

The Crystal and Molecular Structure of Rhodan Hydrate

ASBJØRN HORDVIK

Chemical Institute, University of Bergen, Bergen, Norway

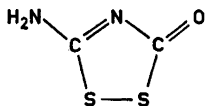
The crystal and molecular structure of rhodan hydrate, a five-membered cyclic unsaturated disulphide, has been solved by systematic application of Sayre's equation, and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the $h0l$, $hk0$, and hhl reflections, and the final atomic coordinates have been corrected for the rigid-body libration of the molecule.

The rhodan hydrate molecule is approximately planar. Two of the found C-N bond lengths, 1.336 ± 0.017 Å and 1.337 ± 0.018 Å, agree with the aromatic C-N bond length, 1.340 Å in pyridine, while the third C-N bond length, 1.408 ± 0.017 Å, deviates significantly from this value. Other bond lengths in the molecule are, S-C = 1.767 and 1.784 ± 0.015 Å, C-O = 1.223 ± 0.017 Å and S-S = 2.061 ± 0.007 Å.

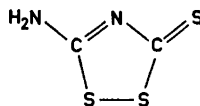
The bond lengths show that the molecule is stabilized through π -orbital delocalization, which is more pronounced in the carbon-nitrogen part than in the carbon-sulphur part of the molecule, but the conjugation in the ring probably also extends over the sulphur-sulphur bond.

The molecules are in the crystal arranged in pairs over centers of symmetry. The molecules in a pair lie approximately in the same plane and are held together through N-H...N hydrogen bonds of length 2.97 ± 0.02 Å. Between pairs there are N-H...O hydrogen bonds of length 2.87 ± 0.02 Å.

Rhodan hydrate (I) and xanthan hydride (II) are unsaturated five-membered cyclic disulphides. The relatively high stability of these compounds as contrasted with saturated five-membered cyclic disulphides, is probably due to some aromatic character of the ring.

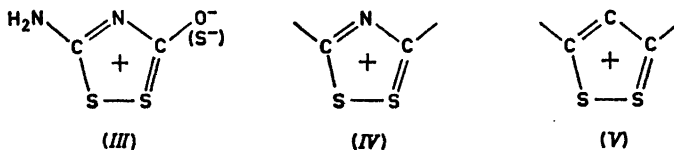


(I)



(II)

In formally polar forms of rhodan hydrate and xanthan hydride, as for example III, the ring atoms possess a sextet of π -electrons available for bonding. Equivalent resonance forms, IV and V, appear to play an important role in the structures of the thiuret ion¹⁻⁴ and the 1,2-dithiolium ion,^{5,6} respectively.



In the unsaturated five-membered cyclic disulphides so far investigated, the disulphide group is essentially planar.¹⁻⁸ Foss¹ suggests that delocalized π -bonding may account for the planarity and the relatively high stability of the compounds. As a contrast, the saturated five-membered cyclic disulphide, 1,2-dithiolane-4-carboxylic acid may be mentioned.⁹ There the disulphide group has a dihedral angle of $27 \pm 1^\circ$ and the 1,2-dithiolane ring is rather unstable.

The most pronounced ring-conjugation so far found in an unsaturated five-membered cyclic disulphide, occurs in 3-phenyl-1,2-dithiolium iodide.⁶ In that compound even the sulphur-sulphur bond, 2.00 ± 0.01 Å, has appreciable π -bond character.

The sulphur-sulphur bond length in 3,5-diamino-1,2-dithiolium iodide⁴ has been found to be 2.08 ± 0.02 Å. For the analogous compound, thiuret hydroiodide, two different refinement procedures^{1,4} led to sulphur-sulphur bond lengths of 2.088 ± 0.012 Å and 2.083 ± 0.015 Å, respectively, and in thiuret hydrobromide² the sulphur-sulphur bond length is found to be 2.081 ± 0.009 Å. Also the carbon-sulphur bonds are longer in the latter compounds than in 3-phenyl-1,2-dithiolium iodide. The reason seems to be that the amino nitrogens in the thiuret ion and the 3,5-diamino-1,2-dithiolium ion strongly engage themselves in π -bonding, at the expense of the conjugation in the carbon-sulphur part of the unsaturated disulphide ring.

Accordingly, in order for a stable planar disulphide group to occur, one may assume that only weak conjugation in the carbon-sulphur part of the ring is necessary. The sulphur-sulphur bond lengths mentioned above for 3,5-diamino-1,2-dithiolium iodide, thiuret hydroiodide and hydrobromide, indicate that the sulphur-sulphur bonds in these compounds are pure single bonds, while the sulphur-sulphur bond length of 2.071 ± 0.004 Å (corrected for rigid-body libration), found in thiuret hydrochloride hemihydrate,³ may indicate that the conjugation there also extends over the sulphur-sulphur bond. There are, however, in the former compounds linear $X \cdots S - S \cdots X$ arrangements in which close contacts between halogen ions (X) and sulphur atoms may influence the length of the sulphur-sulphur bond. The partial covalent bonding between halogen and sulphur probably arises through a transfer of charge from the halogen ions to those *p*-orbitals of the sulphur atoms already engaged in the sulphur-sulphur σ -bond, at the expense of this bond.

Rhodan hydrate and xanthan hydride are according to their unit cells and space groups,¹⁰ well suited for X-ray crystallographic structure investigation. The purpose of working out both structures was mainly to obtain two independent determinations of the same unsaturated five-membered disulphide ring. The results from the structure investigation of xanthan hydride have been reported.⁸

EXPERIMENTAL

The unit cell and space group of rhodan hydrate have been reported by Foss.¹⁰ The crystals are monoclinic, $a = 12.50 \text{ \AA}$, $b = 5.24 \text{ \AA}$, $c = 14.67 \text{ \AA}$, and $\beta = 95\frac{1}{2}^\circ$. The experimental error was estimated to be within 0.5 %. Of the two possible space groups $C2/c$ and C/c , the former is indicated by "average test" and "zero moment test".¹¹ There are eight molecules in the unit cell.

The intensities of the $h0l$, $hk0$ and hhl reflections were estimated by eye from sets of Weissenberg photographs, taken with $\text{CuK}\alpha$ radiation. Small crystals were used in order to minimize absorption effects. 257 independent reflections were obtained and measured. The intensities were corrected for Lorenz and polarization effects but not for absorption. Common reflections in $h0l$, $hk0$ and hhl were used to put all the reflections on the same scale.

