.4 19.8
-6 21.5 24.1	-9 15.7 15.2	-12 11.6 19.8	-4 23.2 27.3	-3 10.4 13.8	-1 23.2 26.1	-12 15.0 22.3
-7 22.4 25.4	-10 17.8 24.1	$k=2 l=10$	-5 6.3 5.3	-4 14.5 18.9	-2 22.2 26.3	$k=3 l=9$
$k=2 l=6$	$k=2 l=8$	-2 12.5 16.3	$k=3 l=2$	-7 23.2 26.9	-4 16.3 18.1	-1 11.0 9.4
-1 12.6 10.9	-2 13.5 16.7	-5 13.9 15.3	-2 2.5 5.8	-8 29.1 36.4	-5 23.2 26.9	-5 9.8 13.5
-2 12.6 14.1	$k=2 l=9$	-6 11.8 11.0	-3 7.7 10.0	-9 15.5 18.1	$k=3 l=6$	-8 13.5 16.4
-3 19.9 23.6	-2 11.6 18.1	$k=2 l=11$	-5 17.4 20.3	$k=3 l=4$	-1 13.5 15.0	-9 14.5 19.8
-5 14.3 13.0	-3 23.0 30.6	-8 11.9 17.2	-6 9.7 11.5	-2 7.8 7.4	-2 13.5 15.8	$k=3 l=11$
-6 13.4 16.3	-4 23.6 26.5	$k=3 l=1$	$k=3 l=3$	-7 19.3 23.2	$k=3 l=7$	-2 19.3 26.1
-8 16.4 20.2	-6 19.6 23.9	-1 24.2 29.9	-1 10.0 12.4	-9 9.9 14.0	-1 11.6 16.0	-3 14.5 18.7
$k=2 l=7$						

Table 3. Bond lengths and angles in piperidinothiosemicarbazide. Estimated standard deviations in parenthesis refer to the last decimal positions of respective values.

<i>i</i>	<i>j</i>	<i>D_{ij}</i>	<i>i</i>	<i>j</i>	<i>k</i>	$\angle ijk$
S	C(1)	1.67(4) Å	S	C(1)	N(1)	127(3)°
N(1)	C(1)	1.26(6)	S	C(1)	N(2)	119(3)
N(1)	C(2)	1.41(7)	N(1)	C(1)	N(2)	114(4)
N(1)	C(6)	1.48(6)	C(1)	N(1)	C(2)	126(4)
N(2)	C(1)	1.49(6)	C(1)	N(1)	C(6)	117(4)
N(2)	N(3)	1.39(5)	C(1)	N(2)	N(3)	121(3)
C(2)	C(3)	1.63(8)	C(2)	N(1)	C(6)	117(4)
C(3)	C(4)	1.57(8)	C(2)	C(3)	C(4)	111(4)
C(4)	C(5)	1.63(8)	C(3)	C(2)	N(1)	105(4)
C(5)	C(6)	1.55(8)	C(3)	C(4)	C(5)	105(4)
N(2)—H...N(3a)		3.03(7)	C(4)	C(5)	C(6)	108(4)
N(3)—H...S(b)		3.39(5)	C(5)	C(6)	N(1)	109(4)
N(3)—H...S(c)		3.28(5)				
N(3).....C(2d)		3.47(7)				
symmetry code						
		<i>x</i>	<i>y</i>	<i>z</i>		
<i>a</i>		- <i>x</i>	-1/2+ <i>y</i>	1/2- <i>z</i>		
<i>b</i>		- <i>x</i>	- <i>y</i>	- <i>z</i>		
<i>c</i>		- <i>x</i>	1- <i>y</i>	- <i>z</i>		
<i>d</i>		- <i>x</i>	1/2+ <i>y</i>	1/2- <i>z</i>		

are shown in Fig. 2 and 3. In the molecular packing there are two kinds of the continuous hydrogen bonding framework.

One is of the type N—H...S of the length 3.28 and 3.39 Å in which the amino nitrogen atom forms hydrogen bond with the sulfur atom which is related by the inversion center. This hydrogen bond forms infinite zigzag chain parallel to the *b* axis.

The other is N—H...N type of the length

3.03 Å. The imino nitrogen atom forms hydrogen bond to the amino nitrogen atom of the other molecule related by the two-fold screw axis. This frame work continues in the spiral form around the two-fold screw axis.

