DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 17, No. 2, 1973.
Printed in Republic of Korea

Morpholinothiosemicarbazide의 結晶 및 分子構造

具廷會 · 金勳燮 · 申鉉昭* · 李榮子**

서울大學校 文理科大學 化學科

(1972. 12. 27 接受)

The Crystal and Molecular Structure of Morpholinothiosemicarbazide

Chung Hoe Koo, Hoon Sup Kim, Hyun So Shin* and **Yungja Lee****

Department of Chemistry, College of Liberal Arts and Sciences,
Seoul National University, Seoul, Korea

(Received Dec. 27, 1972)

요 약. 몰포리노치오세미카바자이드의 결정구조가 X—선해석에 의하여 결정되었다. 세포상수는 $a=4.19(2)$, $b=6.56(2)$, $c=26.67(4)$ A°이고, 단위세포는 4분자를 포함하며, 공간군은 $P2_12_12_1$이다. 원자좌표치는 최소자승법으로 정밀화 하였으며 R값은 651개의 관측반사를 써서 계산한 결과 0.07이다. 아미노 질소원자는 a-축에 평행한 2회의 나선축에 의하여 옮겨지는 다른 분자의 황원자와 3.48 및 3.49 A°의 수소결합을 하고 있으며 이미노 질소원자는 a-축에 평행한 2회의 나선축에 의하여 옮겨지는 다른 분자의 아미노 질소원자와 3.04 Å의 수소결합을 하고 있다. 이들 3개의 수소결합은 분자들을 2회의 나선축 부근에 배열하게 한다. 수소결합 이외로 분자들을 연결하는 힘은 van der Waals의 힘이다.

Abstract. The crystal structure of morpholinothiosemicarbazide has been determined by single crystal X-ray analysis. The lattice constants are $a=4.19(2)$, $b=6.56(2)$ and $c=26.67(4)$ Å. The unit cell contains 4 molecules and the space group is $P2_12_12_1$. The atomic parameters have been refined by least-squares method to a final R value of 0.07, based on the 651 observed reflexions. The amino nitrogen atom forms hydrogen bonds to the sulfur atoms of the other molecules related by the two-fold screw axis parallel to the a-axis, the distances of the hydrogen bonds being 3.48 and 3.49 Å. On the other hand, the imino nitrogen atom forms a hydrogen bond to the amino nitrogen atom of the other molecule related by the two-fold screw axis parallel to the a-axis, the distance of the hydrogen bond being 3.04 Å. These three hydrogen bonds arrange the molecules around the two-fold screw axis. Apart from the hydrogen bonding system the structure is held together by van der Waals forces.

* Department of Polymer Science, College of Engineering, Dongguk University

** Department of Chemistry, College of Liberal Arts and Sciences, Ewha Womans University

Introduction

As a part of effort to establish the chemical and biological properties of organic compounds

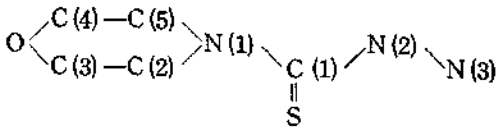

Fig. 1. The numbering of atoms exclusive of hydrogen atoms in the morpholinothiosemicarbazide molecule.

containing sulfur atom, we are undertaking the structure determinations of sulfur compounds which have a biologically active group by X-ray diffraction. This paper describes the crystal and molecular structure of morpholinothiosemicarbazide which has a thioureido group. (*Fig.* 1)

Experiment

Needle-shaped crystals of morpholinothiosemicarbazide elongated along the *a*-axis were obtained by slow evaporation from an aqueous solution at room temperature.

Unit cell dimensions were determined by a least-squares refinement of fifteen 2θ values measured on $0kl$ and $h0l$ Weissenberg photographs calibrated with superimposed NaCl powder lines, using Cu $K\alpha$ radiation (λ=1.5418 Å).

The density was measured by floatation in a mixture of benzene and chloroform. The crystal data are given in Table 1.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken at room temperature about the *a* (5 layers, $0kl$ to $4kl$) and *b* (2 layers, $h0l$ to $h1l$) axes, with Ni-filtered Cu Kα radiation, using two different crystals. The approximate dimensions of the crystals were 0.2×0.2×1.0 and 0.2×0.15×1.0 mm respectively.

The intensities were corrected for Lorentz and polarization effects and for spot extension[1], but they were not corrected for absorption. An IBM 1130 computer program for data correction[2] was used.

Structure Determination and Refinement

After the structure amplitudes were scaled and normalized to E values by means of a Wilson plot[3], a three-dimensional sharpened Patterson function was synthesized with E^2 as coefficients, using the 651 observed reflexions.

Trial positional parameters for the sulfur atom was obtained from inspection of the three-dimensional Patterson map. The remaining 9 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 sulfur atom.

The initial R factor, $R=\sum||F_0|-|F_c||/\sum|F_0|$ based on these positions was 0.30 for all reflexions. Three cycles of isotropic block diagonal least-squares refinement reduced the R factor to 0.18, and two cycles of anisotropic block diagonal least-squares refinment[4] lowered it to 0.07. The weighting scheme proposed by Cruickshank[5] was used.

