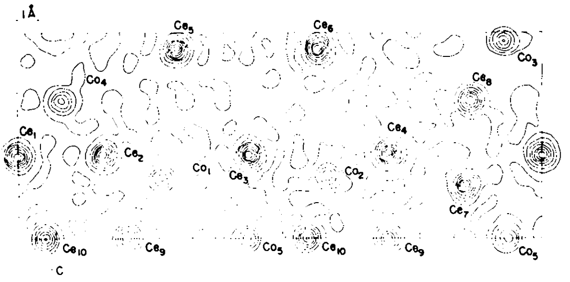

Fig. 1. Electron density in $Ce_{24}Co_{11}$ on the mirror $(x, 2x, z)$ plane. The outer contour is 0 e.Å^{-3}. The contour interval at the Co atoms is 10 e.Å^{-3} and at the Ce atoms 20 e.Å^{-3}.

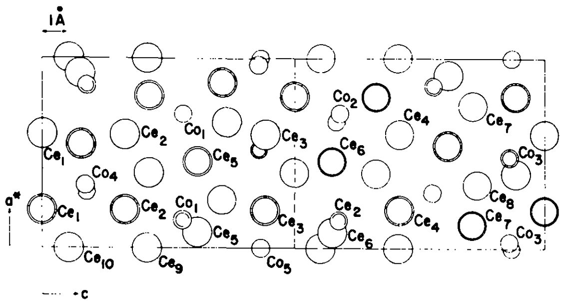

Fig. 2. Projection of the structure of $Ce_{24}Co_{11}$ on a plane normal to the b axis.

Discussion of the structure

A projection of the structure normal to the b axis is shown in Fig. 2. The interatomic distances are listed in Table 2. The neighbors given are those which satisfy the definition of Frank & Kasper (1958). Some of the Ce–Co distances are exceptionally short. The smallest known Ce–Ce distance is 3·09 Å in $CeCo_2$. The radius of Co is about 1·25 Å so one might expect a minimum Ce–Co distance of about 2·80 Å. Distances as short as 2·61 Å are found in this compound. The standard deviations given in Table 2, aside from systematic errors, are overestimates because the fact that the atoms are in special positions has not been taken into account.

We are indebted to V. O. Struebing for the preparation and heat treatment of the alloy.

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The Crystal Structure of Rhodanine, $C_3H_3ONS_2$*

By D. van der Helm,† Arthur E. Lessor, Jr.‡ and Lynne L. Merritt, Jr.
Department of Chemistry, Indiana University, Bloomington, Indiana, U.S.A.

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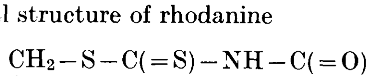
The structure of rhodanine has been determined by three-dimensional Fourier and least squares methods using an I.B.M. electronic computer. The crystals are monoclinic having the unit-cell dimensions $a_0 = 10{\cdot}02$, $b_0 = 7{\cdot}67$, $c_0 = 7{\cdot}28$ Å; $\beta = 102°\ 38'$. There are four molecules per unit cell and the space group is $P2_1/n$. The molecule is planar. There are two strong N · · · O hydrogen bonds around the center of symmetry, binding the molecules in pairs.

Introduction

The crystal structure of rhodanine


$$\underbrace{CH_2-S-C(=S)-NH-C(=O)}$$

is one of several investigations being carried out in this laboratory on chelate compounds and organic compounds forming chelates. An earlier communication with the unit cell dimensions has appeared (Merritt & Lessor, 1955). Rhodanine has been long used as an intermediate in the preparation of phenylalanine. The analytical properties were not discovered until Feigl (1926) reported the formation of the water-insoluble complex of rhodanine and silver ion. He also found that similar complexes were formed in acidic solution with univalent mercury and copper ions. In basic solution almost all metallic ions give precipitates containing rhodanine which decompose

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* Contribution No. 1077 from the Chemical Laboratories of Indiana University.

† Present address: Department of Chemistry of Oklahoma, Norman, Oklahoma.

‡ Present address: The International Business Machines Corp., Kingston, New York.

more or less rapidly to the sulfides. The silver atom supposedly forms bonds with the nitrogen and the sulfur atom outside the ring (Feigl, 1949).

Experimental

Rhodanine was recrystallized from ethyl alcohol. When grown from this solvent the crystals are elongated, hexagonal plates. Oscillation photographs were taken about all three crystallographic axes and the unit cell dimensions were found to be

$$a_0 = 10{\cdot}02 \pm 0{\cdot}10,\ b_0 = 7{\cdot}67 \pm 0{\cdot}08,\ c_0 = 7{\cdot}28 \pm 0{\cdot}07\ \text{Å};\quad \beta = 102°\ 38'.$$

Cu $K\alpha$ radiation was used ($\lambda = 1{\cdot}542$ Å). The density was 1·549 g.cm.$^{-3}$ (flotation) and a direct calculation of the number of molecules per unit cell yields 3·8 molecules, which may be rounded off to 4·0. The three principal indices of refraction were $n_\beta = 1{\cdot}77$ (parallel to the b-axis of the crystal), $n_\alpha = 1{\cdot}59$ (49° in obtuse β with the a-axis) and $n_\gamma = 1{\cdot}80$.

Systematic extinctions were observed for ($h0l$) when $h+l \neq 2n$ and for ($0k0$) when $k \neq 2n$. This determines the space group uniquely as $P2_1/n$. The multiple film technique was used to obtain X-ray intensity data. Intensities were estimated visually by comparison with a standard intensity strip. Three-dimensional data were used for the structure determination after being corrected in the usual way.

