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Salicylaldehyde-4-piperidinothiosemicarbazone의 결정 및 분자구조

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The Crystal and Molecular Structure of Salicylaldehyde-4-piperidinothiosemicarbazone

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요 약 살리실알데히드-4-피페리디노티오세미카르바존의 분자 및 결정구조를 X-선 회절법으로 밝혔다. 이 화합물의 결정은 직각바둥축정계에 속하며 공간군은 $P2_12_12_1$이다. 단위세포상수는 a=6.52(2), b=13.42(4), c=14.92(4)Å으로서 4개 분자를 포함하고 있다. 원자의 좌표는 중원자법을 이용하여 결정하였고 최소자승법으로 정밀화하였다. 1019개의 구조인자에 대한 최종 R값은 0.10이다. 티오세미카르바존 화합물에서 C=S결합은 N—NH 결합에 대해 트랜스 위치에 존재하는 경우가 많은데 살리실알데히드-4-피페리디노티오세미카르바존에서는 시스위치에 있다. 히드록실기의 산소원자는 O—H···N의 분자내수소결합과 N—H···O의 분자간수소결합에 참여하는데 그 수소결합길이는 각각 2.56Å과 3.00Å이다. 분자간에는 N—H···O 수소결합에 의하여 a축에 평행한 나선축을 따라 나선형 분자띠를 이루고 있으며 이들 분자띠는 반데르왈스힘으로 결합되어 있다.

ABSTRACT. The crystal structure of salicylaldehyde-4-piperidinothiosemicarbazone, $C_{13}H_{17}N_3OS$, has been determined by single crystal X-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions a=6.52(2), b=13.42(4), c=14.92(4) Å. There are four formular units in a unit cell. The structure was solved by the heavy atom method and refined by isotropic block diagonal least-squares methods to a final R value of 0.10 for 1019 observed reflections. The oxygen atom of the hydroxyl group is involved in two hydrogen bonds, one as donor in the intramolecular O—H···N hydrogen bond and the other as acceptor in the intermolecular N—H···O hydrogen bond, the distances of the hydrogen bonds 2.56 and 3.00 Å respectively. The molecules are joined into infinite columns by the N—H···O hydrogen bonds which form spirals along the two fold screw axis parallel to the a axis. The molecular columns are held together by van der Waals forces.

INTRODUCTION

Thiosemicarbazones are a large group of organic derivatives whose biological activities are dependent on their complexing abilities. Gin-

gras[1] has shown a direct relationship between the antifungal activity of the thiosemicarbazone and the chelation of the thiosemicarbazone with copper ions. Apparently a knowledge of the conformation and bond lengths is essential for a final explanation of the requirements for biological activity in these compounds. Therefore, a crystal structure analysis of salicylaldehyde-4-piperidinothiosemicarbazone was undertaken as part of a program devoted to the electronic structures, chelating properties and biological activities of thiosemicarbazones.

EXPERIMENTAL

Crystals were obtained as transparent yellow thick plates elongated along the *a* axis by slow evaporation of an ethanol solution at room temperature.

Oscillation and Weissenberg photographs showed the crystal system to be orthorhombic. Unit cell dimensions were measured from *0kl* and *hk0* Weissenberg photographs, upon which Debye-Scherrer diagrams with NaCl powder as standard were superimposed, using Cu$K\alpha$ radiation (λ=1.5418 Å).

The density of single crystals was measured by the flotation method in a mixture of carbon tetrachloride and benzene. The crystal data are as follows:

Salicylaldehyde-4-piperidinothiosemicarbazone, $C_{13}H_{17}N_3OS$

M. W. =263.36

a=6.52(2) Å

b=13.42(4)

c=14.92(4)

Z=4

Space group: $P2_12_12_1$, from systematic absences $h00$ for $h=2n+1$, $0k0$ for $k=2n+1$, $00l$ for $l=2n+1$.

D_c=1.34 g·cm^{-3}

D_m=1.33 g·cm^{-3}

The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs corresponding to reciprocal levels *hkl*, h=0 to 5, using Cu$K\alpha$ radiation from a nearly cylindrical specimen of mean diameter 0.3 mm cut and ground along the *a* axis. The *hk*0 and *hk*1 data were also collected to facilitate interlevel scaling. The intensities were visually estimated by comparison with a calibrated film strip.

The intensities were corrected for Lorentz and polarization effects and for spot-shape differences, and they were reduced to structure factors without corrections for absorption. The structure factors for various layers were placed on a common scale by correlating those of the equivalent reflections. A total of 1019 observed independent structure factors were thus prepared for use in the structure analysis. Then these structure factors were put on an absolute scale by Wilson's method[2] which gave an overall temperature factor of 3.75 Å^2.

STRUCTURE DETERMINATION and REFINEMENT

The normalized structure factors, $E(hkl)$, were calculated. A statistical test of the distribution of the normalized structure factors gave a strong indication for a noncentrosymmetry.

The sulfur-sulfur Harker peak was easily identified, and a search for inter- and intramolecular sulfur to light atom vectors suggested positions for the thirteen atoms except the five carbon atoms of the piperidyl group in the molecule.

Structure factors using the approximate coordinates for the thirteen atoms were computed and the R value for the 785 largest of them was 0.32. The remaining 5 atoms exclusive of the hydrogen atoms in an asymmetric unit were located in a three-dimensional Fourier synthesis phased on the atomic parameters of the thirteen

atoms. Three cycles of isotropic block diagonal least-squares refinement[3] reduced the R value to 0.12.

At this stage a three-dimensional difference Fourier synthesis was computed using only low-order reflections with $\sin\theta/\lambda<0.35$. The subsequent map showed peaks for all the 17 hydrogen atoms in plausible positions although there were some spurious peaks. One cycle of least-squares refinement of the positional parameters of the hydrogen atoms with all fixed $B=3.0$ Å^2 and with fixed positional and thermal parameters for the heavier atoms gave a final R value of 0.10.

The weighting scheme proposed by Cruickshank[4] was used. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=(1.00+|F_o|+0.045|F_o|^2)^{-1}$. The atomic scattering factors were taken from International Tables for X-ray Crystallography[5].

The final positional and thermal parameters of the atoms are listed in *Table* 1 together with their estimated standard deviations.

The computation described were performed on an IBM 1130 computer using programs written by Shiono[3].

The observed and calculated structure factors are compared in *Table* 2.

DISCUSSION

The intramolecular bond lengths and angles are listed in *Table* 3 and shown in *Fig.* 1, which also indicates the atomic numbering.

The C—C bond lengths in the benzene ring vary from 1.36 to 1.43 Å with a mean value of 1.39 Å, which shows good agreement with the value of 1.395 Å quoted for the mean aromatic C—C bond length.

Bond lengths and angles in the piperidyl group correspond to normal values, and the ring has the chair form. The C(2)—N(1)—C(6) angle is in agreement with the value found in 1-*p*-(oximinoethyl)phenoxyacetylpiperidine[6].