Table 1. Crystal data for morpholinothiosemicarbazide

Formula weight: 161.23
Crystal system: orthorhombic
a=4.19(2) Å
b=6.56(2) Å
c=26.67(4) Å
Z=4
Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd.
Space group: $P2_12_12_1$ (from systematic absences and intensity statistics)
D_c=1.41 g.cm^{-3}
D_m=1.42 g.cm^{-3}

The function was $\sum\omega(F_0-F_c)^2$, where $\omega^{-1}=4.00+|F_0|+0.0187|F_0|^2$. The atomic scattering factors were taken from International *Table* for X-ray Crystallography[6].

A structure factor calculation of all the

Table 2. Observed and calculated structure factors for morpholinothiosemicarbazide. Columns are: Index, 10|*Fobs*|, 10|*Fcalc*|, 10 *A*calc, 10 *B*calc.

H=0	K=0			
4	309	334	334—	0
6	267	274	274—	0
8	79	90	90—	0
10	547	463	463	0
12	169	170	170	0
14	217	209	209	0
16	181	179	179—	0
18	15	21	21	0
20	229	233	233—	0
22	198	199	199	0
24	348	354	354	0
30	93	92	92—	0
H=0	K=1			
3	346	339	0	339
4	138	141	0	141
5	685	692	0	692—
6	105	103	0	103
7	267	270	0	270—
8	111	94	0	94—
9	285	286	0	286—
10	164	161	0	161
11	574	612	0	612
12	97	84	0	84—
13	351	338	0	338
14	79	77	0	77—
15	88	78	0	78—
16	60	60	0	60—
17	293	241	0	241—
18	34	32	0	32—
19	231	198	0	198—
20	58	56	0	56—
21	149	146	0	146
22	144	140	0	140—
25	77	69	0	69
26	20	17	0	17
27	42	41	0	41—
28	30	27	0	27
29	66	65	0	65—
31	39	39	0	39—
H=0	K=2			
0	78	79	79—	0
1	14	10	10	0
2	171	167	167	0
3	120	136	136	0
4	296	272	272	0
5	304	291	291	0
6	485	551	551	0
7	168	167	167—	0
8	183	161	161	0
9	173	170	170	0
10	201	177	177—	0
11	210	210	210	0
13	225	229	229—	0
14	134	112	112—	0
16	202	196	196	0
18	208	181	181	0
19	89	81	81—	0
20	55	54	54	0
21	40	40	40—	0
26	18	18	18	0
28	71	61	61	0
30	77	78	78	0
H=0	K=3			
1	355	406	0	406—
2	252	272	0	272
3	177	176	0	176—
5	199	211	0	211
6	31	31	0	31—
7	109	108	0	108
8	102	100	0	100—
10	113	121	0	121—
11	139	133	0	133—
13	105	100	0	100—
14	67	64	0	64
17	122	111	0	111
19	100	98	0	98
21	92	89	0	89—
22	104	92	0	92—
23	125	124	0	124—
25	78	77	0	77—
29	52	50	0	50
H=0	K=4			
0	358	378	378	0
2	127	124	124	0
4	112	95	95—	0
6	319	276	276—	0
9	172	165	165	0
10	285	261	261	0
11	181	154	154	0
12	161	143	143	0
13	184	179	179—	0
14	228	194	194	0
15	68	74	74—	0
18	113	108	108—	0
22	60	57	57	0
24	106	103	103	0
28	43	43	43—	0
H=0	K=5			
1	72	60	0	60
2	69	80	0	80—
5	214	179	0	179—
6	54	52	0	52—
9	194	180	0	180—
11	291	257	0	257
13	143	137	0	137
15	125	95	0	95—
17	122	108	0	108—
19	104	100	0	100—
27	32	30	0	30—
H=0	K=6			
0	314	256	256—	0
3	26	25	25	0
4	75	74	74	0
6	109	106	106	0
10	40	39	39—	0
16	71	67	67	0
20	68	62	62	0
22	35	32	32—	0
H=0	K=7			
3	53	49	0	49—
4	51	50	0	50
5	62	59	0	59
8	55	51	0	51—
11	76	69	0	69—
13	58	52	0	52—
16	44	42	0	42
17	29	29	0	29
H=0	K=8			
0	49	47	47	0
3	45	40	40—	0
5	37	34	34—	0
6	42	39	39—	0
9	25	23	23	0
H=1	K=0			
1	277	286	0	286—
2	440	408	408—	0
3	591	659	0	659—
4	782	835	835	0
5	303	276	0	276—
6	124	128	128—	0
7	60	63	0	63
8	246	242	242—	0
9	158	143	0	143
10	478	466	466—	0
11	129	123	0	123
13	110	115	0	115—
14	228	220	220	0
15	70	62	0	62—
16	276	234	234	0
18	137	125	125—	0
19	135	134	0	134
20	225	268	268—	0
21	187	184	0	184
22	93	91	91	0
23	52	53	0	53
24	64	58	58—	0
25	48	46	0	46—
26	48	48	48	0
27	85	84	0	84—
28	45	43	43	0
H=1	K=1			
0	161	169	0	169
1	931	839	527—	653
2	466	375	276	253—
3	400	356	36—	354
4	247	229	24	228—
5	165	137	41—	131
6	189	187	9—	187—
7	281	280	30	278—
8	376	328	325—	49—
9	288	277	55—	271—
10	192	164	143—	81—
11	114	95	26	92
12	179	186	6	186—
14	160	158	153	38—
15	245	220	5	220
16	173	147	132	63—
20	106	99	23—	96—
21	167	163	4	163—
22	72	74	72—	14—
23	129	125	103—	71—
24	36	34	31	14
25	131	123	55—	110
26	47	50	45	22—
27	71	71	22—	67
28	28	29	19	21—
29	28	28	4	28
30	26	26	11—	23—
31	64	63	3	63—
32	42	42	41—	6
H=1	K=2			
0	252	269	0	269
1	247	246	85—	231—
2	326	316	304—	84
3	98	104	73	74
4	243	279	270—	71
5	89	109	109—	4—
6	43	41	38	15
7	83	79	71—	36—
8	103	101	94	37
9	207	217	192	101—
10	306	297	293	47—
11	269	264	230—	130—
12	161	163	71—	147—
13	202	181	71—	167
14	221	240	239—	29—
15	96	101	79	63
16	85	91	90—	17—
17	78	83	45—	70
19	69	68	3	67—
20	121	130	130	2—
22	61	69	60	34
23	46	48	28—	40
24	56	58	43—	39
26	79	85	84—	17
H=1	K=3			
0	14	13	0	13
1	197	219	147—	162—
2	357	309	260—	168—
3	175	209	28—	208—
4	130	152	108—	107—
5	112	104	54	88—
6	85	104	99—	32
7	104	128	16	127
8	144	146	131	66—
9	216	246	53—	240
10	142	164	142—	80—