Determination of the structure

The most intense reflection was (211). The molecule was expected to be almost flat. A three-dimensional Patterson synthesis was computed to find the positions of the two sulfur atoms and possibly a reasonable trial structure. In order to get as much information as possible the amplitudes were modified to sharpen the Patterson peaks. After considering several modification functions (Patterson, 1935; Lipson & Cochran, 1955; Shoemaker, Baricau, Donohue & Lu, 1953), the function

$$\left(\sum_i Z_i^2 / \sum_i f_i^2\right) \exp\left[(-4\pi^2/p) + 2B\right] \sin^2\theta/\lambda^2$$

was found to be the most appropriate. The value of p was taken to be 7·25. The functions proposed by Shoemaker and co-workers need an accurate value of the temperature factor so as not to get disturbing series termination errors or, on the other hand, so as not to diminish the high reflections too quickly. At this stage only an inaccurate value for the temperature factor was available, which was used in the equation above.

In the Harker section $P(u, \frac{1}{2}, w)$ there were three high peaks. These are S–S peaks; one of them is a non-Harker peak. The sulfur atoms therefore must have about the same y parameters. This was proved by the Harker line $P(\frac{1}{2}, v, \frac{1}{2})$. This, together with the real Patterson peaks gave quite accurate parameters for the sulfur atoms.

To get reliable information about the positions of the other atoms, a Patterson superposition method in three dimensions using seven of the possible ten S–S peaks was carried out (Shoemaker *et al.*, 1953; Donohue & Bryden, 1955). This gave unambiguously the positions of three other atoms. It also indicated two other probable positions which were reasonable as far as the form of the molecule is concerned. All the Patterson peaks of one of these latter atoms lay near S–S peaks and several of the Patterson peaks of the other atom were considerably distorted by the two-fold axis. In the first three-dimensional Fourier synthesis these last two probable positions were left out. The R, $R = \Sigma(F_c - kF_o)/\Sigma kF_o$, of this first calculation was 0·35 and gave the positions of the two remaining atoms (which agreed well with the probable positions obtained from the superposition of the Patterson maps). New three-dimensional structure factors were calculated ($R = 0{\cdot}23$), using an overall isotropic temperature factor. A difference Fourier indicated only small shifts in parameters. The molecule thus found lay near the $(2\bar{1}1)$ plane.

Refinement of the structure

It was decided to refine the structure with least-squares calculations on the parameters and the individual isotropic temperature factor of each atom. The parameter corrections were calculated from a diagonal matrix, except for cross-terms $\Sigma(\partial F/\partial x_i)(\partial F/\partial z_i)$. After four cycles of structure factor and least-square calculations the R was reduced to 0·17. The weighting factor in the least-squares calculation was taken as $1/F_o$, and for F_o's lying between F_o minimum and $3F_o$ minimum, as $1/(3F_o\ \text{min.})$. The function minimized was $\sum_q w(|F_o| - |F_c|)^2$. After the fourth time there were only a few small shifts. A three-dimensional difference Fourier gave indications of the positions of the three hydrogen atoms. These were included in all the following structure factor calculations, assigning them arbitrarily a value of B of 1·00 in the temperature factor expression. The Fourier section at $(2\bar{1}1)$ showed

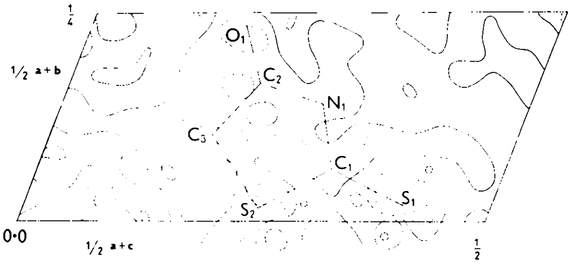

Fig. 1. Difference Fourier of the section $(2\bar{1}1)$. Contours at 0·5 e.Å^{-3}. Dotted contours are negative. The maximum electron density at the centers of the sulfur atoms on the Fourier synthesis was 42 e.Å^{-3}.

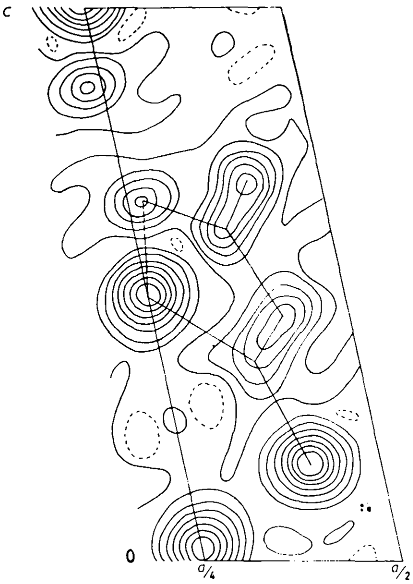

Fig. 2. Final Fourier electron density projection on (010). Contours at 2 e.Å^{-2}, except around the sulfur atoms where the contours are at 2, 4, 8, 12, 16, 20 and 24 e.Å^{-2}. Zero line is dotted.

that the two sulfur atoms and the oxygen atoms, especially, have strong anisotropic movements. The directions and lengths of the axes of the vibration ellipsoids for these three atoms were calculated from the difference Fourier (Cochran, 1951; Rollett & Davies, 1955; Davies & Blum, 1955; Leung, Marsh & Schomaker, 1957). New structure factors were calculated with anisotropic temperature factor parameters for the sulfur and oxygen atoms and isotropic temperature factor parameters for the remaining atoms. The next difference Fourier through the section $(2\bar{1}1)$ showed only a small improvement, although the R was reduced to 0·15. A least-squares calculation showed only small shifts. Newly calculated structure factors, optimalized as well as possible with respect to the anisotropic temperature parameters, gave the values for the final difference Fourier through the section $(2\bar{1}1)$, (Fig. 1). A few reflections with high intensities, which were obviously unreliable because of extinction, were left out of this calculation. Although a fair improvement could be seen, the anisotropy is still present. A final least-squares calculation did not give any significant shifts and further refinement was considered to be without any value, taking into account the other possible errors. The final R for all the observed reflections was 0·14. A projection on (010) is shown in Fig. 2. The final parameters are given in Table 1, the temperature factors in Table 2 and direction cosines of the axes of the vibration ellipsoids for the sulfur and the oxygen atoms are given in Table 3. The observed and calculated structure factors are presented in Table 4.