The calculated structure factors in Table 11 are based on the atomic scattering curves of Berghuis *et al.*¹² for oxygen, nitrogen, and carbon, Tomiie and Stam¹³ for sulphur, and Viervoll and Øgrim¹⁴ for hydrogen.

STRUCTURE DETERMINATION

Direct solution. The structure was solved in the b -axis projection by means of Harker Kasper inequalities and systematic use of Sayre's equation,¹⁵ and a brief account of this has been reported earlier.¹⁶ A more detailed description of the procedure is given here.

Observed $h0l$ structure factors were put on an absolute scale by means of Wilson's method,¹⁷ and unitary structure factors were calculated for the

Table 1. Unitary structure factors and probable signs for the $h0l$ reflections used in the direct structure determination.

h	l	$100u$	sign	h	l	$100u$	sign
6	0	25	$-abc$	-10	10	42	cd
8	0	44	$-b$	-10	14	50	a
0	8	36	$-ab,d$	12	10	30	$-c$
0	12	45	ac	-12	2	55	$-a$
0	14	33	b	-12	4	57	$-bc,d$
2	4	27	ab	-12	10	46	$-ad,b$
2	10	37	ad	14	2	31	$-b$
2	12	63	-				
-4	4	46	c	12	0	35	+
-4	8	41	ad	2	18	26	-
-4	16	74	a	-4	12	30	+
6	2	58	+	6	14	39	-
6	6	41	acd	-6	10	26	+
-6	4	50	$-a$	-6	16	34	+
-6	6	46	d	8	6	31	-
-6	12	49	b	8	12	34	+
8	14	40	-	12	2	40	-
-10	2	46	c	-12	8	26	+

strongest reflections. The signs for 2,0,12 and 602 were chosen positive, and combination of these two reflections in a Harker Kasper inequality gave the sign for 8,0,14. The signs for $\bar{4}$,0,16, $\bar{6}$,0,12, $\bar{4}$ 04, and $\bar{6}$ 06 were denoted a , b , c , and d , respectively, and sixteen sets of probable signs were derived, by means of Sayre's equation $S_{h'} \cdot S_{h''} \approx S_{h'+h''}$, for the 25 first reflections in Table 1. This could be reduced to four sets of probable signs by taking into account the derived relationship between a , b , c , and d ; see for instance derived signs for 008, $\bar{1}\bar{2}$,0,4 and $\bar{1}\bar{2}$,0,10 in Table 1. Furthermore, one of the remaining four sets could be regarded as unlikely because it had all signs positive.

Sign combinations which fit into Cochran and Woolfson's equation¹⁵ $S(h) \approx S(\sum_{h'} U_{h'} U_{h+h'})$ were then sought among the 25 signs so far determined. This led to probable signs for 10 additional reflections for each of the three sets of probable signs. The corresponding Fourier maps were computed, and the molecule was recognized in one of them. This Fourier map is shown in Fig. 1.

The signs in Table 1 correspond to the origin which was used in the subsequent refinement. Therefore 2,0,12 is negative in Table 1, and the correct solution corresponds to a , b , c , and d also negative. All derived signs later proved right.

Structure refinement. The b -projection of the structure was first refined by Fourier syntheses, and after three cycles, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ was 0.115. A difference map was then calculated in order to locate the hydrogen atoms,

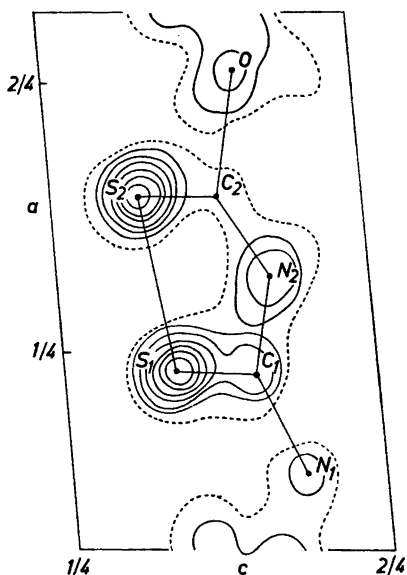


Fig. 1. Fourier map of rhodan hydrate in the b -axis projection, based on the 35 reflections in Table 1, with $a = -$, $b = -$, $c = -$, and $d = -$. Contours at arbitrary but equal intervals.

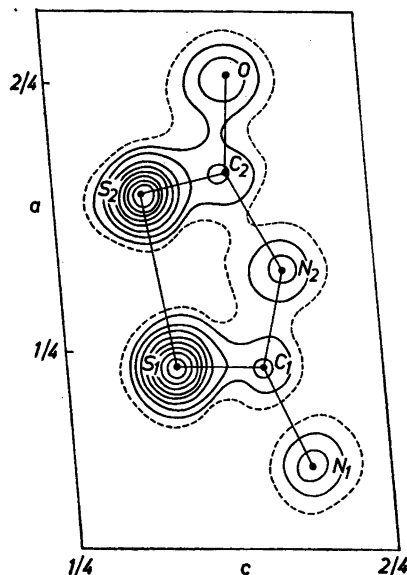


Fig. 2. Final Fourier map of rhodan hydrate in the b -axis projection. Contours at arbitrary but equal intervals.

and the map indicated that both hydrogen atoms belonged to the exocyclic nitrogen. The scattering contribution from the hydrogen atoms were then included in the structure factor calculation. Approximate y -coordinates were found by taking into account that the molecules, as in xanthan hydride, were arranged in pairs across centers of symmetry through N—H...N hydrogen bonds.

The complete set of data, comprising $h0l$, $hk0$ and the diagonal zone hhl , was refined by a least squares procedure. The program which was used, is written by Hirshfeld for the electronic computer WEIZAC, of the Weizmann Institute. A similar but not identical program has been described in the literature.¹⁸ This program seeks to minimize the function

$$r = \frac{\sum w(k^2 F_o^2 - |F_c|^2)^2}{wk^4 F_o^4}$$

by a diagonal approximation of the matrix, and the interaction between k and an average isotropic temperature parameter is taken care of by means of a two by two matrix according to a method of Cruickshank.¹⁹ The weighting factor w for the $h0l$ and hhl reflections was taken as F_o^{-3} for $F_o > 2$ and as $2^{-1}F_o^{-2}$ for $F_o < 2$; for the $hk0$ reflections the threshold value was taken as 3 because the reflections on the films of this zone were weaker. The threshold values given are valid for the observed structure factors as listed in Table 11. Some

Table 2. Final atomic coordinates from the least squares refinement, and standard deviation in coordinates in fractions of corresponding cell edges.

