The Crystal and Molecular Structure of Xanthan Hydride

ASBJÖRN HORDVIK*

The Department of X-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

The crystal and molecular structure of xanthan hydride has been solved by direct sign determination and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the $h0l$, $0kl$ and $1kl$ reflections.

Average lengths of C—N bonds in the molecule is 1.339 Å, and no C—N bond deviates significantly from this value. Other bond lengths in the molecule are, C—S = 1.761 ± 0.008 Å and 1.756 ± 0.008 Å, C=S = 1.653 ± 0.009 Å and S—S = 2.063 ± 0.005 Å.

The bond lengths indicate that the molecule is stabilized through π-orbital delocalization which is most pronounced in the

$$\begin{array}{c}\diagdown \\ \diagup\end{array}\!N-\underset{|}{C}\!=\!N-\underset{|}{C}\!= \text{ part, where no C—N bond length differs signifi-}$$

cantly from the aromatic C—N bond length 1.340 Å in pyridine. The C—S bonds are less shortened through π-bonding and the S—S bond only to a small degree.

The molecules are in the crystal held together in pairs through N—H···N hydrogen bonds, of length 2.952 ± 0.012 Å. There are N—H···S hydrogen bonds of length 3.356 ± 0.010 Å between the pairs.

So far X-ray structure determinations of two unsaturated five-membered cyclic disulphides have been reported in the literature, namely of thiuret hydroiodide [1] and 4-methyl-trithione,[2,3] and preliminary reports on the structures of rhodan hydrate [4] and xanthan hydride.[5] The relatively high stability of these compounds as contrasted with saturated five-membered cyclic disulphides, may be assumed to be due to some aromatic character of the ring. Structure determinations of two 1,2,4-dithiazolidine derivatives, xanthan hydride and rhodan hydrate, and also of some substituted 1,2-dithiolium salts have been undertaken in order to test this idea. The present paper is the first in this series.

---

* Present address: Chemical Institute, University of Bergen, Norway.

EXPERIMENTAL

The unit cell and space group of xanthan hydride have been reported by Foss.[6] The crystals are monoclinic prismatic, with $a = 4.05$ Å, $b = 10.59$ Å, $c = 12.78$ Å and $\beta = 97°$. The experimental error was estimated to be within 0.5 %. The space group is $P2_1/c$ and there are four molecules in the unit cell.

The intensities of the $h0l$, $0kl$ and $1kl$ reflections were estimated visually from Weissenberg photographs, taken with $CuK\alpha$ radiation. Small crystals of cross-section $ca.$ 0.05×0.05 mm were chosen in order to minimize absorption effects, and no absorption correction was then considered necessary (the linear absorption coefficient of xanthan hydride for $CuK\alpha$ radiation is 109 cm⁻¹). 460 independent reflections were obtained, with a range of intensities of 10 000 to 3. The intensities were corrected in the usual way to give sets of relative structure factors. Common reflections in $h0l$, $0kl$ and $1kl$ were used to put all the reflections on the same scale.

The calculated structure factors in Table 9 are based on the atomic scattering curves of Berghuis et al.[7] for nitrogen and carbon, Tomiie and Stam [8] for sulphur and Viervoll and Ögrim [9] for hydrogen.

DETERMINATION OF THE STRUCTURE

The structure was solved in the a-axis projection by means of direct methods, and a brief account of this has been reported earlier.[5] A more detailed description of the procedure is given here. Observed $0kl$ structure factors were put on an absolute scale by means of Wilson's method,[10] and unitary structure factors were calculated for the strongest reflections. The signs for 03,15 and 076 were chosen positive, and the signs for 040, 008, 00,12 and 060 were denoted a, b, c, and d, respectively. Sixteen sets of probable signs were now derived, by

Table 1. Unitary structure factors and probable sings for the $0kl$ reflections used in the direct structure determination. Sign marked with asterisk later proved wrong.

k	l	u	sign	k	l	u	sign
4	0	0.58	a	10	9	0.36	—
6	0	0.44	d	11	2	0.35	−ab
10	0	0.35	ad	11	4	0.34	−abc
0	8	0.59	b	11	6	0.59	a
0	12	0.74	c				
1	5	0.25	abc				
1	7	0.23	ab	8	0	0.25	+
1	15	0.27	a	0	10	0.32	+
2	12	0.25	acd	1	13	0.33	+
3	5	0.25	bc	1	14	0.30	—
3	7	0.31	b	2	11	0.39	— *
3	15	0.44	+	2	13	0.41	+
4	8	0.42	ab	3	11	0.25	+ *
4	12	0.48	ac	3	13	0.34	—
5	5	0.25	abcd *	4	13	0.43	—
5	6	0.26	ad	5	14	0.33	+
6	8	0.40	bd	7	2	0.26	+
6	12	0.36	cd	7	13	0.42	+
7	1	0.24	− b *	8	1	0.40	—
7	5	0.34	abcd	8	5	0.32	—
7	6	0.52	+	8	7	0.33	—
10	1	0.38	−b	8	9	0.27	+
10	8	0.40	abd	12	1	0.40	+