Table 1. *Atomic coordinates*

	x/a	y/b	z/c
S_1	0·410	0·043	0·173
S_2	0·248	0·036	0·473
C_1	0·366	0·129	0·358
C_2	0·871	0·164	0·096
C_3	0·770	0·291	0·148
N_1	0·417	0·283	0·440
O_1	0·909	0·030	0·184
H_1	0·510	0·354	0·440
H_2	0·817	0·339	0·289
H_3	0·676	0·258	0·195

Table 2. *Temperature-factor coefficients*

	α	β	γ	δ	ε	η	B
S_1	0·693	0·635	0·498	0·025	−0·260	0·485	
S_2	0·578	0·483	0·533	−0·265	−0·073	0·523	
O_1	0·818	0·580	0·578	−0·293	−0·413	0·790	
C_1							1·48
C_2							1·38
C_3							2·13
N_1							1·55
H_1							1·00
H_2							1·00
H_3							1·00

Table 3. *Axes of vibration ellipsoids*

Atom	i	g_{i1}	g_{i2}	g_{i3}	B_i
S_1	1	−0·2921	0·3946	0·7889	1·41
	2	0·5507	0·8021	−0·0782	2·75
	3	0·7769	−0·4271	0·6038	3·01
S_2	1	0·0000	0·7312	0·6648	1·88
	2	0·6269	0·5415	−0·4109	1·33
	3	0·7769	−0·4271	0·6038	2·96
O_1	1	−0·2921	0·3946	0·7889	1·24
	2	0·5507	0·8021	−0·0782	2·13
	3	0·7769	−0·4271	0·6038	4·17

Computations

All computations were made on an I.B.M. 650 electronic computer. All the programs used were written in this laboratory. A general program, without limitations as to the number of amplitudes was written for Patterson and Fourier summations. The speed is difficult to define. An actual example with 600 amplitudes took 20 hr. of machine time to compute 31,250 points in space. The structure factor, Fourier and least-squares programs used in this analysis are now superseded by faster programs.

The scattering factors for carbon, nitrogen and oxygen were the values of Berghuis *et al.* (1955). The scattering factors of sulfur were based on the values given by Tomiie & Stam (1958).

Description of the structure

All of the atoms lie very nearly in a plane. The least-squares-best plane is given by the equation $2{\cdot}127x-1{\cdot}302y+1{\cdot}087z=1$, and the average deviation of the atoms from this plane is 0·012 Å, the maximum

Table 4. *Table of structure factors of rhodanine*

The star indicates an unobserved reflection. The listed value of F_o in that case is the minimal structure factor amplitude which is observable at the position of the reflection