Table 2 (Cont).

11	100	104	88—	56
12	76	73	31	66—
13	93	114	76—	85—
14	77	82	17	80—
15	138	151	30—	148—
18	70	69	62	31
19	76	76	24	72
20	76	76	47	59—
21	82	84	9—	83
22	97	98	94	28—
23	56	58	38—	45
25	50	61	29—	54—
26	51	46	35—	30—
27	38	45	2—	45—
28	36	38	38—	1—
H=1 K=4				
0	60	58	0	58
1	38	40	39	7
2	128	130	126	29
3	135	155	45—	148—
4	142	146	132	61
5	104	106	105—	7—
6	57	59	1—	59
7	131	131	97—	89
8	79	92	62—	68
9	153	179	101	147
10	232	236	232—	42—
11	127	144	90—	112
12	108	126	30	122—
13	97	112	16—	111—
14	140	156	154	21—
15	72	79	22	76—
16	42	44	37	23
17	73	79	52—	60—
18	40	48	22—	43
19	57	58	29—	50
20	90	104	103—	13
21	45	53	19—	49
26	43	39	38	10
27	30	31	4	31—
H=1 K=5				
1	137	138	38	133
2	71	90	90	11
3	132	133	7—	133
4	82	81	54	60—
5	90	87	1—	87
6	45	43	12	42—
7	144	160	22—	159—
8	109	126	108—	63—
9	77	79	31—	72—
10	74	83	82—	10—
11	73	82	45—	68
12	56	62	9	61
13	58	57	38—	42—
14	77	88	83	29—
15	96	111	34—	106
16	73	71	68	23—
17	37	37	11—	35
21	48	59	0	59—
23	32	32	19	25—
25	36	38	5	37
H=1 K=6				
1	46	49	40—	28
3	64	76	33—	69
4	103	124	124—	4
8	51	55	44	33
10	111	111	109	18
11	48	46	44—	12—
12	28	26	22—	13—
13	52	45	38—	24
14	91	76	75—	15
16	57	59	59—	10
21	36	36	16—	32—
22	21	19	19—	3
H=1 K=7				
0	79	79	0	79—
1	67	73	5	73—
3	49	50	12—	49—
5	28	23	20	12—
7	26	24	7	23
8	35	37	36	9
9	53	56	1	56
11	46	43	42—	11
12	31	27	1	27—
13	38	34	28—	19—
15	38	34	5—	33—
H=1 K=8				
0	40	35	0	35—
2	33	30	28	11—
4	33	31	30	9
5	32	30	28—	11—
6	30	28	2—	27
H=2 K=0				
0	293	336	336—	0
1	274	279	0	279
2	177	189	189	0
3	114	96	0	96
4	168	138	138	0
5	53	60	0	60—
6	108	108	108—	0
7	201	198	0	198—
8	55	56	56—	0
9	149	151	0	151
10	167	159	159—	0
11	263	270	0	270
12	154	147	147—	0
13	252	226	0	226
14	54	51	51—	0
15	38	42	0	42
17	136	137	0	137—
18	78	77	77—	0
20	87	90	90	0
21	50	41	0	41
23	96	91	0	91
24	62	57	57—	0
25	59	59	0	59
26	47	44	44	0
29	35	33	0	33—
H=2 K=1				
0	115	106	106—	0
1	251	241	227	79—
2	260	253	235—	95
3	153	147	54	136—
4	274	259	172	194
5	133	114	35—	109
6	259	275	263	80
7	115	109	0	109
8	87	89	83	31
9	90	96	41	86
10	64	75	52—	55—
11	106	107	66	85—
12	216	214	212—	24
13	57	54	18—	51—
14	33	34	14—	31
15	43	49	3	49
16	67	75	73	15
17	98	105	6—	104
18	191	172	169	31—
19	86	84	73	41
20	74	65	14	63—
21	87	77	43—	63—
22	77	80	78—	18—
23	31	30	13—	26—
24	61	53	52—	6—
25	49	54	45	30—
26	45	45	34—	30
28	60	59	53	26
30	39	39	34	19
H=2 K=2				
0	199	200	200	0
1	270	269	60	262—
2	131	133	111	73—
3	260	273	17	273
4	138	136	132—	35
5	199	208	31—	206
6	259	257	257—	11—
7	341	352	193	294
8	63	72	70—	14
9	110	124	59	109—
10	134	137	48	128—
12	30	32	22	23
13	69	81	63	50—
14	86	55	27	48
15	95	93	86—	35
16	79	75	74—	13
17	116	141	59—	129
18	118	121	120—	14—
19	76	90	12	89
20	38	42	33—	26—
21	68	80	16—	79
22	45	42	33	25
23	119	122	1—	122—
24	66	63	61	13—
25	38	38	19	33—
27	28	31	12—	28
28	32	36	35—	11—
H=2 K=3				
1	40	43	0	43
2	178	197	195	28—
4	107	103	77—	69
5	84	94	23—	91—
6	64	68	68—	5—
7	90	92	9	92—
8	146	143	136—	45—
9	66	68	49	47
10	57	56	55	9
11	136	155	27	153
12	278	336	336	11—
13	149	146	12—	146
16	62	65	44—	47
17	58	60	11	59—
18	116	119	119—	6—
19	55	54	29	45—
20	32	29	26	13—
22	51	60	58	15
23	29	30	7	29
H=2 K=4				
0	92	91	91—	0
1	200	194	10	194
2	112	110	80—	76—
3	47	53	2	53—
6	62	65	64	13
7	148	147	83	121—
8	63	64	35—	54
9	126	119	22	117
10	70	67	35—	57—
11	72	70	20—	67
13	103	101	40	92
15	37	40	33—	22
17	79	76	27—	71—
22	35	34	23—	25
23	75	83	0	83
24	33	33	31—	12—
H=2 K=5				
0	65	67	67—	0
1	32	25	13—	21—
2	61	59	56—	19
3	39	37	36	10
4	76	89	89	9
6	123	124	122	26—
8	80	80	36	72—
9	87	82	35—	74
11	56	53	12—	52—
12	64	63	63—	7—
15	63	60	32	51
16	61	58	39	42
17	25	30	22	20
18	79	76	75	11
H=2 K=6				
0	72	71	71	0
1	52	51	26—	44—
4	62	58	56—	18