means of the multiplication rule [11] $S_{\mathbf{h}} \cdot S_{\mathbf{h'}} \approx S_{\mathbf{h+h'}}$, for the 28 first reflections in Table 1. This could be reduced to eight sets of probable signs because two combinations strongly indicated that $S_{00,12} = c$ should be negative, namely $S_{076} \cdot S_{0\bar{7}\bar{6}} \approx S_{00,12}$ and $S_{011,6} \cdot S_{0\bar{1}\bar{1},6} \approx S_{00,12}$, for which the average values in unitary structure factors are 0.59 and 0.64, respectively. Sign combinations which fit into Cochran and Woolfson's equation [12] $S(\mathbf{h}) \approx S(\Sigma_{\mathbf{h'}} U_{\mathbf{h'}} \cdot U_{\mathbf{h+h'}})$ were then sought among the 28 signs so far determined. This led to probable signs for 17 additional reflections for each of the eight sets of probable signs.

Fourier maps corresponding to the eight sets of 45 probable signs were then computed, and the molecule was recognized in one of them. This Fourier map which is based on $a = -$, $b = -$, $c = -$ and $d = +$ is shown in Fig. 1.
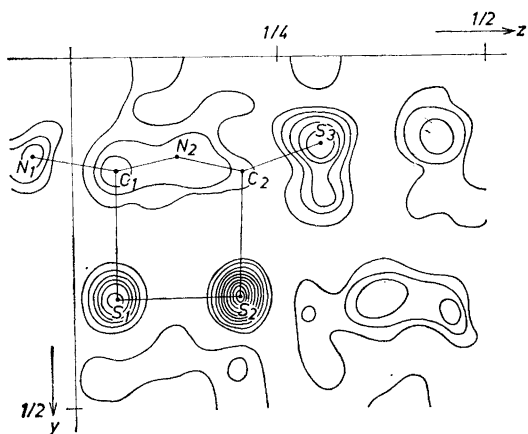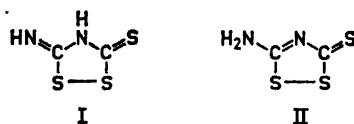

Fig. 1. Fourier map of xanthan hydride in the a-axis projection, based on the 45 reflections in Table 1. with $a = -$, $b = -$, $c = -$ and $d = +$. Contours at arbitrary but equal intervals.

The 17 signs in the last part of Table 1 which are derived by Cochran and Woolfson's equation correspond to these signs for a, b, c, and d. Four signs, marked with asterisks in Table 1, later proved wrong.

The reflections with $k + l$ odd in Table 1 have opposite signs of the corresponding reflections in Table 9. This is because the origin fixed by choosing the signs of two reflections arbitrarily, was different from the origin eventually used in the refinement. The origin on the Fourier map in Fig. 1 is the one used in the subsequent calculations, and thus corresponds to reversed signs of the $k + l$ odd reflections in Table 1. The structure was first refined by Fourier synthesis, and after three refinements $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ was 0.18. Difference synthesis was now used and after the fifth cycle R had dropped to 0.12.

The two hydrogen atoms in the molecule had so far been excluded from the structure factor calculations because there were two possibilities for placing them. They could either belong to two different nitrogens (I) as anticipated by Hantzsch and Wolvekamp,[13] or they could both belong to the exo-cyclic

$$
\begin{array}{cc}
\underset{\text{I}}{\overset{\displaystyle \text{H}}{\underset{\displaystyle}{HN_{\diagdown}C_{\diagup}N_{\diagdown}C_{\diagup}S}}} & \underset{\text{II}}{H_2N_{\diagdown}C_{\diagup}N_{\diagdown}C_{\diagup}S}
\end{array}
$$

nitrogen (II). Already the third Fourier map [5] seemed to indicate that (II) was more likely than (I), but it was thought better to wait for the correct hydrogen positions to reveal themselves during the difference refinement. Two small maxima near the exo-cyclic nitrogen were still there after the fifth cycle, and it was therefore probable that they represented the two hydrogen atoms. It was at the same time clear from the difference map that anisotropic temperature factors had to be applied to the heavy atoms. By inclusion of the hydrogens in the structure factor calculation R dropped to 0.115.

Attention was then paid to the b-axis projection. The Patterson projection could be interpreted in two ways, and the right solution was picked out by consideration of the molecular arrangement in the unit cell. After three difference refinements R for this zone was 0.17.