h	l	F_o	F_c
k = 0			
2	0	247	-304
4	0	212	-209
6	0	828	-753
8	0	269	267
10	0	49	-31
12	0	176	167
1	1	165	254
1	-1	318	399
3	1	403	-430
3	-1	177	157
5	1	145	-129
5	-1	65	-45
7	1	174	174
7	-1	60	-58
9	1	102	97
9	-1	63	-64
11	1	19*	-27
11	-1	119	-99
0	2	110	115
2	2	77	-42
2	-2	799	-835
4	2	559	538
4	-2	242	266
6	2	126	-110
6	-2	79	-81
8	2	25*	-18
8	-2	436	476
10	2	180	-140
10	-2	202	-220
12	-2	45	41
1	3	57	-68
1	-3	321	321
3	3	143	131
3	-3	88	93
5	3	327	-318
5	-3	24	16
7	3	60	-37
7	-3	269	-257
9	3	24	-23
9	-3	71	-35
11	-3	112	97
0	4	145	-100
2	4	486	-501
2	-4	218	189
4	4	24*	-9
4	-4	700	810
6	4	88	-78
6	-4	118	-110
8	4	255	208
8	-4	269	-276
10	4	22	57
10	-4	323	-311
12	-4	180	180
1	5	317	-309
1	-5	24*	5
3	5	363	369
3	-5	279	-273
5	5	96	-100
5	-5	374	411
7	5	29	68
7	-5	113	-99
9	5	82	-76
9	-5	62	79
11	-5	116	-126
0	6	365	354
2	6	25*	-19
2	-6	130	-123
4	6	64	36
4	-6	27*	-33
6	6	226	-192
6	-6	269	-287
8	-6	79	94
10	-6	56	27
1	7	243	-291
1	-7	174	186
3	7	65	-58
3	-7	25*	-24
5	7	16*	-20
5	-7	237	286
7	-7	162	-179
9	-7	77	67
0	8	86	-113
2	8	92	-95
2	-8	224	-168
4	8	110	108
4	-8	110	71
6	-8	105	85
8	-8	234	239
1	-9	157	164
3	-9	88	-91
5	-9	63	-38
k = 1			
1	0	148	-176
2	0	475	684
3	0	87	68
4	0	174	151
5	0	122	128
6	0	129	-111
7	0	78	60
8	0	126	-128
9	0	25*	-24
10	0	25*	27
11	0	68	-60
12	0	33	-38
0	1	108	-130
1	1	494	603
1	-1	248	352
2	1	949	1253
2	-1	37	-37
3	1	85	99
3	-1	40	46
4	1	176	-160
4	-1	799	-904
5	1	65	-59
5	-1	182	195
6	1	98	-64
6	-1	255	272
7	1	126	-133
7	-1	159	-143
8	1	354	-367
8	-1	43	-42
9	1	26*	32
9	-1	87	100
10	1	151	142
10	-1	266	286
11	1	18*	21
11	-1	115	-96
12	1	11*	-12
12	-1	99	-93
0	2	108	-121
1	2	244	277
1	-2	33	12
2	2	135	153
2	-2	94	-79
3	2	247	-217
3	-2	136	123
4	2	54	30
4	-2	113	88
5	2	169	-128
5	-2	21*	-2
6	2	23*	14
6	-2	87	-68
7	2	65	-56
7	-2	43	-43
8	2	25*	-22
8	-2	64	52
9	2	222	203
9	-2	151	-164
10	2	56	-39
10	-2	25*	-14
11	-2	21	34
12	-2	16*	-16
0	3	764	-726
1	3	54	26
1	-3	158	-145
2	3	47	47
2	-3	96	92
3	3	132	125
3	-3	49	18
4	3	120	-92
4	-3	93	79
5	3	34	28
5	-3	177	176
6	3	415	345
6	-3	531	630
7	3	85	-74
7	-3	38	31
8	3	25*	-8
8	-3	188	-200
9	3	101	-94
9	-3	49	-48
10	-3	104	-74
11	-3	136	-110
12	-3	203	-199
0	4	202	234
1	4	324	334
1	-4	179	-161
2	4	138	-138
2	-4	185	-196
3	4	75	-76
3	-4	37	38
4	4	61	62
4	-4	21*	-14
5	4	108	103
5	-4	294	-275
6	4	113	-113
6	-4	311	281
7	4	169	-177
7	-4	162	172
8	4	21*	-19
8	-4	103	80
9	4	15*	38
9	-4	25*	-1
10	4	28	-34
10	-4	136	-128
11	-4	94	87
12	-4	61	-62
0	5	65	62
1	5	64	-41
1	-5	56	-59
2	5	25*	-5
2	-5	485	558
3	5	64	-75
3	-5	176	-172
4	5	301	-311
4	-5	129	-124
5	5	85	68
5	-5	59	34
6	5	26	29
6	-5	182	-142
7	5	43	-52
7	-5	126	122
8	5	17*	-16
8	-5	300	-329
9	-5	25*	7
10	-5	119	151
11	-5	56	-45
12	-5	50	36
0	6	103	102
1	6	54	-28
1	-6	273	-312
2	6	33	-33
2	-6	87	64
3	6	132	-131
3	-6	261	289
4	6	49	39
4	-6	143	-64
5	6	251	234
5	-6	54	-54
6	6	58	-45
6	-6	148	120
7	-6	202	186
8	-6	61	-68
9	-6	151	-156
10	-6	23*	22
11	-6	64	58
0	7	94	-104
1	7	104	102
1	-7	45	-42
2	7	195	193
2	-7	90	-88
3	7	98	-107
3	-7	104	-85
4	7	94	86
4	-7	247	-226
5	7	61	-56
5	-7	124	82
6	-7	120	86
7	-7	26	-5
8	-7	92	68
9	-7	98	73
10	-7	135	182
0	8	21*	32
1	8	117	91
1	-8	23*	-45
2	8	36	-41
2	-8	23*	-26
3	8	158	-137
3	-8	234	223
4	-8	33*	-43
5	-8	169	-143
6	-8	54	-34
8	-8	15*	-5
0	9	103	-98
1	-9	15*	-28
2	-9	15*	-3
3	-9	50	40
4	-9	126	115
5	-9	13*	1
k = 2			
0	0	516	586
1	0	255	-363
2	0	89	-83
3	0	193	178
4	0	67	67
5	0	162	-159
6	0	421	-416
7	0	158	141
8	0	125	121
9	0	67	-53
10	0	20*	-16
11	0	63	56
12	0	155	138
0	1	309	-405
1	1	443	-543
1	-1	22	-16
2	1	100	91
2	-1	258	316
3	1	108	125
3	-1	13*	1
4	1	356	369
4	-1	157	-156
5	1	57	47
5	-1	228	220
6	1	99	68
6	-1	161	-141