The bond lengths found in the thiosemicarba-

Table 1. Final positional and isotropic thermal parameters in salicylaldehyde-4-piperidinothiosemicarbazone. (Key to atomic numbering is given in *Fig.* 1. The estimated standard deviations given in parentheses refer6 to the last decimal positions.)

Atom	x	y	z	B
S	0.2470(5)	0.6929(2)	0.6804(2)	4.70(5)
N(1)	0.498(1)	0.8189(7)	0.7641(6)	4.9(2)
N(2)	0.629(1)	0.7408(6)	0.6425(5)	4.1(2)
N(3)	0.609(1)	0.6763(6)	0.5687(5)	3.9(2)
C(1)	0.465(2)	0.7546(7)	0.6961(6)	3.8(2)
C(2)	0.337(2)	0.8446(9)	0.8275(9)	5.7(3)
C(3)	0.406(2)	0.8268(9)	0.9231(8)	5.1(2)
C(4)	0.605(2)	0.8799(9)	0.9431(9)	5.7(3)
C(5)	0.775(2)	0.8527(8)	0.8754(7)	5.1(2)
C(6)	0.692(2)	0.8729(8)	0.7798(8)	5.2(3)
C(7)	0.776(2)	0.6427(7)	0.5386(6)	4.2(2)
C(8)	0.765(2)	0.5724(6)	0.4615(5)	3.5(2)
C(9)	0.941(2)	0.5223(9)	0.4374(8)	5.2(3)
C(10)	0.933(2)	0.4533(10)	0.3644(9)	5.9(3)
C(11)	0.748(2)	0.4351(8)	0.3205(7)	5.0(2)
C(12)	0.575(2)	0.4847(8)	0.3436(7)	4.9(2)
C(13)	0.586(2)	0.5567(7)	0.4148(6)	3.5(2)
O	0.407(1)	0.6044(5)	0.4369(4)	4.1(1)
H(N2)	0.75	0.78	0.64	
H(C2)	0.21	0.78	0.82	
H′(C2)	0.27	0.92	0.82	
H(C3)	0.44	0.74	0.92	
H′(C3)	0.28	0.84	0.97	
H(C4)	0.60	0.96	0.93	
H′(C4)	0.65	0.86	0.00	
H(C5)	0.74	0.78	0.88	
H′(C5)	0.88	0.91	0.89	
H(C6)	0.79	0.85	0.75	
H′(C6)	0.64	0.93	0.77	
H(C7)	0.91	0.67	0.56	
H(C9)	0.06	0.54	0.47	
H(C10)	0.06	0.42	0.35	
H(C11)	0.75	0.38	0.26	
H(C12)	0.46	0.48	0.31	
H(O)	0.42	0.64	0.48	

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

h=0	k=0	15	5.86	4.70	17	3.47	3.51	1	4.25	5.54	16	5.22	4.62	h=1	k=6
2	11.81	10.78	16	5.28	4.69	h=0	k=8	6	4.89	4.92	17	6.41	6.17	1	14.08	14.90
4	45.76	39.05	18	7.05	6.03	0	20.34	19.20	7	6.55	7.61	18	3.94	3.95	2	5.44	5.08
6	3.89	4.35	h=0	k=4		1	7.25	8.10	h=0	k=15		h=1	k=3		3	40.82	38.97
8	74.53	70.48	0	29.51	34.65	2	8.30	9.50	3	6.97	9.57	0	55.96	55.78	4	30.98	29.19
10	25.53	27.34	1	1.75	0.42	3	10.42	10.54	6	3.64	3.46	1	67.97	68.16	5	54.71	45.53
12	6.61	6.29	2	43.15	39.67	5	11.47	11.34	h=0	k=16		2	73.08	70.60	6	18.92	18.87
16	9.22	9.93	3	51.07	51.31	7	5.78	6.03	0	10.17	9.82	3	22.28	22.61	7	11.14	10.59
h=0	k=1	4	38.32	38.83	8	13.75	13.54	2	4.05	4.63	4	20.92	17.79	9	12.64	11.27
1	53.21	46.66	5	35.82	36.27	9	5.72	4.08	h=1	k=0		5	9.64	7.96	11	15.81	12.77
2	32.31	29.87	6	36.48	34.58	10	6.16	6.48	1	85.20	80.43	6	24.92	24.53	13	7.89	7.42
3	6.55	4.83	7	40.57	37.62	12	12.97	12.95	2	59.55	54.93	7	36.07	32.01	h=1	k=7	
4	26.56	26.82	8	9.19	6.74	13	4.50	5.05	4	78.11	69.86	8	6.28	4.95	1	30.59	28.85
5	22.00	20.83	9	22.92	23.48	14	8.67	9.43	5	24.53	21.64	9	17.22	16.98	2	4.27	5.24
6	11.75	9.42	10	6.25	6.58	h=0	k=9		6	15.95	13.50	10	7.75	8.62	3	12.61	9.59
8	12.92	15.70	11	5.08	4.57	1	10.08	12.11	10	5.47	4.07	11	7.19	7.88	4	29.31	27.16
9	34.59	36.29	15	3.94	5.33	2	4.77	6.72	11	5.86	4.75	12	5.30	5.84	5	9.55	10.02
10	5.89	6.88	18	5.66	4.38	3	14.64	15.44	12	17.75	17.05	13	8.19	7.17	6	15.11	15.05
11	13.95	12.34	h=0	k=5		4	8.30	7.77	13	7.61	8.84	14	7.94	7.05	7	17.06	15.14
12	4.19	5.31	1	27.67	25.53	5	6.33	6.92	16	8.25	7.43	15	7.19	8.22	8	13.70	12.54
13	11.61	11.02	2	46.74	45.68	6	6.16	7.98	17	5.36	4.19	16	7.94	7.13	9	8.03	8.47
15	5.55	4.82	3	9.11	8.94	9	8.94	9.04	h=1	k=1		17	7.14	4.84	10	9.83	8.24
16	3.55	3.84	4	6.64	4.39	10	6.50	7.57	0	34.29	34.12	h=1	k=4		11	5.91	4.13
18	4.14	3.12	5	3.97	4.82	11	4.75	7.23	1	41.10	38.01	0	38.90	36.01	12	8.97	8.07
h=0	k=2	6	27.90	24.11	h=0	k=10		2	32.31	29.63	1	14.81	16.41	14	5.55	4.93	
0	42.74	44.12	7	13.36	10.80	0	6.30	7.60	3	42.54	39.11	2	18.23	16.19	h=1	k=8	
1	44.68	43.00	9	10.89	11.65	1	4.25	4.33	4	29.42	30.01	3	23.14	25.45	0	15.89	20.69
2	66.66	62.88	10	21.03	22.05	2	4.50	5.54	5	29.67	28.68	4	12.17	15.35	1	8.58	9.86
3	37.04	35.73	11	5.39	5.37	4	5.86	5.97	6	21.23	18.91	5	26.98	26.05	2	22.56	22.54
4	6.69	4.40	12	5.30	6.08	7	6.55	8.14	7	45.57	43.71	6	25.53	22.70	4	16.89	17.70
5	68.61	66.83	18	8.42	6.79	8	8.97	11.57	8	13.03	12.65	7	7.94	8.33	6	8.97	8.36
6	15.14	18.06	h=0	k=6		9	12.19	12.97	9	34.79	30.44	9	13.20	11.83	7	12.11	8.86
7	30.40	28.73	0	28.48	26.23	12	5.97	5.94	10	7.47	8.01	10	18.39	16.02	8	16.86	17.48
8	6.86	7.21	1	57.96	49.54	15	2.86	3.50	12	8.42	6.67	11	19.73	15.87	9	7.55	7.46
10	9.97	9.81	2	8.44	7.09	h=0	k=11		13	27.09	22.22	12	6.78	6.40	10	10.53	11.26
11	5.30	4.65	5	39.57	34.83	2	6.36	7.51	14	8.00	6.84	13	8.39	8.94	11	7.22	5.98
13	11.36	10.16	6	4.69	4.87	3	6.03	8.65	15	8.11	7.06	15	6.22	6.71	12	12.31	11.20
14	4.33	4.52	7	23.26	22.39	4	6.11	6.90	16	8.22	6.59	17	5.55	3.99	16	4.25	3.63
15	5.41	4.88	8	4.66	5.61	8	7.25	6.45	18	4.50	3.26	h=1	k=5		h=1	k=9	
16	7.05	7.02	9	6.94	7.98	10	10.25	9.98	h=1	k=2		0	5.25	5.23	0	23.26	24.28
18	2.80	2.31	10	3.61	3.21	11	8.14	8.22	0	15.08	15.95	1	12.36	10.65	1	24.76	25.94
h=0	k=3	11	5.05	5.23	h=0	k=12		1	65.77	64.24	2	31.73	33.68	2	14.25	15.50	
1	3.75	5.95	12	10.97	10.62	0	4.05	5.19	2	48.40	46.43	3	32.51	28.76	4	5.64	7.13
2	128.38	166.01	15	5.89	5.77	1	6.44	9.12	3	60.69	61.32	4	17.14	16.56	5	7.25	7.07
3	109.32	120.83	17	2.86	2.58	5	7.50	12.21	4	56.05	50.87	5	53.46	47.02	6	7.78	7.83
4	13.31	15.26	h=0	k=7		7	4.41	5.74	5	32.54	30.50	6	44.35	40.98	7	18.48	17.73
5	43.57	44.37	2	17.42	18.06	9	5.22	6.27	6	8.64	6.17	7	16.61	14.14	8	13.53	12.20
6	37.76	38.78	3	12.36	12.17	13	3.72	5.37	7	6.75	7.11	8	10.89	11.87	11	8.14	7.77
7	28.81	28.53	4	26.20	26.68	h=0	k=13		8	10.33	8.35	9	5.69	7.59	h=1	k=10	
8	9.50	11.88	6	12.44	10.48	3	4.52	4.43	9	23.73	22.81	10	12.00	9.58	0	6.16	5.43
10	20.14	19.49	7	13.42	14.31	4	7.00	8.80	10	5.94	6.82	11	9.44	6.38	1	11.14	10.98
11	6.36	6.11	9	8.58	7.39	6	8.50	10.07	11	33.37	28.30	13	10.08	7.38	2	8.42	10.16
12	4.25	2.75	10	8.39	8.73	h=0	k=14		12	16.47	14.35	14	19.20	16.22	3	16.22	13.78
13	4.61	3.61	11	11.69	12.70	0	4.91	6.86	14	6.03	6.05	15	5.22	3.81	4	13.33	14.93