Atom	x	y	z
S ₁	0.2350 0.00030	0.1636 0.00065	0.3365 0.00021
S ₂	0.3958 0.00030	0.1967 0.00070	0.3199 0.00023
C ₁	0.2379 0.0011	0.4354 0.0023	0.4067 0.0007
C ₂	0.4157 0.0009	0.4800 0.0029	0.3854 0.0008
N ₁	0.1463 0.0009	0.5048 0.0025	0.4391 0.0007
N ₂	0.3256 0.0009	0.5777 0.0017	0.4237 0.0007
O	0.5025 0.0009	0.5876 0.0016	0.3925 0.0007
H ₁	0.047 0.012	0.418 0.026	0.435 0.011
H ₂	0.145 0.010	0.645 0.024	0.474 0.007

Table 3. Components of atomic vibration tensors U^r in \AA^2 , referred to crystallographic axes.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S ₁	0.0557	0.0344	0.0519	-0.0096	-0.0128	0.0092
S ₂	0.0557	0.0432	0.0551	-0.0003	-0.0085	0.0138
C ₁	0.0604	0.0377	0.0368	0.0026	-0.0056	0.0115
C ₂	0.0400	0.0373	0.0562	-0.0124	-0.0037	0.0064
N ₁	0.0580	0.0487	0.0551	-0.0256	-0.0210	0.0129
N ₂	0.0479	0.0294	0.0540	-0.0066	-0.0097	0.0134
O	0.0549	0.0578	0.0703	-0.0177	-0.0132	0.0124

Final isotropic temperature factors for H₁ and H₂ are $\exp[-4.9(\sin^2\theta/\lambda^2)]$ and $\exp[-0.95(\sin^2\theta/\lambda^2)]$, respectively.

reflections which were supposed to be affected by secondary extinction were given zero weight.

The least squares refinement was carried out with isotropic temperature factors until all parameter shifts were small compared with the respective standard deviations in parameters. Thereafter anisotropic temperature factors were applied to all atoms except the hydrogens, and the refinement was continued until r had converged. The final value of the conventional agreement factor R is 0.078 when the reflections which are given zero weight are neglected.

Atomic coordinates and components of atomic vibration tensors, corresponding to the last stage of refinement, are given in Tables 2 and 3, respectively. The observed and calculated structure factors are listed in Table 11, and the final Fourier map of the b -axis projection is shown in Fig 2. Standard deviations as listed in Table 2 are based on a diagonal approximation. For a sufficiently large number of reflections and a structure that is not overly regular, this approximation is usually quite adequate provided that the coordinates are referred to approximately orthogonal axes.²⁰ These conditions are probably fulfilled in the present investigation, and the good agreement of the bond lengths in rhodan hydrate and the related compound xanthan hydride⁸ indicates the same.

Thermal analysis. The anisotropic vibrations which are given in Table 3 may be supposed to arise primarily from rigid-body oscillations of the whole molecule. Cruickshank²¹ has shown how the rigid-body libration and translation can be deduced from anisotropies of the different atoms in a rigid molecule. His method presupposes that the axes of libration intersect in a known point, such as a centre of symmetry. Hirshfeld²² suggests that even if one makes the reasonable assumption that the principal axes intersect in a common point, one can not locate this point *a priori*. Therefore the three coordinates of the libration centre have to be determined from the "observed" anisotropies, along with the six components of translational vibration and the six components of libration. Hirshfeld²² has shown how to do this.

An analysis of the rigid-body vibrations of rhodan hydrate has been undertaken, although the refinement was not based on complete three-dimensional data. By including the diagonal zone hhl , however, one probably avoids systematic errors in the derived anisotropic vibrations due to incorrect relative

Table 4. Origin, and direction cosines of the axes L, M, N of the molecular coordinate system, referred to crystal axes.

	a	b	c
L	0.9860	0.0957	-0.2312
M	-0.0026	0.8302	0.5552
N	0.1674	-0.5494	0.7990
Origin at $x = 0.3211$		$y = 0.3673$	$z = 0.3734$

Table 5. Atomic coordinates in Å units in the molecular coordinate system, (a) final coordinates from the least squares refinement, (b) the latter values corrected for rigid-body libration. Isotropic standard deviations in coordinates times 10^3 are given in parentheses.

Atom	(a)			(b)		
	L (Å)	M (Å)	N (Å)	L (Å)	M (Å)	N (Å)
S_1	-1.038	1.184	-0.025	-1.040	1.191	-0.024 (4)
S_2	1.017	1.180	0.021	1.021	1.188	0.022 (4)
C_1	-1.104	-0.570	0.021	-1.107	-0.574	0.022 (14)
C_2	1.182	-0.585	0.015	1.187	-0.588	0.015 (14)
N_1	-2.308	-1.139	0.009	-2.315	-1.147	0.010 (12)
N_2	-0.009	-1.325	-0.006	-0.008	-1.333	-0.006 (10)
O	2.282	-1.108	-0.030	2.291	1.113	-0.030 (10)
H_1	-3.561	-0.733	0.003	-3.573	-0.737	0.005 (150)
H_2	-2.372	-2.034	0.012	-2.379	-2.046	0.013 (120)

Table 6. Components of atomic vibration tensors V^r in Å² as found by the least squares refinement (exp) and as calculated from the rigid-body parameters (RB).