7	1	205	216
7	-1	20*	-6
8	1	145	-140
8	-1	52	-27
9	1	44	-52
9	-1	62	-63
10	1	20*	-40
10	-1	26*	-4
11	1	16*	-4
11	-1	52	-33
12	-1	15*	10
0	2	91	-82
1	2	20*	-29
1	-2	49*	0
2	2	156	-157
2	-2	873	-968
3	2	328	365
3	-2	142	109
4	2	628	728
4	-2	181	169
5	-2	173	-133
5	2	135	-93
6	2	62	-47
6	-2	107	89
7	2	144	-151
7	-2	239	247
8	2	29	29
8	-2	392	417
9	2	49	-64
9	-2	112	-108
10	2	279	-270
10	-2	80	-80
11	2	107	112
11	-2	50	-49
12	-2	52	-45
0	3	124	-123
1	3	62	-61
1	-3	215	235
2	3	28	16
2	-3	228	-228
3	3	178	162
3	-3	306	-275
4	3	153	-105
4	-3	215	-216
5	3	135	-122
5	-3	20*	7
6	3	24*	1
6	-3	89	56
7	3	23*	12
7	-3	161	-172
8	3	37	-34
8	-3	188	215
9	3	69	-63
9	-3	206	217
10	3	121	111
10	-3	22*	29
11	-3	26	-6
12	-3	107	-113
0	4	185	194
1	4	58	-56
1	-4	28	14
2	4	442	-473
2	-4	62	-40
3	4	142	118
3	-4	124	108
4	4	80	75
4	-4	351	461
5	4	23*	3
5	-4	137	-130
6	4	23*	-5
6	-4	255	-246
7	4	23*	28
7	-4	22	11
8	4	162	161
8	-4	69	69
9	4	49	-46
9	-4	62	-43
10	-4	258	-221
11	-4	47	53
12	-4	93	107
0	5	111	108
1	5	49	-22
1	-5	29	14
2	5	175	187
2	-5	125	-131
3	5	201	213
3	-5	287	-320
4	-5	156	-143
4	-5	309	314
5	5	23*	4
5	-5	84	69
6	5	20*	18
6	-5	60	40
7	5	18*	31
7	-5	41	27
8	5	25	-60
8	-5	41	-22
9	-5	220	198
10	-5	145	-133
11	-5	82	-90
0	6	298	332
1	6	115	-93
1	-6	197	-244
2	6	145	164
2	-6	108	-100
3	6	147	-111
3	-6	54	-32
4	6	20*	-24
4	-6	228	-201
5	6	26	-50
5	-6	29	21
6	6	170	-148
6	-6	275	-295
7	6	112	106
7	-6	101	101
8	-6	178	161
9	-6	62	-48
10	-6	89	75
11	-6	58	57
0	7	106	-106
1	7	161	-144
1	-7	183	172
2	7	37	-37
2	-7	88	-85
3	7	63	77
3	-7	76	-80
4	7	18	-15
4	-7	82	71
5	7	112	-125
5	-7	173	158
6	-7	156	-112
7	-7	152	-143
8	-7	18*	-6
9	-7	15*	22
0	8	62	-68
1	8	34	20
1	-8	94	-74
2	8	30	40
2	-8	172	-144
3	8	13*	-6
3	-8	54	38
4	-8	23	15
5	-8	54	40
6	-8	152	117
7	-8	84	60
8	-8	64	72
1	-9	127	175
2	-9	76	-87
3	-9	132	-133
4	-9	49	-33
k = 3			
1	0	158	-185
2	0	245	280
3	0	29	-25
4	0	165	152
5	0	183	182
6	0	177	-161
7	0	58	41
8	0	35	-34
9	0	21*	-8
10	0	70	-43
11	0	78	-78
0	1	176	-212
1	1	214	226
1	-1	15*	-8
2	1	411	458
2	-1	15*	8
3	1	318	-352
3	-1	250	-261
4	1	20*	-3
4	-1	383	-473
5	1	19*	-33
5	-1	148	129
6	1	171	157
6	-1	54	61
7	1	75	-99
7	-1	54	-28
8	1	271	-314
8	-1	55	52
9	1	252	212
9	-1	140	147
10	1	18	20
10	-1	257	229
11	1	38	-35
11	-1	55	-47
12	-1	82	-90
0	2	117	-128
1	2	44	-74
1	-2	63	-79
2	2	472	-515
2	-2	35	37
3	2	165	-211
3	-2	285	313
4	2	77	73
4	-2	357	-410
5	2	181	186
5	-2	234	-215
6	2	145	144
6	-2	163	-133
7	2	21*	-17
7	-2	20*	-26
8	2	241	202
8	-2	35	6
9	2	19*	-7
9	-2	48	-9
10	2	77	-75
10	-2	204	183
11	2	9*	-28
11	-2	102	91
12	-2	78	58
0	3	594	-645
1	3	183	179
1	-3	252	303
2	3	17*	-16
2	-3	237	251
3	3	133	-133
3	-3	145	-124
4	3	20*	-8
4	-3	18*	-19
5	3	215	234
5	-3	204	191
6	3	367	379
6	-3	305	325
7	3	97	-78
7	-3	247	-255
8	3	120	-115
8	-3	119	-117
9	3	16*	6
9	-3	50	15
10	3	12*	-34
10	-3	68	70
11	-3	54	-44
12	-3	140	-149
0	4	183	201
1	4	167	184
1	-4	122	-114
2	4	153	-125
2	-4	119	-120
3	4	51	20
3	-4	17*	-2
4	4	52	-46
4	-4	61	-64
5	4	91	67
5	-4	224	-225
6	4	110	-69
6	-4	241	268
7	4	105	-89
7	-4	149	135
8	4	55	45
8	-4	21*	-15
9	4	17	-31
9	-4	20*	23
10	-4	17*	-17
11	-4	129	115
0	5	104	115
1	5	119	-107
1	-5	227	229
2	5	129	126
2	-5	258	277
3	5	50	-60
3	-5	183	-217
4	5	245	-235
4	-5	233	-227
5	5	170	140
5	-5	51	-28
6	5	46	-45
6	-5	31	-18
7	5	46	41
7	-5	171	-158
8	5	12*	27
8	-5	202	-189
9	-5	157	150
10	-5	139	127
11	-5	49	-35
0	6	26	-21
1	6	108	145
1	-6	124	-150
2	6	68	66
2	-6	270	316
3	6	115	-75
3	-6	24*	-6
4	6	235	214
4	-6	23*	12
5	6	50	49
5	-6	24*	-41
6	6	63	-52
6	-6	86	-56
7	-6	203	198
8	-6	194	-186
9	-6	91	-90
10	-6	29	-3
0	7	51	66
1	7	58	66
1	-7	48	-22
2	7	203	176
2	-7	167	-161
3	7	17*	13
3	-7	20*	7