5	13.50	11.54	12	5.02	4.46	1	44.21	40.19	2	17.20	15.91	7	4.02	5.08	1	16.61	14.35
6	5.83	6.98	13	7.44	9.67	2	5.28	7.80	3	14.25	13.06	h=2		k=15	2	27.76	27.46
7	7.61	7.00	14	20.70	20.34	3	19.50	21.76	4	5.25	5.44	0	7.14	7.31	3	15.81	16.26
8	13.00	12.62	17	4.22	4.19	4	3.61	3.50	5	16.34	15.75	1	4.55	4.72	4	5.86	8.21
12	4.77	4.55	h=2		k=1	6	11.31	12.03	6	25.23	25.90	3	5.05	5.98	5	21.75	21.95
h=1		k=11	0	3.80	3.64	7	18.92	19.23	7	26.81	24.64	h=3		k=0	6	9.11	9.24
0	9.72	8.31	1	13.47	12.42	8	5.00	5.99	8	23.87	24.17	2	32.29	36.88	8	11.50	12.26
1	9.30	9.10	2	44.38	45.62	9	7.03	6.45	9	4.27	5.45	3	10.22	8.91	9	8.61	9.82
3	5.05	4.76	3	22.50	23.02	11	12.03	10.65	10	4.58	4.88	4	16.97	15.32	10	9.97	11.24
5	10.67	12.23	4	9.28	9.58	12	7.44	7.39	11	5.30	4.83	5	14.72	10.78	11	3.50	4.58
6	10.25	10.67	5	20.75	18.29	13	6.05	8.59	14	7.30	8.00	6	15.59	17.71	12	9.36	9.21
8	5.02	6.46	6	5.53	3.63	15	6.00	5.82	16	3.77	4.10	7	5.28	6.85	13	8.75	8.93
14	6.69	5.69	7	3.72	3.91	h=2		k=5	h=2		k=9	8	3.33	3.93	14	4.61	5.53
h=1		k=12	8	8.25	10.38	0	20.62	22.51	1	10.17	11.62	10	15.08	14.96	16	6.33	5.71
0	5.97	6.41	9	14.70	14.36	1	10.81	10.50	3	18.03	18.33	11	5.53	4.33	h=3		k=4
1	13.64	13.79	10	6.25	6.61	2	27.81	25.96	5	15.36	15.30	12	4.33	4.97	0	10.78	10.42
2	8.19	9.80	11	4.58	5.68	3	6.30	5.52	6	8.03	9.70	14	3.02	3.72	1	17.25	15.45
3	5.11	5.86	14	6.11	6.01	4	36.57	35.24	7	6.00	6.75	15	5.66	4.19	2	23.39	22.00
4	4.83	4.90	15	8.25	8.77	5	15.84	16.76	11	5.14	5.41	16	2.69	3.79	3	15.97	16.68
9	6.25	5.41	17	5.55	4.64	6	9.86	10.49	12	3.75	2.80	17	2.64	1.81	4	6.28	7.34
10	4.58	4.31	h=2		k=2	7	14.53	17.19	h=2		k=10	h=3		k=1	5	19.89	21.06
13	2.94	3.03	0	34.45	36.39	8	18.09	19.81	1	14.17	15.45	0	19.28	14.31	6	9.33	9.68
h=1		k=13	1	42.43	39.68	9	10.25	8.60	2	13.36	15.13	1	25.31	22.23	7	6.83	7.83
0	19.14	17.91	2	4.64	6.70	10	14.08	15.94	3	10.00	11.76	2	21.25	19.18	8	9.14	9.72
2	8.89	8.44	3	6.08	5.97	11	10.28	10.99	5	13.86	12.53	3	9.80	9.99	9	18.23	18.69
3	4.72	4.98	4	46.54	40.20	12	16.11	13.54	6	6.05	8.38	4	34.09	30.99	10	5.58	5.89
6	7.80	8.97	5	22.25	21.89	16	4.47	4.16	7	5.64	4.88	5	5.53	6.04	12	3.80	5.53
7	6.25	6.09	6	33.70	33.16	h=2		k=6	8	5.61	8.62	6	16.28	17.28	13	4.36	5.36
8	10.36	10.64	7	18.98	20.01	0	6.36	7.15	10	6.47	8.14	7	24.84	27.11	16	2.41	2.05
h=1		k=14	8	9.42	8.60	1	39.43	34.51	12	4.33	4.53	8	4.33	5.87	17	3.52	3.49
0	5.30	3.50	9	17.42	18.12	2	10.39	7.94	13	5.30	4.66	9	5.97	6.56	h=3		k=5
1	6.66	6.73	11	12.06	12.47	3	20.28	18.64	h=2		k=11	10	8.25	8.38	0	74.86	72.10
2	4.66	4.15	12	13.22	13.31	4	17.34	16.50	2	4.55	4.12	11	10.03	9.81	1	2.50	3.74
3	6.53	6.99	13	9.22	9.84	5	10.56	10.39	3	21.17	21.61	12	12.14	11.34	2	7.94	9.23
4	4.72	5.33	14	7.14	5.26	6	13.81	13.45	4	10.39	11.18	14	5.61	6.41	3	4.66	5.06
5	4.77	4.34	15	7.44	7.90	7	16.89	15.63	5	17.64	16.67	15	5.66	6.07	4	8.58	9.58
h=1		k=15	h=2		k=3	8	11.94	11.32	9	6.44	7.71	17	2.25	1.80	5	9.83	10.77
2	5.97	6.40	0	13.08	11.62	9	18.00	18.95	10	9.86	9.28	h=3		k=2	6	6.00	8.37
h=1		k=16	1	24.62	26.23	10	10.19	9.26	11	8.86	10.01	0	7.92	8.43	7	7.55	7.29
0	6.11	4.23	2	26.37	26.50	13	5.44	7.42	12	4.44	4.23	1	11.72	8.99	8	29.29	31.28
2	5.05	5.39	3	38.07	36.27	17	3.27	3.71	h=2		k=12	2	47.32	48.72	9	23.14	23.95
3	4.66	5.27	4	42.01	35.30	h=2		k=7	0	4.30	6.16	3	31.87	34.25	10	6.05	8.83
4	4.77	4.83	5	6.66	5.58	0	3.52	1.39	1	11.69	13.42	4	4.22	4.59	11	5.39	5.39
6	3.05	5.15	6	16.36	16.88	1	9.30	8.67	2	10.39	11.94	5	14.81	16.72	12	5.05	5.36
h=2		k=0	7	8.11	9.75	2	11.33	11.20	4	6.58	7.95	6	15.28	16.20	13	4.66	4.65
0	37.29	38.57	8	14.17	15.29	3	28.81	28.77	10	5.50	5.72	7	5.75	5.65	16	5.83	5.79
1	5.80	5.96	9	10.86	10.24	4	10.72	11.95	h=2		k=13	8	6.33	7.12	h=3		k=6
2	22.20	25.45	10	13.39	14.44	5	20.28	22.09	0	8.05	7.45	9	8.83	9.59	0	16.56	16.22
3	44.71	43.11	11	14.70	16.22	6	10.69	11.87	2	5.22	5.54	10	14.64	14.72	1	22.89	22.22
4	2.33	1.17	12	18.03	17.68	7	6.91	6.85	3	4.36	4.56	11	17.95	20.02	2	5.47	7.82
5	21.62	22.70	13	5.86	6.75	8	10.22	10.89	8	4.52	4.51	12	3.80	5.34	3	15.20	16.24
6	58.41	55.42	14	5.78	5.66	9	9.25	7.78	10	3.72	4.67	14	3.14	3.37	4	12.42	11.94
7	23.14	21.07	16	4.64	5.45	10	10.36	12.36	h=2		k=14	16	3.39	3.39	5	10.31	10.08
8	16.00	12.42	17	6.28	6.15	h=2		k=8	0	10.31	11.27	17	4.19	3.28	7	14.78	15.06
10	5.72	6.30	h=2		k=4	0	19.25	17.85	1	6.80	7.05	h=3		k=3	8	13.00	14.68
11	12.08	12.67	0	47.54	44.52	1	18.59	20.14	2	5.75	4.40	0	20.89	21.60	9	12.42	15.42