Table 2 (Cont).

5	73	74	14−	72
6	39	43	43−	7
7	80	76	10	76
10	72	69	40	56−
11	52	50	17	47−
12	37	37	37	7
13	40	39	16−	35−
14	42	38	22	30
17	52	56	5−	55
H=2 K=7				
1	55	54	42−	34
2	44	47	47	3
3	37	41	21−	35
4	37	36	6−	35−
5	35	32	5−	31−
6	32	31	31−	4−
7	36	36	18	31−
H=3 K=0				
1	59	59	0	59
3	111	111	0	111
4	52	55	55−	0
5	27	28	0	28−
6	32	32	32−	0
7	127	130	0	130−
8	43	44	44	0
9	148	143	0	143−
10	87	91	91−	0
11	87	84	0	84−
13	77	83	0	83
15	87	87	0	87
16	37	37	37−	0
17	32	40	0	40
21	59	70	0	70−
H=3 K=1				
0	48	49	0	49
2	239	230	229−	12
3	89	83	83−	12−
4	119	113	111−	20−
5	132	124	116	42
6	41	40	40−	4−
7	122	110	110	0
8	150	139	139	5
9	97	98	98	8−
10	85	81	80	14−
13	29	35	24	25−
14	97	100	99−	13−
15	46	48	40	26
16	56	62	61−	7
17	89	98	97	12−
19	42	41	38	13−
20	52	63	62	10−
21	33	36	36−	1−
22	94	83	83	7
23	21	21	21	0
24	29	29	26−	13
25	25	20	20−	3
26	59	58	58−	4
28	29	29	29−	2−
H=3 K=2				
0	95	77	0	77−
1	60	62	52	34
2	44	39	20−	34
3	258	238	49−	233−
4	68	62	52−	53
5	152	140	21	139−
6	56	60	44	41
7	51	48	22	43
8	42	47	6−	47−
9	176	168	42−	162
10	63	75	25−	71−
11	125	125	9	125
13	140	155	14−	154−
14	74	72	24	68−
15	110	129	29−	126−
17	54	66	27	60−
18	14	18	17−	4−
19	123	123	5−	123
20	37	36	15	32
21	52	61	15−	59
H=3 K=3				
0	20	15	0	15−
1	43	42	42	1
2	182	185	185	9
3	50	51	28	43
4	71	74	74	1
5	27	31	28	12−
5	56	55	46−	29−
7	43	42	41	8−
8	236	249	249−	17
9	47	53	36	39
12	33	35	27−	23−
14	65	63	61	16
15	39	37	18	33−
16	108	115	115	1
17	24	23	21	9
20	33	32	32−	5
22	75	80	80−	2−
H=3 K=4				
1	27	28	28	1
3	106	112	22−	109
4	40	38	37	7−
5	40	41	6	41
6	20	22	22−	1
8	61	60	2	60−
9	64	73	11−	72−
10	37	37	17	32−
11	74	69	6−	69−
13	70	80	10−	80
14	46	52	18−	48−
15	34	34	9−	32
16	28	27	4	27−
19	70	62	2−	62−
21	45	44	8−	43−
H=3 K=5				
1	32	34	12−	31
2	65	72	72−	1−
3	53	51	51	4−
4	38	45	45−	1−
5	44	41	41	6−
6	22	19	14−	12−
7	46	45	41	18
8	49	46	46	4
10	39	38	38	6
11	26	29	29−	4−
13	33	31	30−	6
14	52	45	44−	9
18	14	16	14	6−
20	23	22	22	2
H=3 K=6				
0	54	57	0	57−
1	28	31	0	31−
2	28	38	6−	32−
3	44	50	1	50−
6	36	40	11	38
7	40	38	3	38
9	58	62	8	61
10	36	34	15	30−
11	35	32	6−	31
13	41	39	8−	39−
14	31	29	8−	28−
H=4 K=0				
0	67	64	64−	0
1	135	123	0	123−
5	90	72	0	72
6	53	50	50	0
7	45	46	0	46
8	45	51	51−	0
9	33	30	0	30−
10	68	73	73−	0
11	71	71	0	71−
12	11	10	10	0
13	54	46	0	46−
14	68	73	73−	0
17	43	42	0	42
H=4 K=1				
0	36	35	35	0
1	71	68	51−	46−
2	45	46	45	4