4	7	15*	5
4	-7	235	-217
5	7	44	-45
5	-7	78	60
6	-7	117	96
7	-7	18*	7
8	-7	149	122
9	-7	37	32
0	8	16	36
1	8	149	150
1	-8	34*	-37
2	8	104	-122
2	-8	102	103
3	-8	114	132
4	-8	165	-165
5	-8	165	-145
6	-8	15*	7
7	-8	51	51
k = 4			
0	0	405	438
1	0	350	-348
2	0	76	-87
3	0	109	-118
4	0	145	155
5	0	179	-187
6	0	352	-384
7	0	250	250
8	0	20*	2
9	0	29	-10
10	0	16*	17
11	0	76	82
0	1	405	-433
1	1	20	-15
1	-1	13*	-9
2	1	15*	-4
2	-1	80	87
3	1	24	19
3	-1	89	98
4	1	59	70
4	-1	56	-48
5	1	36	-24
5	-1	105	78
6	1	317	307
6	-1	217	-233
7	1	87	-61
7	-1	150	-135
8	1	76	-62
8	-1	132	-118
9	1	76	36
9	-1	44	-59
10	1	44	-53
10	-1	104	89
11	1	36	43
11	-1	13*	2
0	2	66	58
1	2	134	-137
1	-2	289	-373
2	2	37	-45
2	-2	271	-359
3	2	148	158
3	-2	251	292
4	2	216	210
4	-2	220	155
5	2	264	-259
5	-2	52	-39
6	2	103	-88
6	-2	20*	-30
7	2	131	134
7	-2	125	121
8	2	43	29
8	-2	148	167
9	2	87	-89
9	-2	199	-168
10	2	87	-59
10	-2	136	-120
11	-2	76	62
0	3	73	-85
1	3	51	10
1	-3	172	214
2	3	154	-176
2	-3	338	-400
3	3	37	-60
3	-3	75	-59
4	3	303	-318
4	-3	55	-58
5	3	137	-158
5	-3	20*	-25
6	3	134	128
6	-3	75	-79
7	3	41	74
7	-3	85	-53
8	3	118	127
8	-3	194	216
9	3	15*	3
9	-3	45	30
10	-3	55	39
11	-3	44	-33
0	4	138	157
1	4	184	-244
1	-4	18*	6
2	4	279	-323
2	-4	158	154
3	4	197	193
3	-4	266	301
4	4	95	-105
4	-4	189	184
5	4	23*	-5
5	-4	322	-331
6	4	20*	19
7	4	104	121
6	-4	115	-113
7	-4	16*	-13
8	4	186	162
8	-4	31	-3
9	-4	163	-137
10	-4	131	-126
11	-4	194	202
0	5	41	41
1	5	170	-153
1	-5	137	165
2	5	237	275
2	-5	72	71
3	5	20	31
3	-5	88	-114
4	5	56	-35
4	-5	252	290
5	5	16*	-31
5	-5	118	81
6	5	55	-52
6	-5	34	-46
7	5	105	106
7	-5	65	-49
8	-5	61	-39
9	-5	125	112
10	-5	128	-135
0	6	139	145
1	6	103	-77
1	-6	31	-27
2	6	43	-41
2	-6	61	-47
3	6	29	-14
3	-6	34	-14
4	6	67	48
4	-6	20*	-19
5	6	15*	-17
5	-6	217	-180
6	6	92	-67
6	-6	154	-137
7	-6	132	114
8	-6	88	80
9	-6	13*	11
0	7	212	-291
1	7	120	-127
1	-7	62	33
2	7	115	114
2	-7	58	50
3	7	40	40
3	-7	23*	-18
4	7	36	42
4	-7	18*	9
5	-7	175	172
6	-7	268	-257
7	-7	111	-101
8	-7	11*	22
0	8	80	-98
1	8	65	52
1	-8	24	4
2	-8	137	-129
3	-8	66	65
4	-8	118	115
5	-8	95	66
6	-8	137	112
k = 5			
1	0	132	129
2	0	171	197
3	0	17	-25
4	0	264	287
5	0	167	-128
6	0	20*	18
7	0	97	47
8	0	160	-189
9	0	26	-34
10	0	171	-144
0	1	46	24
1	1	286	288
1	-1	53	41
2	1	192	233
2	-1	126	160
3	1	276	-315
3	-1	260	-314
4	1	116	-150
4	-1	281	-314
5	1	143	121
5	-1	355	391
6	1	21*	8
6	-1	75	67
7	1	138	-157
7	-1	49	-31
8	1	111	-76
8	-1	40	-54
9	1	103	81
9	-1	83	78
10	1	32	25
10	-1	126	107
11	-1	163	-174
0	2	134	-174
1	2	16*	-21
1	-2	102	108
2	2	239	-275
2	-2	16*	0
3	2	19*	-32
3	-2	29	27
4	2	94	85
4	-2	241	-270
5	2	100	-56
5	-2	51	-26
6	2	93	92
6	-2	78	-69
7	2	17*	-2
7	-2	31	-51
8	2	148	122
8	-2	51	45
9	2	47	22
9	-2	55	-22
10	-2	94	97
11	-2	27	23
0	3	133	-140
1	3	283	323
1	-3	201	254
2	3	49	-63
2	-3	100	103
3	3	24*	18
3	-3	41	39
4	3	40	-31
4	-3	116	113
5	3	75	71
5	-3	231	227
6	3	78	39
6	-3	77	86
7	3	189	-152
7	-3	213	-250
8	3	15*	-1
8	-3	133	-129
9	3	34	36
9	-3	66	53
10	-3	32	-13
0	4	359	454
1	4	19	48
1	-4	116	-100
2	4	20*	-20
2	-4	20*	18
3	4	20*	-64
3	-4	122	146
4	4	101	-116
4	-4	53	42
5	4	73	35
5	-4	23*	17
6	4	295	-260
6	-4	250	242
7	4	59	-79
7	-4	16*	0
8	4	98	117
8	-4	16*	11
9	-4	117	-94
10	-4	32	22
0	5	20*	-21
1	5	55	73
1	-5	126	144
2	5	61	53
2	-5	93	99
3	5	130	-138
3	-5	111	-126
4	5	139	-106
4	-5	39	26
5	5	65	28
5	-5	23*	-8
6	5	14*	3
6	-5	22*	-16
7	-5	177	-149
8	-5	91	-94
9	-5	191	177
0	6	91	97
1	6	17*	27
1	-6	68	-103
2	6	16*	18
2	-6	283	305
3	6	108	-71
3	-6	160	120
4	6	191	163
4	-6	19*	-17
5	-6	22*	-32
6	-6	17*	28
7	-6	100	92
8	-6	210	-222
9	-6	114	-113
0	7	89	-93
1	-7	59	-47
2	-7	16*	5
3	-7	158	-133
4	-7	64	-60
5	-7	143	119
6	-7	122	100
2	-8	26	-10