10	9.11	9.23
11	10.08	10.42
12	5.41	6.01
16	3.05	2.29
h=3		k=7
1	10.11	11.84
3	18.81	18.64
5	18.70	17.67
6	8.97	9.65
7	11.86	11.77
8	7.28	8.97
10	4.47	4.76
11	4.19	4.72
13	4.89	5.15
15	3.66	3.28
h=3		k=8
1	4.86	7.05
2	15.53	16.35
3	18.61	18.88
4	8.47	10.66
5	5.58	6.63
6	20.45	21.15
7	10.11	13.53
8	8.78	10.66
9	4.66	6.04
10	12.42	12.32
12	7.08	6.94
h=3		k=9
0	12.42	11.67
1	16.86	15.62
2	8.69	11.00
3	2.52	1.58
4	5.16	5.54
5	6.78	6.90
6	17.45	19.05
7	13.78	13.89
8	4.44	6.54
9	7.08	7.60
11	5.58	4.66
12	4.05	3.77
14	3.97	4.34
h=3		k=10
0	2.61	1.59
1	3.05	2.51
2	9.78	10.58
3	9.94	10.64
4	3.77	5.86
5	3.66	4.66
6	9.36	11.97
10	6.64	7.82
11	5.64	5.69
12	4.80	3.58
h=3		k=11
0	3.55	5.49
1	12.56	12.30
2	2.83	3.04
3	3.27	5.26
4	3.39	5.18
5	3.52	6.18
6	4.14	4.73
7	4.94	6.10
8	7.61	8.73
9	9.19	8.49
12	4.50	4.34
h=3		k=12
0	2.77	4.37
1	3.94	3.87
2	4.39	4.57
3	4.25	5.25
4	11.36	12.07
5	4.64	6.48
h=3		k=13
0	6.69	7.42
1	3.77	4.14
3	4.69	5.69
6	5.33	5.74
8	4.16	5.07
h=3		k=14
0	3.89	3.42
1	4.55	4.58
2	2.72	2.88
3	4.69	6.01
4	3.08	3.62
5	2.47	2.40
h=3		k=15
1	4.41	3.51
h=3		k=16
0	2.61	2.68
2	1.77	2.00
h=4		k=0
0	20.53	17.08
1	4.64	3.68
2	47.13	35.98
3	6.16	7.68
4	17.78	16.80
6	26.98	26.51
8	3.77	3.89
9	4.86	5.41
10	9.05	7.99
12	4.75	4.40
13	6.08	5.25
14	21.56	17.60
15	7.41	5.95
16	2.22	1.65
h=4		k=1
0	4.00	4.89
1	4.39	3.09
2	8.25	8.59
3	8.53	8.54
4	6.69	6.90
5	27.53	25.83
6	2.94	4.62
8	5.78	5.62
9	13.36	11.00
10	4.66	4.13
11	14.45	12.95
13	13.06	12.12
14	3.97	3.17
15	4.30	3.76
h=4		k=2
0	16.56	13.58
1	12.53	13.54
2	16.34	19.42
3	11.61	12.10
4	9.55	9.67
5	11.28	9.33
6	6.50	5.69
7	23.95	19.66
8	13.36	11.01
9	13.25	13.85
10	8.36	7.92
11	5.30	5.54
12	3.41	3.40
13	6.33	5.18
14	6.66	6.46
15	5.36	4.26
16	3.30	2.77
h=4		k=3
0	8.33	10.81
1	1.38	2.31
2	8.55	8.48
3	14.42	15.83
4	22.39	22.35
5	9.67	12.57
6	12.64	10.32
7	8.61	9.28
8	4.75	5.93
9	2.97	3.86
10	4.19	4.24
11	15.36	14.60
12	8.44	8.48
13	2.00	1.63
14	3.39	3.17
15	6.25	4.13
16	7.22	5.47
h=4		k=4
1	2.80	2.07
2	4.69	5.91
3	4.25	4.83
4	4.22	3.99
5	16.67	13.94
6	6.80	5.14
7	26.12	21.76
8	15.67	14.53
9	6.39	6.11
10	5.41	5.80
11	3.00	4.78
12	3.36	4.04
13	8.61	6.33
15	3.94	4.37
16	4.00	3.55
h=4		k=5
1	7.94	5.92
2	8.11	7.70
3	9.00	9.71
4	28.20	24.31
5	4.41	4.16
6	14.61	10.30
7	6.28	4.91
8	6.94	7.53
9	6.47	6.91
10	4.36	3.37
11	4.80	5.44
12	8.69	8.61
14	3.52	2.11
15	2.41	1.36
h=4		k=6
0	10.53	7.75
1	7.83	7.30
2	14.08	12.90
3	8.61	8.91
4	6.05	8.14
5	16.06	16.00
7	4.14	5.36
8	6.86	7.24
9	11.03	10.74
10	3.00	2.69
11	2.77	2.42
13	7.50	6.75
15	3.75	2.83
h=4		k=7
0	9.69	11.03
1	4.80	4.95
3	14.56	12.74
4	6.66	5.83
5	9.86	12.19
7	7.69	6.46
8	4.44	5.72
9	10.03	7.51
10	9.75	9.98
11	4.36	3.86
h=4		k=8
0	18.70	17.09
1	8.19	8.35
2	12.28	11.05
3	4.33	4.44
4	3.89	2.17
5	6.91	5.48
6	13.50	14.03
7	8.30	7.82
8	8.94	6.77
9	5.61	3.89
10	3.39	3.98
11	4.52	3.59
12	2.55	1.68
14	5.72	5.23
h=4		k=9
1	3.05	3.92
3	12.08	10.72
4	5.25	4.87
5	7.92	5.49
6	4.44	4.72
7	5.69	6.03
9	4.27	3.66
10	4.72	4.61
11	3.16	2.76
13	2.02	2.53
h=4		k=10
0	3.14	4.78
1	5.28	4.99
2	8.53	9.67
3	5.75	8.71
4	7.72	6.88
5	14.11	13.62
6	7.61	6.13
7	6.89	6.05
9	3.64	4.41
12	4.80	4.59
h=4		k=11
0	9.69	8.40
2	3.25	3.68
3	11.58	10.74
4	11.83	11.63
8	3.66	2.46
9	3.97	3.81
10	2.91	3.52
11	4.97	4.01
h=4		k=12
0	2.83	2.59
1	5.25	4.64
2	5.94	3.65
4	6.00	5.83
5	4.11	5.46
7	4.36	4.70
9	2.50	2.05
10	2.33	2.31
h=4		k=13
0	7.03	7.67
1	2.91	3.43
2	7.47	6.69
3	4.55	3.36
4	6.55	7.09
6	4.11	3.72
8	2.94	3.50
h=4		k=14
0	5.00	4.96
1	5.75	6.62
2	8.19	7.75
5	2.02	3.12
6	1.91	1.61
h=4		k=15
0	2.27	0.32
1	2.61	2.06
2	2.91	3.61
h=5		k=0
1	4.44	4.81
2	27.90	33.33
3	9.05	13.23
4	20.67	22.04
5	4.89	4.82
6	3.61	4.26
8	7.86	8.89
10	10.14	10.45
12	5.94	4.98
13	2.77	3.06
14	2.77	2.32
h=5		k=1
0	9.08	11.21
1	27.15	24.09
2	3.94	7.24
3	7.22	7.17
4	9.22	8.68
5	7.66	9.62
6	6.47	3.18
7	13.92	12.40
9	11.81	11.90
10	5.89	6.01
12	2.86	2.81
14	2.75	2.49
15	2.58	1.94
h=5		k=2
0	22.84	19.43
2	5.33	6.13
3	18.89	18.81
4	22.14	19.15
5	6.11	7.73
6	6.72	5.38
7	2.77	2.39
8	4.39	5.00
9	3.69	3.47
10	4.39	4.85
11	7.08	7.49
12	5.53	4.98
15	2.58	2.57
h=5		k=3
0	33.04	25.32
1	20.03	20.34
2	15.67	14.68
3	7.03	7.68
4	17.20	16.74
5	16.39	15.42
6	11.14	11.04
7	8.83	8.71
8	9.75	9.53
9	6.97	7.61
10	2.72	2.60