The $1kl$ data were then included in the calculations and from there on the refinement was carried out by three-dimensional methods. The least squares program which was used, is written by Hirshfeld for the electronic computor WEIZAC, of the Weizmann Institute. A similar but not identical program has been described in the literature.[14] This program seeks to minimize the function

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

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.[15] The weighting factor w for the $0kl$ and $1kl$ reflections was taken as $F_o{}^{-3}$ for $F_o > 3$ and as $3^{-1} \cdot F_o{}^{-2}$ for $F_o < 3$; for the $h0l$ reflections the threshold value was taken as 5 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 9. Some reflections which were supposed to be affected by secondary extinction were given zero weight.

Three least squares cycles, with individual isotropic temperature factors, were carried out first. During this refinement r dropped from 0.1465 to 0.0788. Thereafter anisotropic temperature factors were used for all atoms except the hydrogens, and nine additional least squares cycles brought r from 0.0788 to the final value 0.0251. The corresponding R for all the reflections is 0.071, and becomes 0.062 when the reflections which are given zero weight in the least squares refinement are neglected. During the last three least squares cycles, shifts in all parameters were smaller than the corresponding standard deviations.

Final coordinates and temperature parameters are given in Table 2 and 3, respectively. The observed and calculated structure factors are listed in Table 9. Reflections which have been given zero weight because of extinction, are marked with an asterisk. The final Fourier maps of the a- and b-axis projec-

Table 2. Final atomic coordinates and standard deviations in coordinates in fractions of corresponding cell edges.

	x	y	z
S_1	−0.2250	0.3486	0.0519
	0.0009	0.00014	0.0014
S_2	0.0304	0.3394	0.2016
	0.0009	0.00015	0.00014
S_3	0.3737	0.1187	0.2963
	0.0009	0.00017	0.00015
C_1	−0.1443	0.1886	0.0273
	0.0029	0.0006	0.0005
C_2	0.1509	0.1810	0.1920
	0.0029	0.0006	0.0006
N_1	−0.2684	0.1394	−0.0634
	0.0030	0.0006	0.0005
N_2	0.0462	0.1203	0.1014
	0.0025	0.0005	0.0004
H_1	−0.177	0.043	−0.083
	0.034	0.010	0.008
H_2	−0.450	0.213	−0.123
	0.029	0.010	0.008

Table 3. Final temperature parameters β_{ij} and standard deviations in temperature parameters $\sigma(\beta)$. The expression used is $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\,\beta_{12} + kl\,\beta_{23} + hl\beta_{13})$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
S_1	0.0641	0.0035	0.0045	0.0101	−0.0002	0.0041
$\sigma(\beta)$	0.0032	0.0001	0.0001	0.0012	0.0002	0.0011
S_2	0.0572	0.0034	0.0043	0.0023	−0.0015	0.0041
$\sigma(\beta)$	0.0029	0.0001	0.0001	0.0011	0.0002	0.0010
S_3	0.0540	0.0041	0.0051	−0.0024	0.0009	−0.0067
$\sigma(\beta)$	0.0029	0.0001	0.0001	0.0013	0.0002	0.0010
C_1	0.0470	0.0032	0.0036	0.0058	−0.0004	0.0122
$\sigma(\beta)$	0.0102	0.0004	0.0003	0.0048	0.0006	0.0034
C_2	0.0375	0.0032	0.0045	0.0036	−0.0006	0.0073
$\sigma(\beta)$	0.0102	0.0004	0.0003	0.0046	0.0007	0.0034
N_1	0.0784	0.0056	0.0043	0.0012	−0.0007	0.0073
$\sigma(\beta)$	0.0102	0.0005	0.0003	0.0048	0.0007	0.0034
N_2	0.0632	0.0036	0.0034	−0.0013	−0.0006	−0.0017
$\sigma(\beta)$	0.0102	0.0004	0.0003	0.0040	0.0006	0.0031

Final isotropic temperature factors $\exp\,[-B(\sin^2\Theta/\lambda^2)]$ for H_1 and H_2 are $B = 3.45$ Å² and $B = 3.30$ Å², respectively.
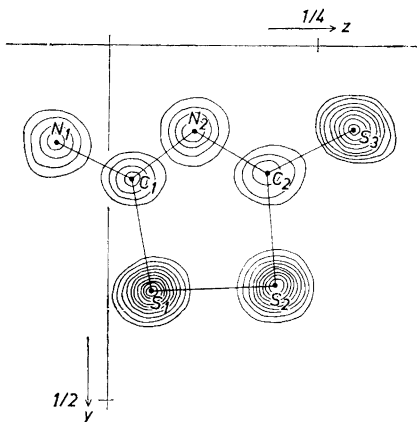
Fig. 2. Electron density projection of xanthan hydride along the *a* axis, showing one asymmetric unit. Plane group *pgg* and origin in center of symmetry. Contour intervals for carbon and nitrogen 2e·Å⁻² and for sulphur 3e·Å⁻². Lowest contour at 3e·Å⁻².
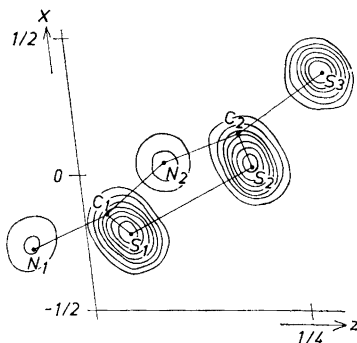
Fig. 3. Electron density projection of xanthan hydride along the *b* axis, showing one asymmetric unit. Plane group *p*2 and origin in center of symmetry. Contour intervals 3e·Å⁻². Lowest contour at 6e·Å⁻².