Table 4 (*cont.*)

h	l	F_o	F_c
	k = 6		
0	0	97	129
1	0	220	-27
2	0	44	-49
3	0	195	233
4	0	36	-19
5	0	264	-265
6	0	25*	-20
0	1	133	-165
1	1	87	83
1	-1	23*	7
2	1	82	95
2	-1	230	309
3	1	23*	16
3	-1	123	-123
4	1	173	197
4	-1	52	44
5	1	29*	-15
5	-1	37	-2
6	1	115	99
6	-1	215	-213
0	2	23*	18
1	2	33	46
1	-2	257	-320
2	2	23*	-2
2	-2	119	-128
3	2	143	178
3	-2	271	370
4	2	65	54
4	-2	26*	31
5	2	251	-190
5	-2	29*	10
6	2	59	-38
6	-2	65	44
0	3	43	44
1	3	24*	-19
1	-3	88	-76
2	3	79	-98
2	-3	255	-349
3	3	82	68
3	-3	76	-57
4	3	268	-260
4	-3	26*	-16
5	3	70	7
5	-3	128	103
6	3	122	98
6	-3	135	128
0	4	23*	15
1	4	150	-145
1	-4	44	-49
2	4	23*	11
2	-4	39	-47
3	4	140	123
3	-4	99	105
4	4	67	51
4	-4	60	61
5	-4	114	-96
6	-4	23*	-19
0	5	52	-17
1	5	71	-24
1	-5	23*	-2
2	5	201	290
2	-5	120	-130
3	-5	40	9
4	-5	290	297
5	-5	83	49
6	-5	20*	20
0	6	23*	-9
1	-6	122	-144
2	-6	48	-42
3	-6	39	-35
4	-6	27	0
5	-6	158	-127
6	-6	16	-26
0	7	212	-197
1	-7	72	41
2	-7	12*	-23
3	-7	31	-13
4	-7	14*	6
5	-7	53	-21
	k = 7		
1	0	25*	2
2	0	171	203
3	0	31*	9
4	0	112	134
5	0	27*	3
6	0	61	-54
0	1	40	-51
1	1	164	205
1	-1	127	141
2	1	40	-10
2	-1	95	-116
3	1	184	-175
3	-1	164	-258
4	1	48	38
4	-1	88	90
5	1	110	73
5	-1	245	187
6	1	23*	32
6	-1	59	53
0	2	134	-186
1	2	96	82
1	-2	135	-193
2	2	162	-203
2	-2	24*	11
3	2	128	89
3	-2	73	-95
4	2	110	112
4	-2	235	-288
5	2	26*	28
5	-2	29*	16
6	2	63	46
6	-2	105	-71
0	3	24*	2
1	3	150	144
1	-3	231	245
2	3	101	111
2	-3	44	-38
3	3	23*	4
3	-3	85	-84
4	3	74	-57
4	-3	56	-75
5	3	184	130
5	-3	147	105
6	3	16*	8
6	-3	52	39
0	4	211	237
1	4	87	-43
1	-4	38	4
2	4	61	-73
2	-4	23*	-20
3	4	63	38
3	-4	19*	-19
4	4	17*	-10
4	-4	23*	-38
5	-4	26*	3
6	-4	276	221
0	5	17*	-3
1	-5	73	83
2	5	54	49
2	-5	21	-30
3	-5	133	-142
4	-5	79	-78
5	-5	57	45
6	-5	44	-20
0	6	50	77
1	-6	75	58
2	-6	177	201
3	-6	15*	-11
5	-6	78	-56
	k = 8		
0	0	75	-100
1	0	110	-152
2	0	30	20
3	0	48	27
4	0	37	-24
5	0	200	-159
6	0	105	94
0	1	184	-239
1	1	50	35
1	-1	54	43
2	1	30	38
2	-1	61	68
3	1	20*	19
3	-1	67	-65
4	1	67	57
4	-1	62	-79
5	1	42	36
5	-1	25*	-66
6	1	119	106
6	-1	221	-165
0	2	28	-17
1	2	156	-147
1	-2	105	-110
2	2	61	-78
2	-2	162	157
3	2	161	170
3	-2	103	105
4	2	25	-35
4	-2	28	-10
5	2	151	-127
5	-2	174	-139
6	2	28	40
6	-2	17*	-45
0	3	88	-123
1	3	53	-82
1	-3	62	-62
2	3	58	-68
2	-3	184	-217
3	3	16*	-18
3	-3	30	48
4	3	106	-97
4	-3	64	-71
5	3	141	108
5	-3	75	55
6	-3	67	-48
0	4	16*	11
1	4	191	-201
1	-4	47	-35
2	4	49	70
2	-4	17*	-22
3	4	92	109
3	-4	86	105
4	-4	48	-51
5	-4	227	-185
1	-5	15*	-8
3	-5	61	46
4	-5	126	163
	k = 9		
1	0	29	50
2	0	115	111
3	0	73	60
4	0	68	57
5	0	116	-80
0	1	20*	-10
1	1	140	136
1	-1	82	65
2	1	105	-111
2	-1	30	49
3	1	113	-122
3	-1	73	-75
4	1	40	32
4	-1	147	139
5	-1	69	73
0	2	20*	-1
1	2	43	-54
1	-2	25	18
2	2	130	-145
2	-2	25	23
3	2	86	66
3	-2	23	-38
4	-2	145	-125
0	3	143	175
1	3	83	85
1	-3	98	100
2	3	60	-80
2	-3	16*	32
3	-3	86	-87