12	7.30	5.94	8	8.50	8.17	6	8.92	8.47	3	3.16	2.18	7	4.14	3.27	0	10.00	8.20
14	2.80	2.32	11	5.55	3.69	7	7.19	5.18	4	2.72	2.09	8	4.36	4.62	1	12.25	8.22
15	5.91	4.52	14	5.69	5.38	9	6.64	5.90	5	5.83	4.22	9	2.47	3.26	2	11.22	9.95
h=5		k=4	h=5		k=6	10	3.30	3.31	7	9.61	7.25	h=5		k=12	3	6.11	5.30
1	9.58	7.80	0	3.11	2.26	11	5.55	3.04	8	2.75	3.00	1	4.86	4.63	4	16.00	11.66
2	12.67	12.34	1	5.64	5.48	12	3.00	2.62	9	2.66	1.81	3	3.97	3.36	6	9.55	7.78
3	4.50	3.80	2	6.39	2.85	13	3.55	2.95	11	2.00	2.41	5	4.83	2.95	10	6.08	4.00
4	5.94	6.78	3	21.48	20.36	h=5		k=8	h=5		k=10	6	2.16	2.35	h=7		l=0
5	6.94	5.77	4	6.83	5.80	0	4.91	3.28	3	3.25	3.68	7	4.16	2.37	3	6.72	4.83
6	4.86	5.01	5	14.86	12.44	1	4.61	3.87	4	2.77	1.87	h=5		k=13	5	6.33	4.06
7	4.86	5.71	7	8.11	6.20	2	9.05	7.08	5	2.83	1.97	0	4.69	4.59	9	3.39	4.53
9	9.33	6.00	9	8.47	8.40	3	3.36	3.70	6	4.89	3.98	1	2.50	2.34	h=7		l=1
11	6.14	4.95	10	7.16	5.71	4	3.86	4.06	7	2.89	3.04	4	3.02	1.96	0	9.80	6.36
h=5		k=5	13	4.44	2.92	6	7.05	7.11	8	2.89	2.30	h=6		l=0	2	5.00	3.16
0	17.45	15.04	h=5		k=7	8	3.19	3.13	9	7.97	4.48	0	43.07	32.30	7	6.97	5.15
1	5.08	5.24	0	2.33	2.07	9	7.11	5.03	10	3.08	3.03	1	8.36	10.83	9	6.64	4.96
2	8.53	8.37	1	2.22	1.39	10	4.55	4.95	h=5		k=11	8	10.97	9.83	h=8		l=0
3	10.69	9.42	2	3.77	3.52	12	4.66	4.09	0	5.89	5.39	9	6.47	5.26	0	9.17	6.59
5	4.80	4.81	3	2.16	1.44	h=5		k=9	1	2.83	2.64	10	3.97	3.35	h=8		l=1
6	13.97	13.07	4	3.52	3.18	1	7.08	6.53	2	2.94	2.22	11	5.72	4.77	1	4.55	3.48
7	3.22	3.71	5	2.83	4.55	2	2.58	2.67	4	2.97	2.31	h=6		l=1	2	4.41	3.25