tions are shown in Figs. 2 and 3. The difference map of the *a*-axis projection corresponding to the final state of refinement is shovn in Fig. 4a with all atoms subtracted, and in Fig. 4b with all atoms but hydrogen subtracted. The standard deviations given in Tables 2 and 3 are based on a diagonal approximation. For a sufficiently large number of reflections and a structure

(a)   *(b)*
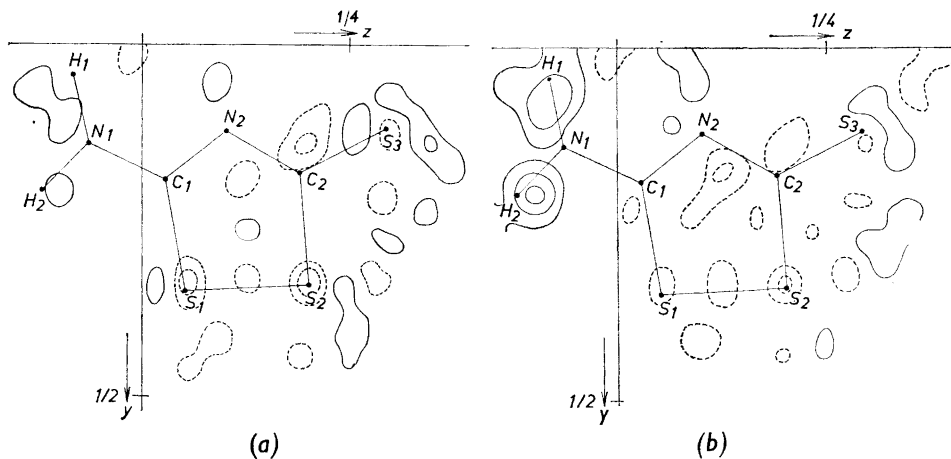
Fig. 4. (a) The final difference projection along the *a* axis of xanthan hydride with all atoms subtracted, and (b) with all atoms except the hydrogen atoms subtracted. Contour lines at intervals of 0.3 e·Å⁻² with negative lines dashed. The zero line is omitted.

that is not overly regular, this approximation is usually quite adequate provided that the coordinates are referred to approximately orthogonal axes.[16] These conditions are probably fullfilled in the present investigation, and the good agreement of the bond lengths in xanthan hydride and the related compound rhodan hydrate [17] indicates the same.

THE XANTHAN HYDRIDE MOLECULE

Bond lengths calculated from the coordinates in Table 2 are listed in Table 4 and shown in Fig. 5a. Standard deviations in bond lengths were calculated from the coordinate standard deviations and an assumed 0.2 % standard deviation in cell dimensions.

Table 4. Bond lengths l and standard deviation in bond length $\sigma(l)$ in the xanthan hydride molecule.

Bond	l (Å)	$\sigma(l)$ (Å)
$S_1 - S_2$	2.063	0.005
$S_1 - C_1$	1.761	0.008
$S_2 - C_2$	1.756	0.008
$C_2 - S_3$	1.653	0.009
$C_1 - N_1$	1.314	0.011
$C_1 - N_2$	1.355	0.011
$C_2 - N_2$	1.347	0.011
$N_1 - H_1$	1.123	0.10
$N_1 - H_2$	1.261	0.10

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

$$3.5859x + 2.8754y - 6.1650z = -0.1405 \text{ Å}$$

where x, y and z are the fractional coordinates with respect to the crystallographic axes.

In order to facilitate a discussion of the thermal vibration of the atoms, a new orthogonal coordinate system L, M, N was chosen. L and M are axes in the least squares plane of the molecule with origin in an approximate center of gravity ($x = 0.01426$, $y = 0.22427$, $z = 0.13569$), and N is perpendicular to the plane. The direction cosines of L, M and N with respect to the crystal axes are given in Table 5, and the atomic coordinates in this orthogonal coordinate system are given in Table 6. The N coordinates in Table 6 give the distances of the atoms from the least squares 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 6 are listed in Table 7 and shown in Fig. 5b. Standard deviations in bond angles were calculated according to Darlow's equation,[18] and use of the L, M, N coordinate system is here an advantage, because the N coordinates can be neglected, and this makes the calculation simpler.

Table 5. Direction cosines of the axes *L, M* and *N* with respect to the crystal axes.

	a	b	c
L	0.4450	−0.2624	0.7959
M	−0.1335	0.9264	0.3668
N	0.8854	0.2715	−0.4824

Table 6. Atomic coordinates in Ångström units in the orthogonal coordinate system *L, M, N,* with standard deviations.