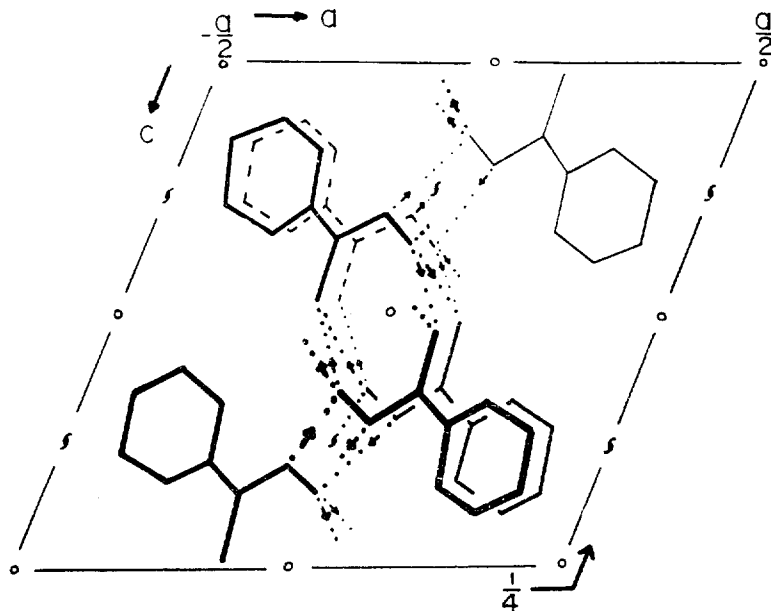
Apart from the hydrogen bonding system the structure is held together by van der Waals forces.

The closest intermolecular contact, N(3)—C(2d), is 3.47 Å.

Table 4. Least-squares planes in piperidinothiosemicarbazide.

Equation for plane: $Ax+By+Cz=D$, where x, y, z are in Å.

Atoms in plane	Atoms out of plane	Distances in Å from best plane	Constant
A. Thiosemicarbazide group			
S		0.01	$A=0.46$
N(1)		0.01	$B=0.79$
N(2)		0.01	$C=0.23$
C(1)		-0.03	$D=1.69$
	N(3)	-0.07	
	C(2)	0.16	
	C(6)	-0.09	
B. Piperidine ring			
C(2)		0.02	$A=-0.24$
C(3)		-0.01	$B=0.92$
C(5)		0.02	$C=-0.21$
C(6)		-0.02	$D=-2.42$
	N(1)	0.64	
	C(4)	-0.78	
C. Ring Substitution			
N(1)		-0.00	$A=0.51$
C(1)		0.00	$B=0.80$
C(2)		0.00	$C=0.13$
C(6)		0.00	$D=1.57$
	S	0.21	
	N(2)	-0.07	

Fig. 2. The crystal structure of piperidinothiosemicarbazide viewed down the b axis. Dotted lines indicate hydrogen bonds with arrows pointing in the donor direction.

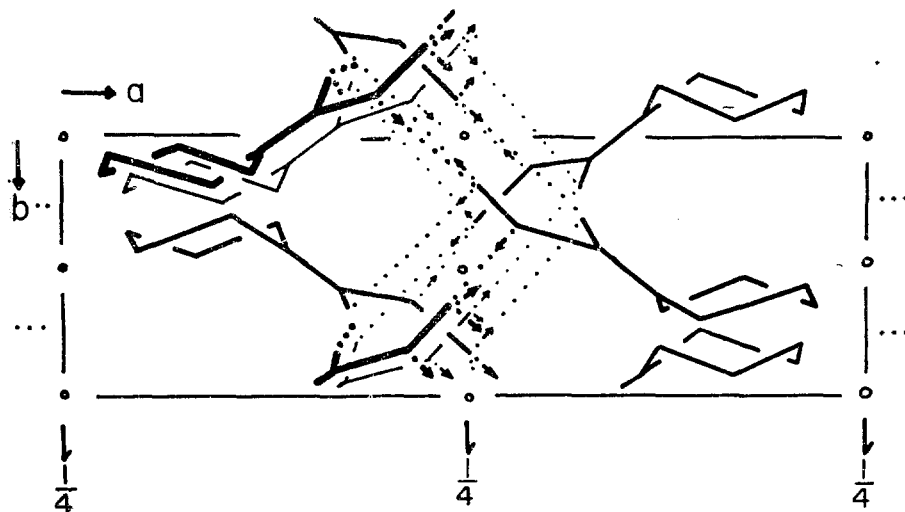


Fig 3. The crystal structure of piperidinothiosemicarbazide viewed down the c axis. Dotted lines are as in Fig 2.

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References

1. C. H. Koo, H. S. Kim, H. S. Shin and Y. Lee, *J. Korean Chem. Soc.*, **17**, 105(1973).
2. A. J. C. Wilson, *Nature, Lond.*, **150**, 152(1942).
3. D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-ray Crystal Structure Analysis", Pergamon Press, New York, 1961.
4. "International Table for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1968.
5. R. Shiono, "IBM 1130 Data Reduction Program, Technical Reports", Dept. of Crystallography, Univ. of Pittsburgh, 1968.
6. R. Shiono, "IBM 1130 Least Squares Program, Technical Report", Dept. of Crystallography, Univ. of Pittsburgh, 1968.
7. R. Restivo and G. J. Palenik, *Acta Cryst.*, **B26**, 1397(1970).
8. E. J. Gabe, M. R. Taylor, J. P. Glusker, J. A. Minkin and A. L. Patterson, *Acta Cryst.*, **B25**, 1620(1969).
9. P. Domiano, G. F. Gasparri, M. Nardelli and P. Sgarabotto, *Acta Cryst.*, **B25**, 343(1969).
10. R. E. Wagner, W. Jensen, W. Wadsworth and Q. Johnson, *Acta Cryst.*, **B29**, 2160(1973).