Table 3. Bond lengths and angles in salicylaldehyde-4-piperidinothiosemicarbazone. The estimated standard deviations are shown in parentheses.

Bond length(Å)		Bond angle(°)	
C(1)—S	1.66(1)	S——C(1)—N(1)	124.1(8)
C(1)—N(1)	1.35(1)	S——C(1)—N(2)	121.8(8)
C(1)—N(2)	1.35(1)	N(1)—C(1)—N(2)	114.1(9)
C(2)—N(1)	1.46(2)	N(1)—C(2)—C(3)	110.9(11)
C(2)—C(3)	1.52(2)	C(2)—C(3)—C(4)	111.6(10)
C(3)—C(4)	1.51(2)	C(3)—C(4)—C(5)	112.1(10)
C(4)—C(5)	1.54(2)	C(4)—C(5)—C(6)	108.1(10)
C(5)—C(6)	1.55(2)	N(1)—C(6)—C(5)	111.0(10)
C(6)—N(1)	1.48(2)	N(3)—C(7)—C(8)	117.3(9)
C(7)—N(3)	1.26(1)	C(7)—C(8)—C(9)	118.1(10)
C(7)—C(8)	1.49(1)	C(7)—C(8)—C(13)	122.1(9)
C(8)—C(9)	1.38(2)	C(9)—C(8)—C(13)	119.8(10)
C(8)—C(13)	1.37(1)	C(8)—C(9)—C(10)	119.1(11)
C(9)—C(10)	1.43(2)	C(9)—C(10)—C(11)	120.1(12)
C(10)—C(11)	1.39(2)	C(10)—C(11)—C(12)	121.0(12)
C(11)—C(12)	1.36(2)	C(11)—C(12)—C(13)	118.4(11)
C(12)—C(13)	1.43(2)	C(8)—C(13)—C(12)	121.5(9)
C(13)—O	1.37(1)	C(8)—C(13)—O	121.9(9)
N(2)—N(3)	1.41(1)	C(12)—C(13)—O	116.5(9)
		C(1)—N(1)—C(2)	121.6(10)
		C(1)—N(1)—C(6)	124.8(10)
		C(2)—N(1)—C(6)	113.6(10)
		C(1)—N(2)—N(3)	118.5(8)
		C(7)—N(3)—N(2)	141.9(9)

zide side chain of various thiosemicarbazones have been tabulated in *Table* 4, together with the distances reported for related compounds. The C(7)—N(3) bond of 1.26 Å should be a double bond. The N(2)—N(3) bond of 1.41Å agrees well with the value reported in 2-formylpyridine selenosemicarbazone[7] and with the accepted single N—N bond length of 1.44 Å. On the other hand, in the structures of 4-formylpyridine thiosemicarbazone[8] and 5-hydroxy-2-formylpyridine thiosemicarbazone[9], the N—N bonds are 1.375 and 1.379 Å, which suggest that other canonical forms may be important. However, there is no evidence for the existence of these forms in this structure.

The C(1)—N(1) and C(1)—N(2) bond lengths of 1.35 Å are significantly shorter than a C(sp^2)—N bond, 1.446 Å, as calculated from the sum of the radii of C(sp^2) and N.[10,11] Thus, these C—N bonds possess some double bond character.

The C=S bond length of 1.66 Å, which is distinctly longer than the corresponding normal double bond, 1.59 Å, is indicative of partial double bond character. On Abraham's scale[12]

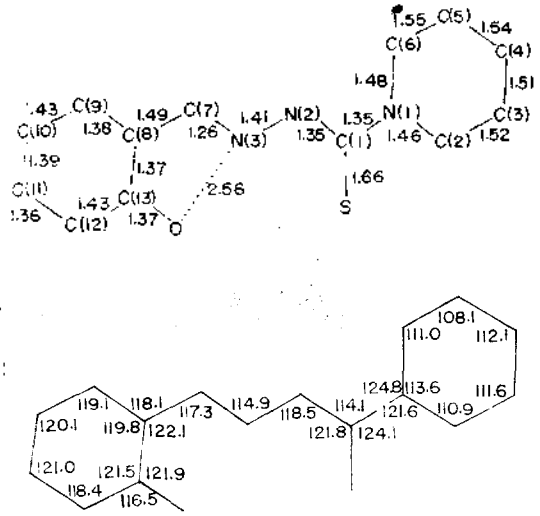

Fig. 1. Bond lengths (Å) and angles(°) in salicylaldehyde-4-piperidinothiosemicarbazone.

the C—S bond has approximately 75 % double bond character. There is a large variation(1.66 to 1.706Å) in the C=S bond lengths in various thiosemicarbazones given in *Table* 4. The lengthening of the C=S bond and the shortening of C—N bonds are a general property of thioureide, —N—C(=S)—N—, groups, which confirms conju-

Table 4. A comparison of the bond lengths(Å) found in thiosemicarbazones and related compounds.