Atom	L (Å)	M (Å)	N (Å)
S_1	−1.6290	0.9563	0.0161
	0.0022	0.0016	0.0034
S_2	0.3797	1.4297	−0.0174
	0.0022	0.0017	0.0032
S_3	2.5749	−0.4771	−0.0048
	0.0023	0.0019	0.0033
C_1	−1.2892	−0.7723	−0.0029
	0.0073	0.0062	0.0108
C_2	0.9393	−0.2344	0.0184
	0.0079	0.0068	0.0110
N_1	−2.2988	−1.6131	−0.0302
	0.0076	0.0063	0.0114
N_2	−0.0024	−1.1980	0.0270
	0.0065	0.0055	0.0095
H_1	−2.063	−2.698	0.140
	0.108	0.104	0.136
H_2	−3.434	−1.067	−0.103
	0.097	0.110	0.118

Table 7. Bond angles and standard deviations in bond angles in the xanthan hydride molecule.

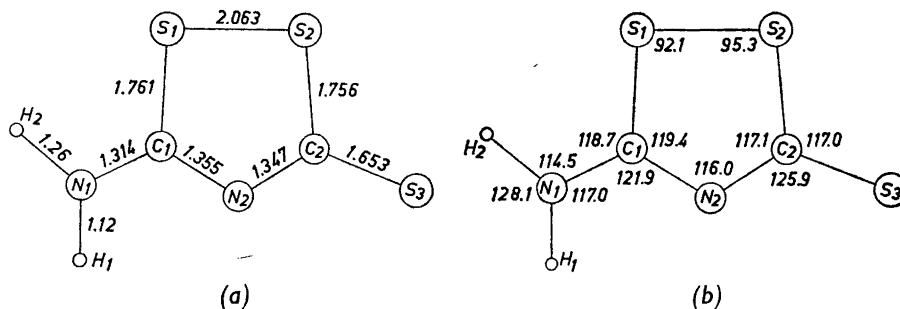|	Angle(°)	Standard deviation(°)
$S_1-S_2-C_2$	95.3	0.3
$S_2-C_2-S_3$	117.0	0.4
$S_2-C_2-N_2$	117.1	0.6
$N_2-C_2-S_3$	125.9	0.6
$C_1-N_2-C_2$	116.0	0.6
$N_1-C_1-N_2$	121.9	0.6
$N_1-C_1-S_1$	118.7	0.6
$S_1-C_1-N_2$	119.4	0.5
$C_1-S_1-S_2$	92.1	0.3
$H_1-N_1-C_1$	117.0	5.5
$H_2-N_1-C_1$	114.5	6.0
$H_1-N_1-H_2$	128.1	7.5

Fig. 5. (a) Bond lengths (Å) and (b) bond angles (°) in the xanthan hydride molecule.

Bond lengths and bond angles in xanthan hydride as listed in Tables 4 and 7, may now be compared with those from other investigations of unsaturated five-membered cyclic disulphides, namely thiuret hydroiodide [1] and 4-methyl-trithione.[3] Of these two the structure analysis of 4-methyl-trithione is the most accurate. The sulphur-sulphur bond in 4-methyl-trithione is found to be 2.047 ± 0.007 Å and in xanthan hydride 2.063 ± 0.005 Å. Both values may not be significantly smaller than the accepted value of 2.08 Å for the length of a sulphur-sulphur single bond. The C=S bond in 4-methyl-trithione is found to be 1.627 ± 0.017 Å and in xanthan hydride 1.653 ± 0.009 Å, and the C—S bonds in 4-methyl-trithione are found to be 1.747 ± 0.017 Å and 1.713 ± 0.017 Å while the corresponding bonds in xanthan hydride are 1.761 ± 0.008 Å and 1.756 ± 0.008 Å. The C=S and C—S bonds in xanthan hydride thus appear to be slightly longer than the corresponding bonds in 4-methyl-trithione. If the lengths of the sulphur-carbon single bond and double bond are taken to be 1.81 Å and 1.61 Å, respectively,[19] the S—C bonds in xanthan hydride are significantly shorter than a single bond, and the S=C bond significantly longer than a double bond.

The average value of the carbon-nitrogen bond lengths in xanthan hydride is 1.339 Å and no C—N bond in the molecule deviates significantly from this value. In thiuret hydroiodide [1] the average value of the C—N bond lengths was found to be 1.34 Å. The C—N bond lengths in xanthan hydride as well as in thiuret hydroiodide are in good agreement with the length of the aromatic C—N bond, which in pyridine [20] has been found to be 1.340 Å.