Atom	V_{LL}	V_{MM}	V_{NN}	V_{LM}	V_{MN}	V_{LN}
S_1 (exp)	0.0522	0.0280	0.0609	0.0051	-0.0024	0.0072
(RB)	0.0504	0.0316	0.0582	0.0055	-0.0041	0.0087
S_2 (exp)	0.0519	0.0390	0.0613	-0.0047	-0.0031	0.0055
(RB)	0.0505	0.0342	0.0653	-0.0003	-0.0027	0.0058
C_1 (exp)	0.0570	0.0321	0.0443	-0.0073	0.0013	0.0073
(RB)	0.0473	0.0319	0.0468	0.0025	-0.0013	0.0088
C_2 (exp)	0.0374	0.0398	0.0558	0.0105	-0.0056	0.0048
(RB)	0.0474	0.0352	0.0546	0.0050	-0.0010	0.0078
N_1 (exp)	0.0504	0.0313	0.0785	0.0144	0.0075	0.0158
(RB)	0.0493	0.0397	0.0733	0.0014	0.0022	0.0081
N_2 (exp)	0.0431	0.0280	0.0583	0.0014	-0.0075	0.0079
(RB)	0.0503	0.0305	0.0572	0.0042	-0.0012	0.0078
O (exp)	0.0497	0.0495	0.0825	0.0105	0.0010	0.0090
(RB)	0.0492	0.0453	0.0845	0.0094	0.0009	0.0083

Table 7. Final rigid-body translation parameters T_{ij} and libration parameters ω_{ij} .

	<i>LL</i>	<i>MM</i>	<i>NN</i>	<i>LM</i>	<i>MN</i>	<i>LN</i>
T (\AA^2)	0.0468	0.0302	0.0410	0.0034	-0.0027	0.0086
ω (rad^2)	0.00983	0.00500	0.00228	-0.00018	-0.00060	0.00048

Table 8. Principal components of rigid-body vibrations, with direction cosines, and coordinates of libration centre, referred to molecular axes.

	<i>L</i>	<i>M</i>	<i>N</i>
$T_1^2 = 0.0529 \text{ \AA}^2$	-0.8185	0.4709	0.3290
$T_2^2 = 0.0372$	-0.0544	0.5065	-0.8604
$T_3^2 = 0.0276$	-0.5718	-0.7222	-0.3889
$\omega_1^2 = 0.0098 \text{ rad}^2$	-0.9967	0.0576	0.0561
$\omega_2^2 = 0.0051$	0.0453	0.9788	-0.1992
$\omega_3^2 = 0.0021$	-0.0664	-0.1960	-0.9783

Libration centre at $L = -0.312$ $M = -0.053$ $N = -0.130$

scaling of zones. It was therefore thought justified to consider atomic coordinates when corrected for rigid-body libration, relevant for bond length calculation. The computer program used is written in FORTRAN II by Hirshfeld, and the calculations were carried out on the IBM 1620^U. In the present investigation the following steps were carried out:

1. An orthogonal molecular coordinate system L, M, N was chosen such that L and M are in the plane of the molecule and N perpendicular to this plane. The origin is in an approximate centre of gravity and the directions of L , M , and N are the directions of the principal axes of inertia. The directions cosines of L , M , and N with respect to the crystallographic axes are given in Table 4, together with the coordinates of the origin.

2. Atomic coordinates and vibration tensors were transformed to the molecular coordinate system. The transformed values are given in Tables 5a and 6.

3. Rigid-body parameters were calculated according to Hirshfeld's procedure,²² with double weight on the sulphur atoms, and the final values are given in Table 7. Components of atomic vibration tensors as calculated from the rigid-body parameters in Table 7 are listed in Table 6. Principal components of the rigid-body vibrations and their direction cosines with respect to molecular axes are given in Table 8.

4. Atomic coordinates were corrected for rigid-body libration according to Cruickshank's method.²³ The corrected coordinates are listed in Table 5b.

The amplitudes of translational motion in directions of the principal axes are, according to the values in Table 8, 0.17, 0.19, and 0.24 \AA , and the amplitudes of libration about principal axes are 3.0, 4.1, and 5.7°. The libration centre lies 0.31 \AA off the origin of the molecular coordinate system in direction towards the S_1-C_1 bond, and 0.13 \AA under the plane of the molecule.

Maximum libration occurs about an axis through this center and roughly parallel to the molecular L -axis.

The standard deviation of the thermal vibration components, U_{ij}^r , were estimated to average 0.0020 \AA^2 for the sulphur atoms, 0.0065 \AA^2 for the carbon atoms, and 0.0050 \AA^2 for the oxygen and nitrogen atoms. There are thus no significant differences between V_{ij}^r (exp) and V_{ij}^r (RB) in Table 6. The average difference between V_{ij}^r (exp) and V_{ij}^r (RB) is 0.0023 \AA^2 for sulphur, 0.0046 \AA^2 for carbon, and 0.0040 \AA^2 for nitrogen and oxygen, in agreement with the estimated standard deviations.

DISCUSSION

Bond lengths as calculated from the coordinates in Table 5b, are listed in Table 9 and shown in Fig. 3a. Standard deviations in bond lengths were cal-

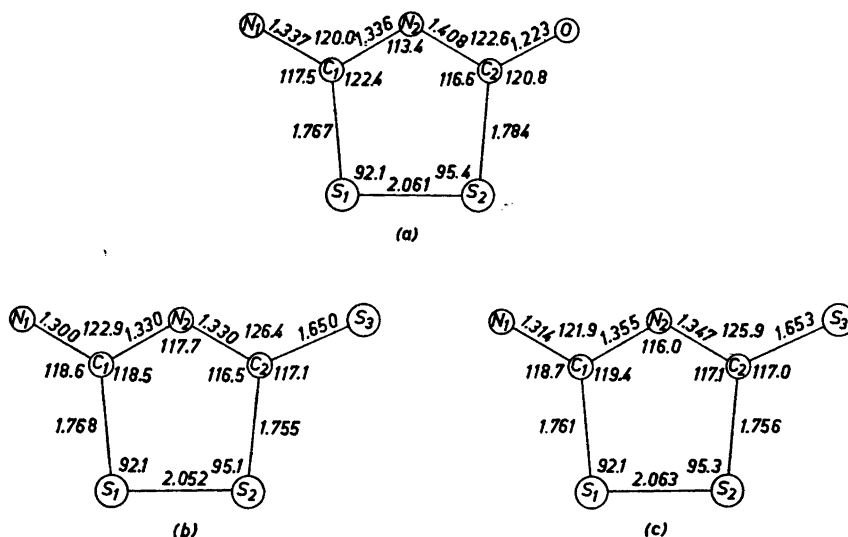


Fig. 3. (a) Bond lengths (Å) and bond angles (°) in the rhodan hydrate molecule. (b),(c) Molecular dimensions of xanthan hydride, (b) as found by Standford, Jr.²⁵ and (c) as found by the author.⁸

culated from the isotropic standard deviations in coordinates given in Table 5b and an assumed 0.2 % standard deviation in cell dimensions.