	C(7)—N(3)	N(2)—N(3)	N(2)—C(1)	C(1)—S
Salicylaldehyde-4-piperidinothiosemicarbazone[13]	1.26(1)	1.41(1)	1.35(1)	1.66(1)
4-Formylpyridine thiosemicarbazone[8]	1.275(3)	1.375(3)	1.354(3)	1.678(2)
5-Hydroxy-2-formylpyridine thiosemicarbazone[9]	1.270(7)	1.379(6)	1.336(7)	1.706(6)
Acetone thiosemicarbazone[9]	1.286(7)	1.398(6)	1.342(6)	1.690(5)
2-Formylthiophene thiosemicarbazone[14]	1.282(4)	1.369(4)	1.343(4)	1.698(3)
2-Keto-3-ethoxybutyraldehyde thiosemicarbazone[15]	1.285(6)	1.371(6)	1.351(6)	1.692(4)
2-Formylpyridine selenosemicarbazone[7]	1.29(2)	1.41(2)	1.35(2)	
Acetone semicarbazone[16]	1.278(3)	1.385(2)	1.361(3)	
Benzaldehyde semicarbazone[16]	1.278(3)	1.378(3)	1.370(3)	
Thiosemicarbazide[17]		1.40	1.34	1.685
1-Phenyl thiosemicarbazide[18]		1.395(2)	1.330(2)	1.696(2)
4-Phenyl thiosemicarbazide[19]		1.431(6)	1.357(7)	1.685(5)
5-Chlorosalicylaldoxime[20]	1.237(16)			
Carbohydrazide[21]		1.416(2) 1.417(3)	1.350(2) 1.349(2)	

gation in them. This is confirmed by the planarity of —N—C(=S)—N—. Also, hydrogen bonds

are important in all the thiosemicarbazones and therefore, small differences in bond lengths may be purturbed by the different hydrogen-bonding patterns. Reference to *Table* 4 shows that the C=S bond in 5-hydroxy-2-formylpyridine thiosemicarbazone[9], of which the S atom is the acceptor for three hydrogen bonds, is the longest one observed in thiosemicarbazones in *Table* 4, while the C=S bond in salicylaldehyde-4-piperidinothiosemicarbazone[13], of which the S atom does not form any hydrogen bond, is the shortest one.

The detailed conformational angles are given in *Fig.* 2. The conformation around the C(1)—N(2) bond is interesting. In salicylaldehyde-4-piperidinothiosemicarbazone the C(1)—S bond is *cis* to the N(2)—N(3) bond, though the *trans* conformation is usually found in the thiosemicarbazones. The *cis* conformation presumably arises from intramolecular steric repulsions between N(3) and —C(6)H_2 group. This *cis* conformation could enable this molecule to function as a tridentate ligand which is O—N—S type.

The least-squares planes are listed in *Table* 5. The benzene ring is planar within the limits of experimental error. The oxygen atom is in this plane, but the C(7) atom is slightly out of it. The benzene ring plane makes an angle of 32.3° with the plane of thioureide group. The piperidyl ring takes a normal chair conformation. The atoms C(4) and N(1) deviate from the mean plane through C(2), C(3), C(5) and C(6) by 0.65 and −0.63 Å respectively. Also, N(1)-substituents, C(1), C(2) and C(6), lie on a plane with the N(1) atom. The planar structure of N(1)-substituents is found in similar compounds.

The crystal structure of salicylaldehyde-4-piperidinothiosemicarbazone projected along the *a* and *b* axes is shown in *Fig.* 3 and *Fig.* 4.

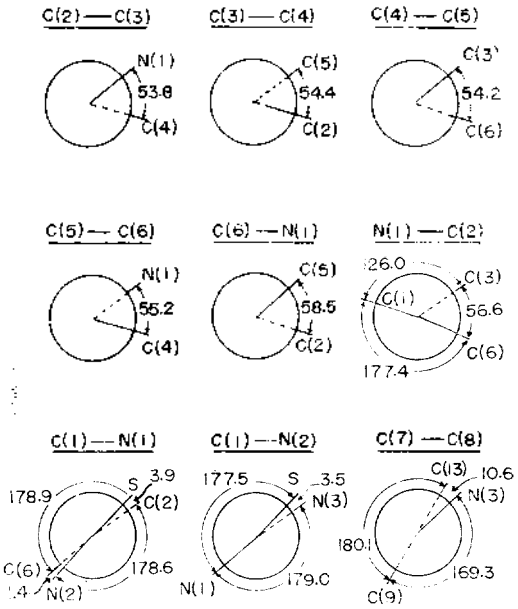

Fig. 2. Conformational angles in degrees in salicylaldehyde-4-piperidinothiosemicarbazone.

An examination for interatomic and intermolecular contacts revealed that the oxygen atom of the hydroxyl group is involved in two hydrogen bonds, one as donor in the intramolecular hydrogen bond and the other as acceptor in the intermolecular hydrogen bond. The internal hydrogen bond involving the hydroxyl oxygen and the N(3) atom has the distance of 2.56 Å and the hydrogen atom is 0.46 Å off the line of O···N centers, thereby making an O—H···N angle of 140.0°. The hydrogen bonding environment about the oxygen atom is shown in *Fig.* 5. On the other hand, the oxygen atom forms a hydrogen bond to the imino nitrogen atom of the other molecule related by the two fold screw axis parallel to the *a* axis, with the distance of 3.00 Å. The hydrogen atom deviates from a line of centers by 0.45 Å.

From *Fig.* 3 it may be seen that the molecules are joined by the hydrogen bonds involving

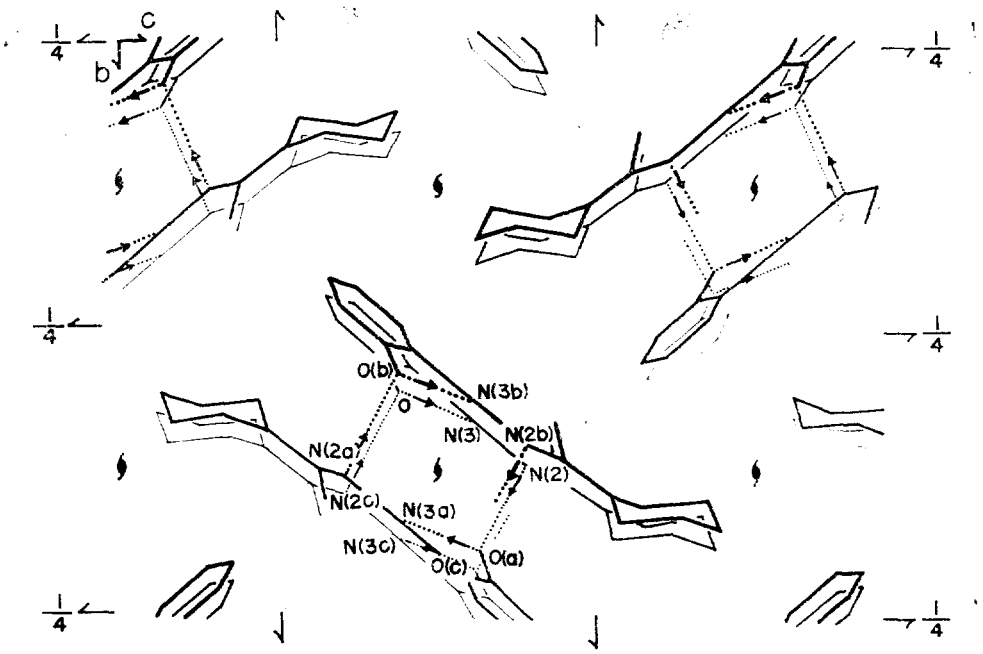

Fig. 3. The crystal structure of salicylaldehyde-4-piperidinothiosemicarbazone viewed down the *a* axis. Dotted lines are hydrogen bonds; arrows indicate donor direction.