The shape of the five-membered ring in xanthan hydride is much the same as in 4-methyl-trithione. The S—S—C angle on the thione side of the ring is in both structures found greater than the other S—S—C angle, and the same has been found for the corresponding angles in rhodan hydrate.[17]

One may conclude that the xanthan hydride molecule is stabilized by π-orbital delocalization. This seems to be most pronounced in the $>$N—C=N—C= part of the molecule. The C—S bonds in the ring are less shortened by π-bonding, and the S—S bond, if shortened relative to a single bond, is only so to a small degree. The bond orders for the C—S and S—S bonds, which for

Table 8. Mean square vibrational displacements along principal axes of thermal ellipsoids, and projections of these values on to the axes L, M, and N in the orthogonal coordinate system. The dimension is $Å^2$.

Atom	principal axis	m.s.d	$L_{m.s.d}$	$M_{m.s.d}$	$N_{m.s.d}$
S_1	1	0.0560	0.0210	0.0088	0.0513
	2	0.0363	0.0313	0.0112	−0.0147
	3	0.0166	−0.0057	0.0156	−0.0003
S_2	1	0.0471	0.0215	−0.0010	0.0419
	2	0.0364	0.0323	0.0027	−0.0166
	3	0.0174	−0.0010	0.0174	0.0009
S_3	1	0.0592	−0.0093	−0.0254	0.0525
	2	0.0304	0.0282	0.0073	0.0085
	3	0.0226	−0.0075	0.0196	0.0082
C_1	1	0.0458	0.0372	0.0111	0.0242
	2	0.0239	0.0138	−0.0063	−0.0183
	3	0.0133	−0.0006	0.0124	−0.0047
C_2	1	0.0394	0.0382	0.0101	0.0020
	2	0.0290	−0.0024	0.0034	0.0287
	3	0.0162	−0.0040	0.0155	−0.0022
N_1	1	0.0643	0.0372	−0.0024	0.0513
	2	0.0358	0.0284	−0.0076	−0.0204
	3	0.0299	0.0058	0.0292	−0.0028
N_2	1	0.0547	0.0145	−0.0122	0.0513
	2	0.0275	0.0265	0.0004	−0.0074
	3	0.0198	0.0009	0.0193	0.0043

4-methyl-trithione have been calculated by Bergson [21] by a molecular orbital method, should in xanthan hydride presumably be somewhat smaller judging from the experimental results. This will be discussed in a later paper.

The arrangement of molecules in a unit cell of xanthan hydride is shown in Fig. 6. The molecules are arranged in pairs across a center of symmetry through N—H···N hydrogen bonds. Between pairs there are N—H···S hydrogen bonds; these occur not between molecules within a unit cell but between molecules in adjacent unit cells along the a axis.

DESCRIPTION OF THERMAL ELLIPSOIDS

The principal axes of the thermal vibration ellipsoids for the atoms in xanthan hydride, except hydrogen, were derived from the temperature parameters in Table 3. Mean squares of vibrational displacements along each principal ellipsoid axis as well as the projections of these mean square displacements on the axes L, M and N in the orthogonal coordinate system, are given in Table 8. A pictorial representation, with ellipses drawn through points repre-

Table 9. Observed and calculated $h0l$, $0kl$ and $1kl$ structure factors for xanthan hydride based on two molecules. Reflections marked with asterisks were given zero weight in the refinement because of assumed secondary extinction.

k	F_o	F_c ($1k0$)	l	F_o	F_c ($\bar{1}1l$)
1	8.43	+ 10.27	1	19.94 *	+ 26.70
2	14.69	− 16.19	2	54.16 *	− 73.91
3	4.21	− 4.41	3	6.68	+ 7.66
4	8.64	− 8.33	4	15.83	+ 15.03
5	9.86	− 9.74	5	11.10	+ 10.28
6	19.94	+ 20.79	6	15.11	− 14.00
7	11.91	+ 11.62	7	9.46	+ 8.40
8	9.55	− 9.47	8	15.21	+ 14.81
9	6.07	+ 5.67	9	< 1.85	− 1.83
10	10.28	− 9.31	10	14.90	+ 14.81
11	10.89	− 11.31	11	< 1.96	+ 0.89
12	10.28	+ 9.54	12	6.47	− 6.14
13	1.85	− 1.92	13	6.26	− 6.16
			14	8.43	+ 8.02
			15	5.65	− 5.06

l	F_o	F_c ($10l$)	l	F_o	F_c ($12l$)
2	10.07	+ 8.57	1	19.62	+ 20.39
4	6.68	+ 5.90	2	7.80	+ 6.52
6	19.22	+ 18.46	3	32.68 *	− 38.33
8	< 1.75	+ 1.17	4	19.62	− 18.04
10	10.07	+ 9.83	5	16.75	+ 16.39
12	5.23	− 4.82	6	6.26	− 5.34
14	8.01	− 7.20	7	10.37	+ 8.91
			8	< 1.85	+ 0.44
			9	2.67	− 2.20