3	28	27	13	23−
4	76	66	31−	58
5	58	65	29	59
6	116	106	99−	37
7	18	17	3−	17
8	45	37	37−	4
9	56	46	11	44
10	55	52	42	31−
11	60	56	2−	56−
12	77	77	77	7
16	50	47	45−	14
18	71	65	61−	21−
19	44	46	36−	30
20	25	23	1−	23−
21	20	24	8	22
22	24	26	26	3
H=4 K=2				
0	84	78	78	0
1	88	84	40−	74
2	12	12	12	2−
3	77	72	5−	72−
4	37	33	20−	27−
5	95	88	36	80−
6	82	79	79−	5−
7	76	77	21	74−
8	77	71	70−	16−
9	35	33	23	23
10	36	35	24	26
11	29	30	11	28
12	38	45	44	8−
13	29	27	10−	25
14	17	17	16	6−
16	60	59	59−	4
17	39	38	11−	37−
18	42	42	41−	10
19	46	46	26−	39−
H=4 K=3				
0	55	56	56−	0
1	43	42	6	42
2	66	61	61−	7
3	18	18	14	11−
4	23	21	21	2
5	79	75	6	75−
6	25	26	25	7
8	61	60	60	5
9	31	33	18−	27
10	30	29	15−	25−
11	53	49	9−	48
12	89	102	102−	6
13	36	41	6	40
16	29	29	29	3
18	39	38	38	4
H=4 K=4				
0	69	64	64−	0
1	72	70	25−	65−
5	51	49	21	45
7	44	42	20	36
8	39	36	15	33−
9	47	44	5	44−
10	21	21	17−	12
11	35	34	4−	34−
13	38	38	10	37−
H=4 K=5				
0	18	18	18	0
2	29	24	12	21
3	33	31	21−	23−
4	19	20	20−	5−
5	33	31	15−	27
6	54	50	49−	9−
8	34	31	22−	22−
10	20	18	15	11−

Table 3. Final positional and anisotropic thermal parameters
Temperature factors expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$
The e.s.d.'s are shown in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.3352 (5)	0.7602 (3)	0.4149 (1)	0.061 (1)	0.025 (0)	0.0015 (0)	−0.000 (1)	0.000 (0)	−0.0000 (1)
C (1)	0.504 (2)	0.530 (1)	0.4171 (3)	0.057 (4)	0.025 (2)	0.0015 (1)	−0.003 (3)	0.000 (1)	0.0002 (5)
C (2)	0.701 (2)	0.563 (1)	0.3287 (3)	0.068 (5)	0.027 (2)	0.0016 (1)	−0.001 (3)	0.000 (1)	0.0001 (5)
C (3)	0.665 (2)	0.424 (1)	0.2814 (3)	0.066 (5)	0.026 (2)	0.0015 (1)	−0.002 (3)	0.000 (1)	−0.0002 (4)
C (4)	0.774 (2)	0.120 (1)	0.3282 (3)	0.070 (5)	0.027 (2)	0.0016 (1)	0.001 (3)	−0.000 (1)	−0.0001 (5)
C (5)	0.811 (2)	0.246 (1)	0.3775 (3)	0.064 (4)	0.024 (2)	0.0015 (1)	−0.001 (4)	−0.000 (1)	−0.0002 (6)
N (1)	0.642 (2)	0.437 (1)	0.3756 (2)	0.069 (4)	0.026 (2)	0.0015 (1)	−0.001 (3)	0.001 (1)	0.0002 (4)
N (2)	0.520 (2)	0.413 (1)	0.4590 (2)	0.059 (4)	0.026 (2)	0.0014 (1)	0.000 (2)	−0.000 (1)	−0.0001 (4)
N (3)	0.337 (2)	0.475 (1)	0.5036 (2)	0.065 (4)	0.028 (2)	0.0015 (1)	0.001 (3)	0.001 (1)	−0.0003 (4)
O	0.856 (1)	0.244 (1)	0.2852 (2)	0.066 (3)	0.028 (1)	0.0015 (1)	0.000 (3)	0.000 (0)	0.0001 (4)

Table 4. Bond lengths and angles in morpholinothiosemicarbazide
The e.s.d.'s are shown in parentheses.