The rhodan hydrate molecule is approximately planar; the equation for the least squares plane of the molecule, excluding the hydrogen atoms and with double weight on the sulphur atoms is

$$2.0920x - 2.8790y + 11.7208z = 3.9902 \text{ \AA}$$

where x , y , and z are the fractional coordinates with respect to the crystallographic axes. The N -coordinates in Table 5 give the distances of the different atoms from the molecular plane, and, if three times the standard deviation is

taken as a significant figure, show that S_1 and S_2 are slightly out of the plane.

Bond angles calculated from the coordinates in Table 5b are listed in Table 10 and shown in Fig. 3a. Standard deviations in bond angles were calculated according to Darlow's equation.²⁴

Bond lengths and bond angles in the rhodan hydrate molecule may now be compared with those found in the related compound, xanthan hydride, which independently has been investigated by Stanford Jr.²⁵ and the present author.⁸ The two sets of molecular dimensions, supposed to be nearly equally accurate, are given in Fig. 3b and c, and the subsequent discussion is based on the average. It should be mentioned that the bond lengths found in xanthan hydride have not been corrected for rigid-body libration. It appears from the values given in Table 9, that the corrections in bond lengths for rhodan hydrate are in the range 0.004–0.012 Å.

The S–S and S_1-C_1 bond lengths in rhodan hydrate, $S-S = 2.061 \pm 0.007$ Å and $S_1-C_1 = 1.767 \pm 0.015$ Å, are nearly the same as in xanthan hydride, $S-S = 2.058 \pm 0.005$ Å and $S_1-C_1 = 1.765 \pm 0.009$ Å, but the S_2-C_2 bond seems to be somewhat longer in the former, $S_2-C_2 = 1.784 \pm 0.015$ Å, against $S_2-C_2 = 1.756 \pm 0.009$ Å in the latter. The indicated difference in

Table 9. Bond lengths (l) and standard deviation in bond lengths $\sigma(l)$ in the rhodan hydrate molecule; values in parentheses are without correction for rigid-body libration.

Bond	l (Å)	$\sigma(l)$ (Å)
S_1-S_2	2.061 (2.055)	0.007
S_1-C_1	1.767 (1.756)	0.015
S_2-C_2	1.784 (1.772)	0.015
C_1-N_2	1.336 (1.330)	0.017
C_1-N_1	1.337 (1.332)	0.018
C_2-N_2	1.408 (1.403)	0.017
C_2-O	1.223 (1.219)	0.017
N_1-H_1	1.32	0.15
N_1-H_2	0.90	0.12

Table 10. Bond angles and standard deviation in bond angles in the rhodan hydrate molecule; values in parentheses are without correction for rigid-body libration.

	Angle (°)	Standard deviation (°)
$S_1-S_2-C_2$	95.4 (95.5)	0.5
S_2-C_2-O	120.8 (120.8)	1.1
$S_2-C_2-N_2$	116.6 (116.5)	1.0
$O-C_2-N_2$	122.6 (122.6)	1.2
$C_2-N_2-C_1$	113.4 (113.5)	1.1
$N_2-C_1-N_1$	120.0 (120.1)	1.2
$N_2-C_1-S_1$	122.4 (122.4)	1.0
$N_1-C_1-S_1$	117.5 (117.4)	1.0
$C_1-S_1-S_2$	92.1 (92.0)	0.5
$H_1-N_1-C_1$	136	7
$H_1-N_1-H_2$	104	10
$H_2-N_1-C_1$	119	8

bond length is probably related to the difference in electronegativity between the exocyclic atom bonded to C_2 in rhodan hydrate, which is oxygen, and the exocyclic atom bonded to C_2 in xanthan hydrate, which is sulphur. One may assume that the oxygen atom in rhodan hydrate, due to its greater electronegativity, restricts the π -electron on C_2 more extensively than the exocyclic sulphur atom does in xanthan hydrate. The π -bonding in the S_2-C_2 and C_2-N_2 bonds should accordingly be less efficient in rhodan hydrate than in xanthan hydrate, and the bonds longer. Further support for this idea derives from the C_2-N_2 bond length in rhodan hydrate, which is found to be 1.408 ± 0.017 Å and thus is significantly larger than the equivalent bond length in xanthan hydrate.

The C—O bond length in rhodan hydrate is 1.223 ± 0.017 Å in agreement with the length of equivalent C—O bonds, 1.228 ± 0.003 Å, reported by Rabinovich and Schmidt²⁶ for 2,5-dimethyl-1,4-benzoquinone. Values ranging from 1.17 Å to 1.20 Å are suggested for the length of a carbon-oxygen double bond.²⁷ The C—O bond in rhodan hydrate thus seems to be almost a pure double bond.

The cyclic C_1-N_2 and exocyclic C_1-N_1 bonds in rhodan hydrate seems to have approximately equal lengths, 1.336 and 1.337 ± 0.017 Å, respectively, which agrees with the aromatic C—N bond length, 1.340 Å, found in pyridine.²⁸ The corresponding bonds in xanthan hydrate have slightly different lengths, 1.343 and 1.307 ± 0.011 Å, respectively, in agreement with the cyclic and exocyclic C—N bond lengths, 1.346 and 1.309 ± 0.010 Å, in thiuret hydrochloride hemihydrate.³ A similar difference between the C_1-N_2 and C_1-N_1 bonds in rhodan hydrate is not ruled out by the results of the present investigation.

The shape of the five-membered ring in rhodan hydrate is much the same as in xanthan hydrate. Almost identical values have been found both for the $S_1-S_2-C_2$ angles and for the $S_2-S_1-C_1$ angles in the two compounds. The results from a structure investigation of 4-methyl-trithione⁷ show that there the S—S—C angle on the thione side of the unsaturated five-membered disulphide ring is greater than the other S—S—C angle. In accordance with this, the $S_1-S_2-C_2$ angle in rhodan hydrate and xanthan hydrate is found to be greater than the $S_2-S_1-C_1$ angle.