l	F_o	F_c ($\bar{1}0l$)			
2	5.96	− 6.12	10	6.37	− 5.64
4	9.35	− 8.43	11	13.87	+ 13.88
6	19.73	− 19.00	12	5.96	+ 5.09
8	13.78	− 13.03	13	9.46	− 9.30
10	< 1.96	+ 1.29	14	< 1.54	− 0.94
12	< 2.06	− 1.26	15	4.83	− 4.37
14	2.15	+ 2.22			

l	F_o	F_c ($11l$)	l	F_o	F_c ($\bar{1}2l$)
1	15.41	− 15.09	1	24.87 *	+ 30.03
2	11.61	+ 10.28	2	8.32	+ 8.52
3	12.94	− 12.41	3	12.03	− 12.96
4	21.68	+ 20.51	4	6.07	+ 5.50
5	15.72	− 14.86	5	8.94	− 9.73
6	33.70	− 30.21	6	1.45	− 1.57
7	9.55	− 8.34	7	18.29	+ 17.00
8	8.64	+ 8.01	8	11.91	+ 11.08
9	10.07	+ 9.47	9	22.91	− 23.13
10	19.11	− 18.87	10	3.60	− 2.98
11	< 2.06	+ 1.08	11	4.01	+ 3.88
12	6.47	− 6.16	12	2.87	+ 2.79
13	6.37	+ 5.52	13	10.49	− 11.00
14	5.14	+ 4.23	14	< 1.75	− 0.49
15	< 1.12	+ 0.81	15	1.75	− 1.84

	F_o	F_c
l		$13l$
1	15.83	+ 16.80
2	< 1.12	+ 1.12
3	9.04	+ 8.56
4	3.60	+ 3.81
5	21.58	+ 22.14
6	10.18	− 10.42
7	4.93	+ 4.60
8	7.10	+ 7.04
9	6.07	− 6.47
10	8.53	− 8.86
11	4.42	− 4.07
12	< 1.85	+ 0.11
13	9.04	− 8.60
14	1.75	+ 1.61
15	1.12	− 0.92
l		$\bar{1}3l$
1	19.53	− 20.84
2	25.08	− 25.54
3	20.25	− 19.88
4	8.64	+ 8.81
5	8.83	− 8.55
6	2.36	− 2.09
7	18.91	− 17.76
8	10.18	+ 9.61
9	6.07	+ 4.67
10	8.64	+ 7.93
11	3.18	+ 2.79
12	4.42	− 4.02
13	6.58	+ 6.73
14	3.29	+ 3.18
15	11.00	+ 10.08
l		$14l$
1	2.78	− 2.54
2	11.40	− 11.62
3	4.62	+ 4.54
4	8.32	+ 7.63
5	< 1.54	+ 0.78
6	11.61	− 11.47
7	7.19	− 6.66
8	< 1.96	− 0.48
9	< 1.96	+ 0.65
10	2.87	− 3.08
11	6.17	− 5.74
12	< 1.85	+ 0.95
13	< 1.64	+ 1.63
14	7.92	+ 7.31
l		$\bar{1}4l$
1	14.48	− 13.25
2	3.29	+ 3.29
3	8.13	+ 7.95

	F_o	F_c
4	4.42	+ 3.76
5	< 1.54	− 0.43
6	19.32	+ 16.83
7	5.75	+ 5.02
8	2.26	+ 2.25
9	13.36	+ 12.33
10	< 2.06	− 0.06
11	< 2.06	− 0.70
12	< 1.96	− 1.38
13	6.47	+ 5.89
14	2.87	− 2.84
15	1.24	− 1.59
l		$15l$
1	5.14	+ 4.85
2	6.89	− 7.39
3	10.69	+ 11.15
4	16.14	− 15.55
5	< 1.75	− 1.29
6	23.94	+ 25.23
7	12.75	+ 11.84
8	4.01	− 3.88
9	9.15	− 9.49
10	15.51	+ 15.51
11	4.01	+ 3.83
12	5.44	+ 5.76
13	< 1.45	+ 0.31
14	5.56	− 4.62
l		$\bar{1}5l$
1	11.10	− 12.26
2	43.26	+ 44.87
3	14.90	+ 14.07
4	12.85	− 11.69
5	9.97	− 9.41
6	10.28	+ 9.52
7	6.99	+ 6.40
8	18.29	− 15.91
9	5.96	− 5.40
10	16.02	− 14.91
11	6.26	− 6.06
12	3.69	+ 3.48
13	3.60	+ 3.06
14	8.13	− 7.19
15	4.21	− 4.20
l		$16l$
1	8.22	− 7.95
2	10.37	− 10.46
3	21.68	+ 23.26
4	22.51	+ 23.38
5	12.85	− 12.29
6	7.80	+ 7.80
7	4.21	− 4.11
8	2.06	− 1.67