Bond length (Å)			Bond angle (°)	
C (1) - S	1.67 (1)		C (1) - N (1) - C (2)	118.7 (6)
C (1) - N (1)	1.39 (1)		C (1) - N (2) - N (3)	118.7 (6)
C (1) - N (2)	1.36 (1)		C (2) - C (3) - O	111.9 (6)
C (2) - N (1)	1.52 (1)		C (3) - O — C (4)	113.1 (6)
C (2) - C (3)	1.57 (1)		C (4) - C (5) - N (1)	112.4 (6)
C (3) - O	1.43 (1)		C (5) - N (1) - C (2)	115.3 (6)
C (4) - O	1.45 (1)		C (5) - N (1) - C (1)	124.0 (6)
C (4) - C (5)	1.56 (1)		N (1) - C (2) - C (3)	109.2 (6)
C (5) - N (1)	1.44 (1)		N (1) - C (1) - N (2)	112.5 (7)
N (2) - N (3)	1.47 (1)		O — C (4) - C (5)	110.1 (6)
			S — C (1) - N (1)	123.1 (6)
			S — C (1) - N (2)	124.4 (6)
*N (2) - H····· N (3)[a]	3.04 (2)			
*N (3) - H····· S[b]	3.48 (2)			
*N (3) - H····· S[c]	3.49 (2)			

*Hydrogen bonds
Code for symmetry-related atoms:
a $\frac{1}{2}+x, \frac{1}{2}-y, z$. *b* $\frac{1}{2}+x, 1\frac{1}{2}-y, z$. *c* $-\frac{1}{2}+x, 1\frac{1}{2}-y, z$

reflexions showed no serious discrepancies. The observed and calculated structure factors are listed in *Table* 2.

The final positional and thermal parameters of the atoms are listed in *Table* 3. The atoms are numbered according to *Fig.* 1.

Discussion

Intramolecular bond lengths and angles are listed in *Table* 4. The bond lengths, angles and their deviations are those evaluated from the least-squares matrix and no correction for thermal motion effects were made. The molecular dimensions of morpholinothiosemicarbazide are shown in *Fig.* 2. Bond lengths and angles in the morpholyl group correspond to normal values within the error limits, and the ring has the chair form. The exocyclic C—N bond lengths

Table 5. A comparison of bond lengths(Å) obtained from relevant compounds

Compound	C—N	N—N	C=S
Morpholinothiosemicarbazide[10]	1.36 1.39	1.47	1.67
2-p-Methoxyphenol-3, 4-dibenzyl-1, 3, 4-thiodiazolidino-5-thione[11]	1.355	1.420	1.650
1-Thiocarbamoylimidazolidine-2-thione[12]	1.408 1.473 1.378 1.310		1.686 1.673
Tetraethylthiuram disulphide[13]	1.334 1.362		1.662 1.634
6-Mercaptopurine monohydrate[14]	1.384 1.396		1.676
4-Methyl-1:2-dithiacyclopent-4-ene-3-thione[15]			1.627
Dithiouracil[16]	1.401 1.342		1.645 1.684
Thioacetamide[17]	1.324		1.713
Thiosemicarbazide[18]	1.313 1.340	1.40	1.685
mono-Thiosemicarbazide-zinc chloride[19]		1.44	
3-Hydrazino-5-thiol-1, 2, 4-triazole[20]	1.37	1.40	

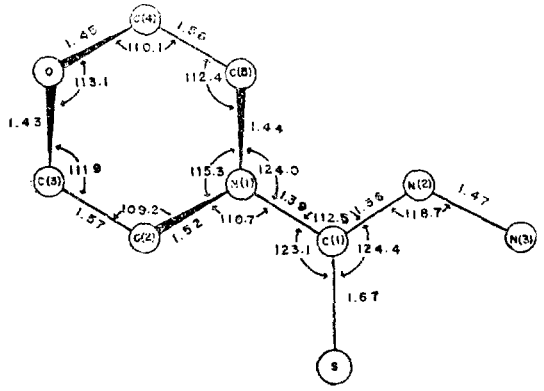

Fig. 2. Molecular dimensions of the morpholinothiosemicarbazide.