The $C_1-N_2-C_2$ angle, $113.4 \pm 1.1^\circ$, in rhodan hydrate does not deviate significantly from the value 116.25° , which is found for the C—N—C angle in pyridine²⁸ by micro-wave methods. However, assuming the C—N—C angles in rhodan hydrate, xanthan hydrate, and the thiuret ion to equal that in pyridine, one may probably expect values less than 116.25° for the C—N—C angle when the compounds are investigated by X-ray crystallographic methods. This is because the centroid of the electron cloud on the cyclic nitrogen atom, due to "atomic" dipole moment, may be displaced from the nucleus in direction of the lone-pair orbital. A thorough discussion of this effect has been given by Coppens and Hirshfeld.²⁹ If the average is taken of the C—N—C angles in rhodan hydrate, xanthan hydrate, thiuret hydroiodide,¹ hydrobromide,² and hydrochloride hemihydrate,³ with weights inversely proportional to the respective standard deviations, one gets the value 114.8° .

Table 11. Observed and calculated $hk0$, $h0l$ and hhl structure factors for rhodan hydrate based on two molecules. Reflections marked with asterisks were given zero weight in the refinement because of assumed secondary extinction.

	F_o	F_c		F_o	F_c
h		$h00$	7	4.79	- 4.95
2	19.83	- 21.19	9	< 1.78	- 0.21
4	3.55	+ 3.88			
6	14.30	- 14.73	h		$h60$
8	18.88	+ 17.79	2	3.44	- 3.77
10	4.48	+ 3.18	4	< 1.88	+ 0.61
12	8.14	+ 7.73	6	4.48	- 5.67
14	3.75	- 3.07			
			l		$20l$
k		$0k0$	2	17.64	- 18.33
2	3.96	+ 3.76	4	23.58	+ 23.16
4	< 2.51	- 2.40	6	8.97	- 8.97
6	5.22	+ 5.82	8	10.96	+ 11.05
			10	14.19	+ 14.53
h		$h10$	12	17.64	- 17.04
1	9.49	+ 9.31	14	< 1.78	- 0.90
3	11.38	+ 11.52	16	5.64	+ 5.80
5	13.57	+ 14.69	18	2.82	- 3.61
7	3.86	- 3.61			
9	2.40	+ 1.20	l		$\bar{2}0l$
11	5.53	+ 3.56	2	23.38	+ 23.50
13	3.96	+ 3.27	4	17.12	- 16.16
			6	9.49	- 9.11
h		$h20$	8	8.97	+ 8.31
2	4.70	+ 3.53	10	2.71	+ 2.31
4	< 1.78	+ 1.49	12	< 1.66	- 1.90
6	13.57	+ 13.41	14	3.34	- 3.55
8	5.84	- 4.65	16	3.34	+ 3.18
10	5.43	- 4.37	18	3.13	+ 1.94
12	3.75	+ 2.83			
14	4.08	+ 2.83	l		$40l$
			2	19.09	- 17.78
h		$h30$	4	< 1.14	- 0.35
1	8.97	+ 8.15	6	< 1.35	+ 0.26
3	2.92	+ 2.44	8	3.75	+ 3.48
5	14.92	- 16.86	10	< 1.66	+ 1.11
7	< 2.61	+ 0.81	12	< 1.78	+ 0.96
9	< 2.71	- 0.04	14	< 1.78	+ 0.32
11	10.22	+ 8.73	16	2.51	- 2.81
13	6.05	- 4.65			
			l		$\bar{4}0l$
h		$h40$	2	17.53	+ 17.31
2	5.53	+ 5.85	4	34.53	- 32.47
4	10.65	- 11.52	6	< 1.26	- 0.54
6	< 2.71	+ 0.72	8	20.04	+ 19.98
8	< 2.61	- 2.78	10	6.69	- 5.89
10	< 2.30	+ 1.95	12	8.66	+ 8.86
12	< 1.78	- 1.19	14	< 1.78	+ 1.37
			16	11.79	- 12.05
			18	2.09	+ 2.37
h		$h50$			
1	7.73	- 6.84	l		$60l$
3	3.75	+ 2.29	2	31.83	+ 31.10
5	4.08	+ 4.16	4	8.77	- 9.44

	F_o	F_c		F_o	F_c
6	17.74	-18.72	<i>l</i>		$\bar{12},0l$
8	8.25	+ 9.14	2	12.73	+ 11.81
10	4.79	- 5.01	4	12.52	-11.93
12	< 1.78	- 1.63	6	2.09	+ 1.73
14	6.36	+ 6.39	8	4.79	+ 4.85
16	< 1.04	- 0.79	10	7.09	- 7.12
			12	3.03	+ 3.20
<i>l</i>		$\bar{6}0l$	<i>l</i>		$14,0l$
2	5.12	+ 5.13	2	4.48	+ 4.07
4	29.32	+28.23	4	< 1.26	- 1.14
6	22.86	-23.44	6	2.18	- 2.27
8					
10	8.45	+ 8.92	<i>l</i>		$\bar{14},0l$
12	12.42	-12.99	2	< 1.47	+ 0.91
14	3.34	+ 3.38	4	2.09	+ 2.15
16	5.22	+ 5.20	6	2.82	- 3.48
			8	1.78	+ 1.77
<i>l</i>		$80l$	10	0.95	+ 1.24
2	3.44	- 2.70	<i>h,l</i>		$h10$
4	8.97	- 8.34	-1,1	6.99	+ 9.31
6	10.01	-10.60	-2,2	3.23	+ 3.53
8	4.48	- 4.78	-3,3	2.30	+ 2.44
10	< 1.78	- 0.07	-4,4	11.17	-11.52
12	5.74	+ 6.32	-5,5	4.79	+ 4.16
14	5.01	- 5.57	-6,6	7.40	- 5.67
			<i>l</i>		$00l$
<i>l</i>		$\bar{8}0l$	2	6.16	- 4.21
2	9.08	- 9.35	4	42.48	-45.02
4	6.88	- 6.23	6	9.39	+ 8.18
6	4.60	+ 4.71	8	22.53	-19.86
8	3.86	- 3.57	10	< 1.88	+ 1.67
10	< 1.78	+ 0.13	12	14.82	+13.23
12	< 1.78	+ 0.43	14	7.83	- 7.65
14	< 1.57	+ 1.01	16	0.83	- 0.23
16	< 1.14	+ 0.34	18	2.82	+ 3.18
			<i>l</i>		$\bar{11}l$
<i>l</i>		$10,0l$	1	5.53	- 5.48
2	5.53	+ 5.46	2	13.14	+13.20
4	< 1.78	- 0.52	3	19.73	+23.45
6	< 1.78	- 0.76	4	17.53	+18.61
8	< 1.78	+ 0.62	5	22.01	-22.32
10	< 1.57	+ 1.57	6	7.31	- 6.68
12	< 1.26	- 1.60	7	5.43	+ 5.41
			8	5.01	- 4.20
<i>l</i>		$\bar{10},0l$	9	9.39	+ 8.32
2	15.13	-14.82	10	6.36	+ 6.02
4	3.55	- 3.42	11	9.08	- 8.46
6	5.74	+ 5.67	12	1.88	- 1.83
8	1.78	- 1.60	13	2.30	+ 2.17
10	8.56	+ 8.96	14	3.03	- 2.79
12	< 1.57	+ 0.07	15	2.30	+ 2.31
14	6.47	- 7.70	16	1.04	+ 1.16
			17	0.73	- 0.80
<i>l</i>		$12,0l$	18	< 0.52	+ 0.40
2	8.66	- 9.18			
4	< 1.66	+ 0.71			
6	2.30	- 2.75			
8	2.82	- 2.49			
10	3.55	+ 4.69			