deviation being 0·024 Å for the C_3 atom. This latter atom is the only one with two attached hydrogen atoms and does not seem to be involved in any resonating structure in the molecule.

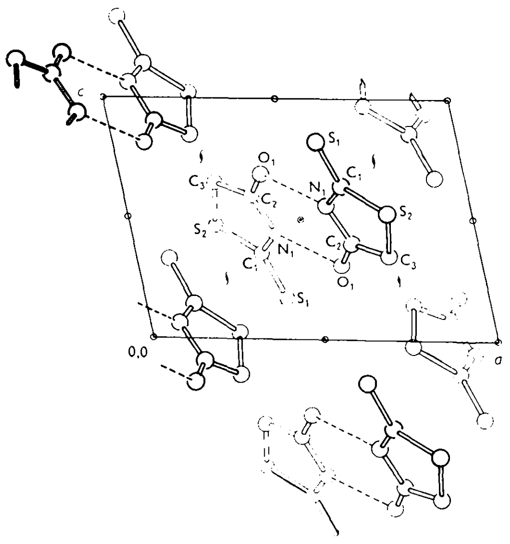

Fig. 3. Projection of the structure of rhodanine, viewed along the *b*-axis. The *b*-axis is up.

A projection of the structure of rhodanine is shown in Fig. 3, viewed along the *b*-axis. Bond distances and angles are shown in Table 5. We estimate the error in the coordinates of atoms as being less than 0·01 Å and, therefore, the error in bond distances as being between 0·01 and 0·02 Å. The error in bond angles is estimated as being less than 1°. These estimates are based upon the changes in bond distances observed in the final stage of refinement. The maximum change in bond distance was actually 0·005 Å for the C_2–C_3 distance.

Table 5. *Bond distances and angles*

Bond distances		Bond angles	
C_1–S_1	1·64 Å	S_1–C_1–S_2	124·1°
C_1–S_2	1·74	S_1–C_1–N_1	124·2
C_3–S_2	1·82	N_1–C_1–S_2	111·8
C_2–C_3	1·51	C_1–N_1–C_2	116·8
C_2–O_1	1·23	N_1–C_2–C_3	112·3
N_1–C_2	1·38	N_1–C_2–O_1	123·3
C_1–N_1	1·37	O_1–C_2–C_3	124·3
		C_2–C_3–S_2	106·3
		C_3–S_2–C_1	92·7

The only bond which does not show some evidence of involvement in a resonating system is the C_3–S_2 bond whose length, 1·82 Å, agrees very well with the expected single bond distance of 1·81 Å (Pauling, 1945), and with measured carbon–sulfur bond distances found in compounds where no resonance is to be expected (1·81 Å in 1,4-dithian, Marsh, 1955; 1·82 Å in dimethyl sulfide, Brockway & Jenkins, 1936; 1·87 Å in N,N'-diglycyl-l-cystine dihydrate, Yakel & Hughes, 1954).

Using Pauling's (1945) tables of bond radii and his table showing the relationship between bond distance and double-bond character, the following approximate double bond percentages can be derived from the experimentally observed bond distances:

C_2–O_1	80%	C_1–S_1	60%
C_2–C_3	–	C_1–S_2	25%
C_2–N_1	20%	C_1–N_1	25%

Thus, a considerable positive charge would be expected to reside on the nitrogen atom making the attached hydrogen atom acidic in nature. Likewise, a considerable negative change would reside on the S_1 atom while a smaller positive charge would be found on S_2 and a small negative charge on O_2. These findings would tend to indicate that the silver rhodanine complex (Feigl, 1926, 1949) would have silver atoms bonded to the N_1 and S_1 atoms. It is not possible to predict the structure of silver rhodanine complex, although a bimolecular complex with two linear N–Ag–S_1 bonds would seem to be the most probable.

The internal angle C_1–S_2–C_3 is 92° 42′ which is just slightly larger than the expected angle of 90° for a single bond but the deviation is in the correct direction for some double-bond character in the C_1–S_2 bond. Likewise the internal angle C_1–N_1–C_2 is found to be 116° 45′ which again tends to show the above-mentioned resonance effects.

The molecule in the plane $(2\bar{1}1)$ forms a pair with the related molecule by a center of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the same plane. The two molecules are bonded together with two N–H $\cdots$ O hydrogen bonds of length 2·85 Å (Fig. 3). The other two molecules lie in the symmetry related plane (211). The planes $(2\bar{1}1)$ and (211) include an angle of 51°. The hydrogen bond angles are $\angle\, C_2\text{–}N_1\text{–}O_1 = 113°\,26'$ and $\angle\, C_2\text{–}O_1\text{–}N_1 = 122°\,5'$.

The crosswise packing of the centrosymmetrical related ‘double’ molecules is similar to that found in many flat organic molecules. Chains of atoms O_1'–(3·6 Å)–O_1–(3·3 Å)–S_2–(3·0 Å)–S_1–(3·5 Å)–S_1'–(3·0 Å)–S_2' etc. extend along $[\bar{1}02]$. The similarity of distances in the chain causes all the S–O peaks in the Patterson to fall on top of the S–S peaks.

Table 6. *Intermolecular distances between reference molecule and molecule related by*

Screw axis $(\frac{1}{4}, 0, \frac{3}{4})$		Screw axis $(\frac{1}{4}, 0, \frac{1}{4})$		Center of symmetry $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	
S_2–O_1'	3·27	C_2–S_1'	3·45	C_2–N_1'	3·63
C_3–O_1'	3·01	N_1–S_1'	3·77	O_1–C_2'	3·66
C_3–C_3'	4·19	N_1–S_2'	3·66	O_1–C_1'	3·87
C_3–S_2'	3·76	S_1–O_1'	3·70	O_1–S_1'	4·18
C_2–S_2'	3·91	S_1–S_2'	4·15	C_2–S_1'	3·80
				N_1–N_1'	3·90
				O_1–O_1'	3·59

The sulfur atoms of two molecules approach to within 3·47 Å of each other. This verifies the finding of Yakel & Hughes (1954), Marsh (1955) and Donohue (1950) that the van der Waals radius of sulfur is less than the value 1·85 Å given by Pauling (1945) and is closer to 1·72–1·73 Å. Other intermolecular distances are given in Table 6. The C_3–O_1' distance is remarkably short.

We do not feel that the temperature factor parameters are highly accurate due to the appearance of the difference Fourier, Fig. 1. The two atoms outside the ring, S_1 and O_1, have the highest temperature factors. The directions of the vibration ellipsoids and also the fact that the ring atoms have relatively lower temperature factors, probably indicate that there exists a torsional vibration around the center of gravity of the five-membered ring.

The difference Fourier may also indicate that the electron distribution around the sulfur atoms is not spherically symmetrical or that the atomic scattering factors are not absolutely correct.

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