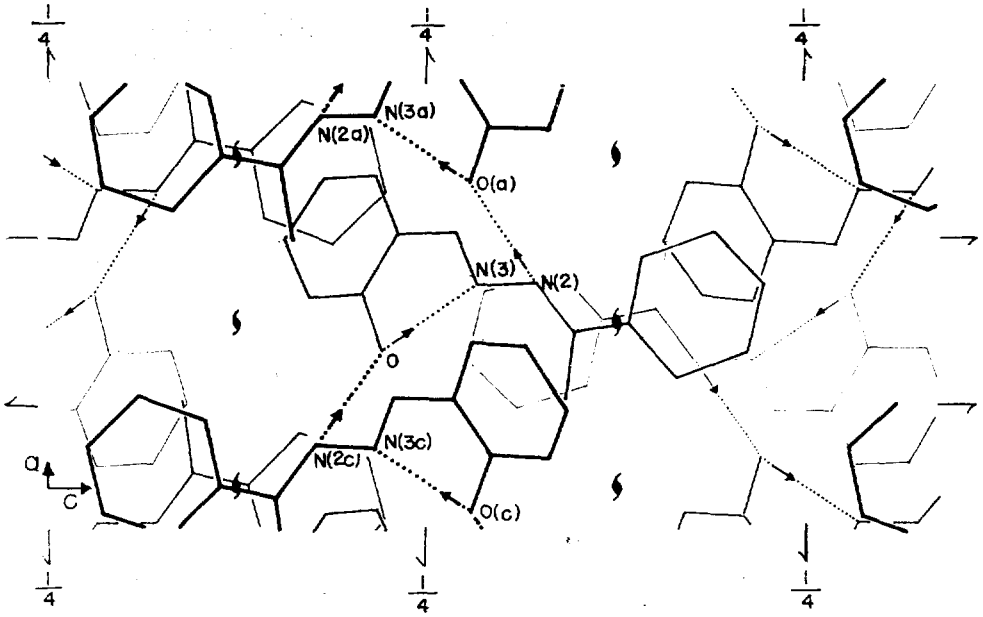

Fig. 4. The crystal structure of salicylaldehyde-4-piperidinothiosemicarbazone viewed down the *b* axis. Dotted lines are hydrogen bonds; arrows indicate donor direction.

Table 5. Least-squares planes in salicylaldehyde-4-piperidinothiosemicarbazone (Equation for plane: $Ax+By+Cz=D$, where x, y, z are in Å)

Atoms included in plane	Atoms not included in plane	Distance from best plane(Å)	Constant
A. Benzene ring			
C (8)		−0.01	$A=$ 0.228
C (9)		−0.01	$B=$ 0.726
C (10)		0.02	$C=-0.649$
C (11)		−0.01	$D=$ 2.260
C (12)		−0.01	
C (13)		0.02	
	N (3)	−0.27	
	C (7)	−0.06	
	O	0.00	
B. Thiosemicarbazone group			
S		−0.00	$A=-0.325$
N (1)		0.01	$B=$ 0.745
N (2)		−0.01	$C=-0.583$
C (1)		−0.01	$D=$ 0.487
	N (3)	0.03	
	C (2)	0.04	
	C (6)	−0.01	
	C (7)	−0.39	
C. Piperidyl group			
C (2)		−0.01	$A=-0.088$
C (3)		0.01	$B=$ 0.975
C (5)		−0.01	$C=$ 0.205
C (9)		0.01	$D=$ 13.399
	N (1)	−0.63	
	C (4)	0.65	
D. Piperidyl ring substitution			
N (1)		−0.01	$A=-0.304$
C (1)		0.01	$B=$ 0.747
C (2)		0.00	$C=-0.591$
C (6)		0.00	$D=$ 0.505
	S	−0.04	
	N (2)	0.01	
	N (3)	0.06	

N(2)—H···O into infinite columns along the *a* axis. The molecular columns are now held together by van der Waals forces.

All other intermolecular distances have normal values and some of the shortest approaches are shown in *Table* 6.

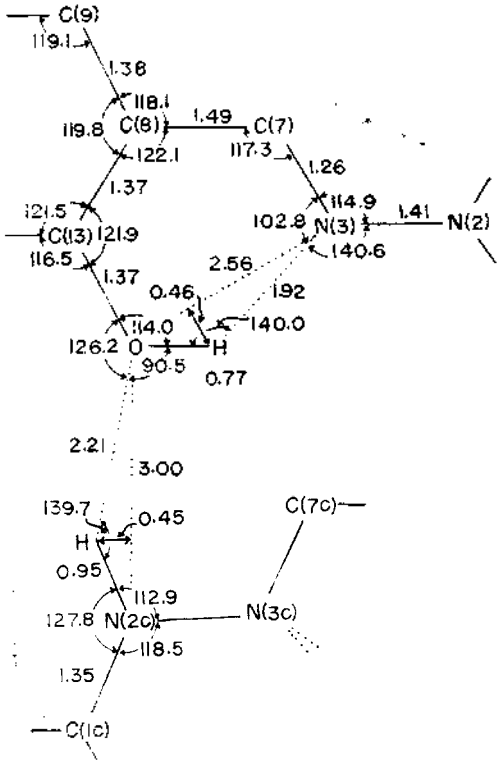

Fig. 5. Hydrogen-bonding environment about the oxygen atom. The dotted lines indicate hydrogen bonds.

Table 6. Some important inter-and intramolecular distances in salicylaldehyde-4-piperidino-thiosemicarbazone.

Hydrogen bonds	
O—H·····N (3)	2.56 Å
N (2)—H····· O (a)	3.00
Other shortest contacts	
C (9)····· O (b)	3.23 Å
C (6)····· C (10c)	3.59
C (4)····· C (13d)	3.42

Symmetry code:

	x,	y,	z
a	$\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$1-z$
b	$1+x$,	y,	z
c	$-\frac{1}{2}+x$,	$1\frac{1}{2}-y$,	$1-z$
d	$1-x$,	$\frac{1}{2}+y$,	$1\frac{1}{2}-z$

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