	F_o	F_c		F_o	F_c
l		11 l	l		33 l
1	17.74*	+27.52	1	5.01	+5.80
2	5.53	-6.23	2	2.40	+2.32
3	36.31*	-45.40	3	6.16	-6.21
4	38.30*	-46.33	4	1.14	+1.19
5	9.39	+8.63	5	5.01	+5.29
6	10.43	-10.05	6	1.78	+1.87
7	21.91	+20.71	7	2.82	+2.53
8	23.17	+22.93	8	5.84	-6.11
9	18.16	-17.23	9	5.12	-5.19
10	3.55	+3.03	10	1.78	-2.04
11	7.31	+6.71	11	1.26	+1.16
12	1.26	-1.39	12	5.12	+5.15
13	4.39	+3.94	13	< 0.95	-0.03
14	1.88	+1.72	14	4.48	-3.99
15	8.35	-8.13	15	< 0.73	-0.06
16	3.13	-2.78	16	0.95	-1.08
17	3.34	+3.22			
18	< 0.42	+0.07	l		33 l
			1	3.13	-3.20
l		22 l	2	4.17	+3.68
1	11.38	+13.14	3	5.95	+5.87
2	10.43	-11.38	4	2.71	-2.94
3	10.01	-10.67	5	< 0.95	-0.18
4	3.03	+2.74	6	5.53	-5.08
5	5.01	-4.63	7	4.70	+4.10
6	3.96	-4.37	8	5.12	+4.16
7	7.83	+7.43	9	1.04	+0.02
8	< 0.95	-0.23	10	4.79	-3.71
9	< 0.95	-0.56	11	5.74	-4.73
10	5.53	+5.34	12	3.44	-2.87
11	4.48	-4.22	13	< 0.83	-0.41
12	1.99	-1.80	14	6.99	+5.74
13	< 1.04	-0.31	15	1.26	+0.87
14	< 0.95	+0.33			
15	2.30	+2.21	l		44 l
16	< 0.73	+0.38	1	7.52	-7.89
17	< 0.62	-0.38	2	4.17	+4.24
			3	10.74	+10.35
l		22 l	4	7.31	+7.64
1	1.35	-0.08	5	1.78	-1.15
2	1.78	+2.05	6	2.30	-2.47
3	2.30	+2.51	7	< 1.04	-0.19
4	12.10	-12.45	8	< 1.04	-0.43
5	10.34	-11.28	9	5.74	+5.57
6	16.08	+15.81	10	1.47	+1.61
7	14.40	+14.74	11	7.92	-8.24
8	7.31	+5.98	12	< 0.83	-0.25
9	7.40	+7.30	13	< 0.62	+0.09
10	8.97	-8.05			
11	12.52	-12.79	l		44 l
12	3.23	+3.06	1	7.21	+7.64
13	2.30	+1.79	2	1.26	-0.90
14	2.92	-2.90	3	4.27	-4.12
15	2.19	+2.37	4	3.34	+3.14
16	2.30	-1.75	5	1.04	+0.87
17	2.71	-2.52	6	3.96	-3.73
			7	1.47	-1.06

	F_o	F_c		F_o	F_c
8	4.08	+ 3.47	3	2.71	+ 2.23
9	2.09	- 2.51	4	< 0.95	+ 0.35
10	1.88	+ 2.17	5	7.73	- 7.52
11	< 0.83	- 0.76	6	8.77	+ 7.78
12	2.61	- 1.80	7	1.88	- 1.42
13	1.66	+ 0.80	8	4.17	- 3.66
l		$\bar{5}5l$	9	6.69	+ 5.26
1	1.14	+ 1.09	10	2.30	- 1.91
2	7.09	- 6.63			
3	6.47	- 6.71	l		$\bar{6}6l$
4	1.66	+ 1.14	1	< 0.52	- 0.41
5	1.14	+ 0.97	2	0.62	- 0.61
6	6.36	+ 6.14	3	< 0.52	+ 0.46
7	7.92	+ 7.46	4	6.69	+ 6.45
8	8.25	- 7.02	5	1.35	- 2.34
9	2.09	- 2.35			
10	1.47	+ 1.38	l		$66l$
11	2.82	- 2.86	1	2.30	+ 1.32
l		$55l$	2	4.79	+ 4.36
1	0.95	+ 0.75	3	4.27	- 4.39
2	3.86	- 3.78			