(1.36 and 1.39 Å) are significantly shorter than the corresponding normal single bond length, 1.44 Å. Reference to Wheatley's order/length curve[7] for C—N bonds indicates 30 % double bond character length in the exocyclic C—N bonds. The C=S bond length is 1.67 Å in morpholinothiosemicarbazide. Valle, Busetti, Mammi and Carazzolo[8] reported a mean value of 1.814 Å for the C—S single bonds in 1, 3, 5, -trithiane, a saturated cyclic compound. On Abraham's scale[9] the C=S bond has approximately 75 % double-bond character. Reference to *Table* 5 shows the extent of the agreement between these, and related C=S and C—N bond lengths in morpholinothiosemicarbazide. The N(2)—N(3) bond length of 1.47 Å agrees with the accepted nitrogen-nitrogen single bond length of 1.44 Å.

The least-squares planes are listed in *Table* 6. In morpholyl ring, the plane through C(2), C(3), C(4) and C(5) is planar to well within the precision of the analysis, and the distances from the plane to the atoms O and N(1) are shown in *Table* 6. The atom O deviates upward from the plane while the atom N(1) deviates downward from the plane by 0.63 and 0.55 Å respectively. Thus, the morpholyl ring takes a normal chair form. The atoms S, C(1), N(1) and N(2) lie nearly on a plane which makes an angle of 6.7° with the least-squares plane included N(1), C(1), C(2), and C(5).

Table 6. Least-squares planes in morpholinothiosemicarbazide
(Equation for plane, $A_x+B_y+C_z=D$, where x, y, z are in Å.)

Atoms included in plane	Atoms not included in plane	Distance from best plane (Å)	Constant
C (2)		0.003	A=0.977
C (3)		−0.003	B=0.104
C (4)		0.003	C=−0.185
C (5)		−0.003	D=1.624
	N (1)	−0.554	
	O	0.634	
C (1)		0.002	A=0.879
N (1)		−0.001	B=0.418
N (2)		−0.001	C=0.231
S		−0.001	D=5.874
	C (2)	0.272	
	C (5)	0.109	
	N (3)	−0.231	
C (1)		0.033	A=0.853
C (2)		0.027	B=0.399
C (5)		0.031	C=0.337
N (1)		−0.091	D=6.902
	C (3)	−0.888	
	C (4)	−0.875	
	N (2)	0.161	
	S	0.012	

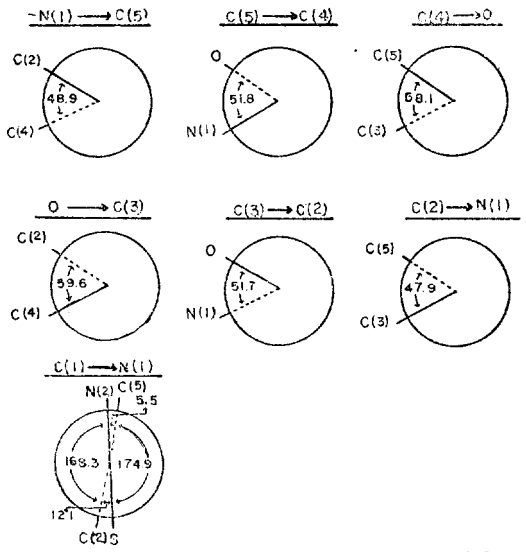

Fig. 3. Conformation angles in degrees, viewed down the N(1)-C(5), C(5)-C(4), C(4)-O, O-C(3), C(3)-C(2), C(2)-N(1), and C(1)-N(1) bonds in the morpholinothiosemicarbazide.

The detailed conformation angles about the N(1)—C(5), C(5)—C(4), C(4)—O, O—C(3), C(3)—C(2), C(2)—N(1) and C(1)—N(1) bonds are given in *Fig*. 3.

Fig. 4 and *Fig*. 5 show the crystal structure projected down the *a* and *b* axes respectively.

An examination of the structure for intermolecular contacts revealed two N—H···S and one N—H···N hydrogen bonds; the amino nitrogen atom forms hydrogen bonds to the sulfur atoms of the other molecules related by the two-fold screw axis parallel to the *a*-axis, the distances of the hydrogen bonds being 3.48 and 3.49 Å.

On the other hand, the imino nitrogen atom forms a hydrogen bond to the amino nitrogen atom of the other molecule related by the two-fold screw axis parallel to the *a*-axis, the distance of the hydrogen bond being 3.04 Å.