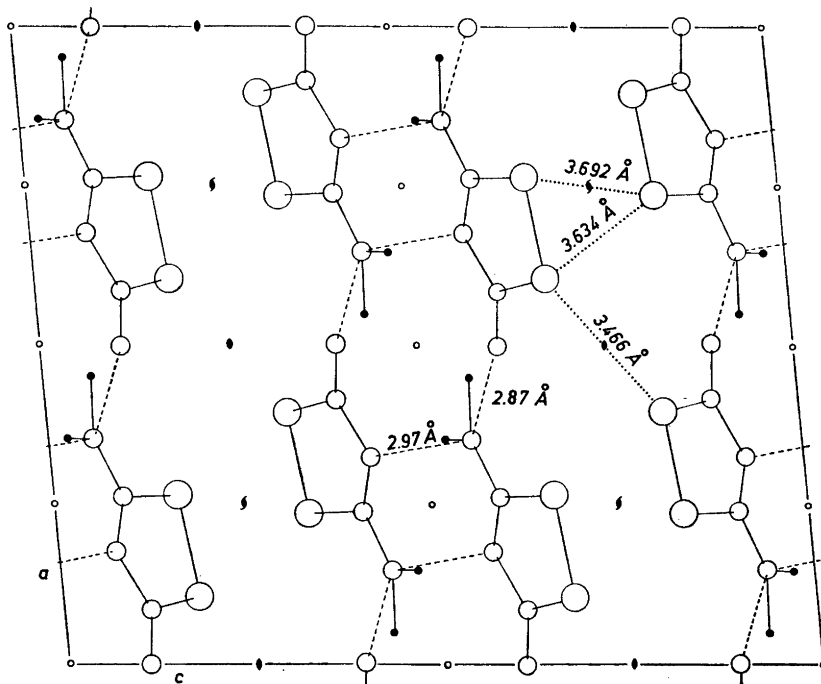


Fig. 4. The arrangement of rhodan hydrate molecules in the unit cell as seen along the b -axis. Broken lines indicate hydrogen bonds.

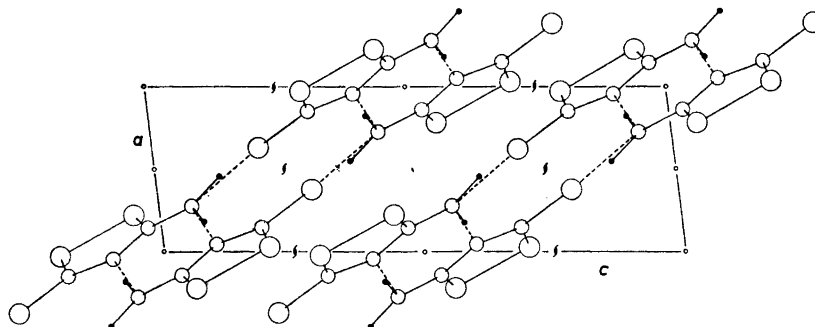


Fig. 5. The arrangement of xanthan hydride molecules in the unit cell as seen along the *b*-axis. Broken lines indicate hydrogen bonds.

All bonds in rhodan hydrate, except the N—H bonds, have been found to be shorter than single bonds, and one may conclude that the molecule is stabilized through π -orbital delocalization. This seems to be most pronounced in the nitrogen-carbon part of the molecule. A comparison of the bond lengths in the carbon-sulphur part of rhodan hydrate ($C-S = 1.767$ and 1.784 ± 0.015 Å, $S-S = 2.061 \pm 0.007$ Å) with the equivalent bond lengths in the saturated five-membered cyclic disulphide, 1,2-dithiolane-4-carbocyclic acid⁹ ($C-S = 1.83$ and 1.85 ± 0.02 Å, $S-S = 2.096 \pm 0.009$ Å), shows that the conjugation in rhodan hydrate probably extends over the entire disulphide group.

The arrangement in the unit cell of rhodan hydrate is shown in Fig. 4. Two and two molecules, one on either side of a symmetry centre, are interconnected through N—H...N hydrogen bonds of length 2.97 ± 0.02 Å. Between such pairs, there are N—H...O hydrogen bonds of length 2.87 ± 0.02 Å, giving rise to layers of molecules parallel to (100). Between layers, only sulphur-sulphur contacts occur, of lengths 3.692, 3.634 and 3.466 ± 0.007 Å.

A somewhat similar arrangement is present in crystals of xanthan hydride. This is shown in Fig. 5.

Acknowledgement. This work has been carried out at the University College of Addis Abeba, the Weizmann Institute of Science, and the University of Bergen. The author wishes to thank the president of the University College of Addis Abeba for his interest and encouragement, Professor G. M. Schmidt and the Weizmann Institute for great generosity and for the use of the computer WEIZAC, and Professor Olav Foss for many helpful discussions.

REFERENCES

1. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
2. Hordvik, A. and Joys, S. *Acta Chem. Scand.* **19** (1965) 1539.
3. Hordvik, A. and Sundsfjord, J. *Acta Chem. Scand.* **19** (1965) 753.
4. Hordvik, A. *Acta Chem. Scand.* **19** (1965) 1039.
5. Bergson, G. *Arkiv Kemi* **19** (1962) 181.
6. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **19** (1965) 935.
7. Jeffrey, G. A. and Shiono, R. *Acta Cryst.* **12** (1959) 447.
8. Hordvik, A. *Acta Chem. Scand.* **15** (1961) 1186; **17** (1963) 2575.

9. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1810.
10. Foss, O. *Acta Chem. Scand.* **10** (1956) 871.
11. *International Tables for X-ray Crystallography*, The Kynoch Press, Birmingham, England, Vol. II, p. 356.
12. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
13. Tomiie, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
14. Viervoll, H. and Øgrim, O. *Acta Cryst.* **2** (1949) 277.
15. Woolfson, M. M. *Direct Methods in Crystallography*, Oxford University Press 1961.
16. Hordvik, A. *Acta Chem. Scand.* **14** (1960) 1218.
17. Wilson, A. J. C. *Nature* **150** (1942) 152.
18. Rossmann, M. G., Jacobson, R. A., Hirshfeld, F. L. and Lipscomb, W. N. *Acta Cryst.* **12** (1959) 530.
19. Pepinsky, R., Robertson, J. M. and Speakman, J. C. (Eds.), *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Pergamon Press, Oxford 1961, p. 42.
20. Hirshfeld, F. L. *Instruction for use of the least squares program for WEIZAC*, The Weizmann Institute of Science, Rehovoth, Israel.
21. Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 754.
22. Hirshfeld, F. L., Sandler, S. and Schmidt, G. M. J. *J. Chem. Soc.* **1963** 2108.
23. Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 757.
24. Darlow, S. F. *Acta Cryst.* **13** (1960) 683.
25. Stanford, R. H., Jr. *Acta Cryst.* **16** (1963) 1157.
26. Rabinovich, D. and Schmidt, G. M. J. *J. Chem. Soc.* **1964** 2030.
27. Abrahams, S. C. *Quart. Rev. (London)* **10** (1956) 407.
28. Bak, B., Hansen-Nygaard, L. and Rastrup-Andersen, J. *J. Mol. Spectry* **2** (1958) 361.
29. Coppens, P. and Hirshfeld, F. L. *Israel J. Chem.* **2** (1964) 117.

Received October 23, 1965.