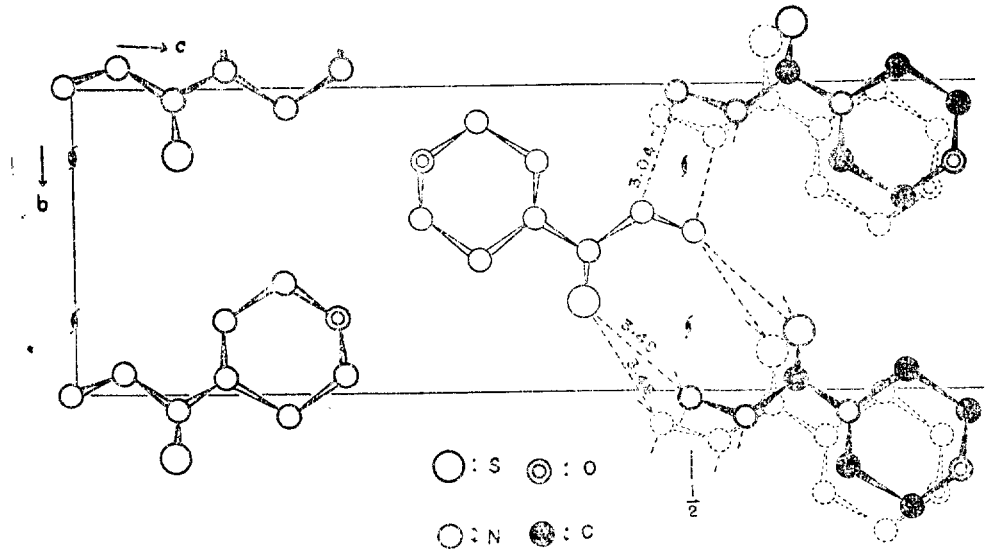

Fig. 4. Projection of the structure along the *a* axis. The dark molecules are above the light ones. Dashed lines indicate intermolecular hydrogen bonds.

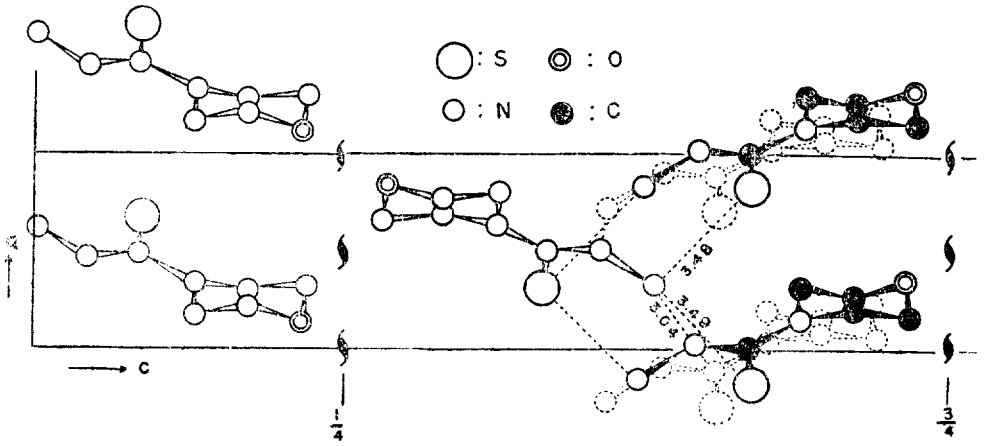

Fig. 5. Projection of the structure along the *b* axis. The dark molecules are above the light ones. Dashed lines indicate intermolecular hydrogen bonds.

From *Fig.* 4 and *Fig.* 5 it may be seen that these three hydrogen bonds arrange the molecules around the two-fold screw axis along the *a*-axis Apart from the hydrogen bonding system the structure is held together by van der Waals forces.

The closest intermolecular approaches (other than the hydrogen bond) are C(2)↔C(4), 3.66 Å; C(5)↔N(3), 3.49 Å; C(3)↔O, 3.41 Å; C(4)↔S, 3.78 Å.

Acknowledgement

It is a pleasure to thank Professor Y. S. Chough and Miss M. Y. Kim, College of Pharmacy, Seoul National University, for helpful discussions. This work has been supported by the research grant from the Ministry of Science and Technology.

References

1. D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).
2. R. Shiono, "IBM 1130 Data Reduction Program, Technical Report", Dept. of Crystallography, Univ. of Pittsburgh, 1968.
3. A. J. C. Wilson, *Nature, Lond.*, **150**, 152 (1942).
4. R. Shiono, "IBM 1130 Least Squares Program, Technical Report," Dept. of Crystallography, Univ. of Pittsburgh, 1968.
5. D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-ray Crystal Structure Analysis", P. 32-78, R. Pepinsky, Robertson and J. C. Speakman, ed., Pergamon Press, New York, 1961.
6. "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1968.
7. P. J. Wheatley, *Acta Cryst.*, **8**, 224 (1955).
8. G. Valle, V. Busetti, M. Mammi and G. Carazzolo, *Acta Cryst.*, **B25**, 1432 (1969).
9. S. C. Abrahams, *Quart. Rev.*, **10**, 422 (1956).
10. This investigation.
11. I. L. Karle and J. Karle, *Acta Cryst.*, **19**, 92 (1956).
12. G. Valle, G. Cojazzi, V. Busetti, and M. Mammi, *Acta Cryst.*, **B26**, 468 (1970).
13. I. L. Karle, J. A. Estlin, and K. Britts, *Acta Cryst.*, **22**, 273 (1967).
14. E. Sletten, J. Sletten, and L. H. Jensen, *Acta Cryst.*, **B25**, 1330 (1969).
15. G. A. Jeffrey and R. Shiono, *Acta Cryst.*, **12**, 447 (1959).
16. E. Sheffner and H. G. Mautner, *J. Amer. Chem. Soc.*, **89**, 1249 (1967).
17. M. R. Truter, *J. Chem. Soc.*, 997 (1960).
18. P. Domiano, G. T. Gasparri, M. Nardelli, and P. Sgarabotto, *Acta Cryst.*, **B25**, 343 (1969).
19. Luigi Cavalca, Mario Nardelli, and Germano Branchi, *Acta Cryst.*, **13**, 688 (1960).
20. M. E. Senko and D. H. Templeton, *Acta Cryst.*, **11**, 808 (1958).