	F_o	F_c		F_o	F_c
9	< 2.06	+ 0.13	l		$18l$
10	8.13	+ 8.74			
11	8.83	− 8.77	1	< 1.96	− 0.10
12	11.30	− 10.02	2	13.57	+ 14.18
13	5.44	+ 4.95	3	7.40	− 7.38
			4	16.86	− 17.80
			5	< 2.06	− 0.06
l		$\overline{16}l$	6	2.87	+ 3.03
			7	8.32	+ 8.58
1	15.93	− 15.12	8	< 1.96	+ 1.16
2	15.72	− 14.89	9	< 1.85	+ 0.69
3	3.29	− 3.50	10	5.44	− 4.94
4	8.94	− 8.65	11	9.04	+ 8.80
5	7.92	+ 6.44	12	6.37	+ 5.45
6	< 1.85	+ 0.80			
7	17.68	− 16.90	l		$\overline{18}l$
8	18.50	− 18.61			
9	10.69	+ 8.97	1	18.91	+ 17.88
10	8.13	+ 7.38	2	6.07	+ 5.49
11	< 1.96	− 1.33	3	2.36	+ 2.34
12	4.42	− 4.08	4	2.47	+ 2.81
13	4.11	+ 3.77	5	2.87	+ 2.27
14	4.01	+ 3.13	6	12.43	− 12.09
			7	< 2.06	− 0.39
			8	10.49	+ 9.62
l		$17l$	9	11.91	− 11.15
			10	4.32	− 4.24
1	11.61	− 11.15	11	< 1.54	− 0.56
2	3.39	+ 3.52	12	4.32	+ 3.96
3	10.18	− 10.72	13	5.04	− 4.61
4	7.19	+ 7.40			
5	19.11	− 19.76	l		$19l$
6	5.86	− 5.94			
7	4.93	− 4.92	1	< 2.06	+ 1.17
8	5.86	− 5.59	2	3.18	+ 2.86
9	< 1.96	+ 2.11	3	3.18	− 3.12
10	< 1.85	+ 0.09	4	2.47	+ 2.70
11	2.78	+ 2.51	5	14.60	+ 15.37
12	5.04	− 4.18	6	8.13	− 8.48
13	6.89	+ 6.51	7	8.74	− 9.41
			8	1.75	− 1.65
			9	9.55	+ 10.20
l		$\overline{17}l$	10	5.75	− 5.40
			11	4.53	− 4.39
1	5.14	+ 4.68			
2	3.29	− 2.75	l		$\overline{19}l$
3	15.32	+ 13.64			
4	< 1.85	+ 0.05	1	11.72	+ 11.25
5	7.92	+ 7.36	2	14.60	− 13.27
6	5.04	− 4.20	3	23.33	− 21.47
7	13.57	+ 12.75	4	3.18	+ 3.22
8	< 2.06	+ 0.77	5	6.99	+ 6.55
9	1.96	+ 2.12	6	< 1.96	+ 0.91
10	< 1.96	+ 0.22	7	13.97	− 13.46
11	< 1.75	− 1.78	8	11.10	+ 9.57
12	2.78	+ 2.43	9	2.67	+ 2.36
13	2.87	− 2.69	10	8.94	+ 8.47
14	1.75	+ 1.61	11	7.92	+ 7.03

l	F_o	F_c
	1,10l	
1	2.47	+ 2.54
2	5.96	+ 5.34
3	7.40	− 6.94
4	11.10	− 11.97
5	5.86	+ 6.09
6	3.50	− 3.68
7	1.64	+ 1.87
8	1.85	+ 1.87
9	< 1.24	+ 0.27
10	2.78	− 2.66

l	F_o	F_c
	$\bar{1}$,10l	
1	3.18	− 2.41
2	10.69	+ 10.72
3	3.69	+ 3.70
4	5.86	+ 5.57
5	4.62	− 4.24
6	< 1.85	+ 1.30
7	9.25	+ 9.36
8	10.89	+ 10.75
9	< 1.45	+ 1.92
10	6.58	− 5.95
11	< 0.72	− 0.99

l	F_o	F_c
	1,11l	
1	4.32	+ 4.40
2	1.85	− 2.06
3	7.80	+ 8.00
4	5.86	− 5.71
5	6.26	+ 6.18
6	6.58	+ 6.15
7	5.04	+ 4.65
8	6.68	+ 6.03

l	F_o	F_c
	$\bar{1}$,11l	
1	< 1.85	− 1.07
2	3.39	+ 3.08
3	2.15	− 2.57
4	< 1.75	− 1.94
5	6.37	− 6.57
6	< 1.54	+ 1.00
7	2.87	− 2.41
8	7.19	− 6.67
9	4.21	− 4.30

l	F_o	F_c
	1,12l	
1	3.90	+ 3.63
2	11.61	− 11.06
3	3.81	+ 3.07
4	14.80	+ 13.99
5	< 1.24	+ 0.44

l	F_o	F_c
	$\bar{1}$,12l	
1	9.67	− 9.08
2	9.67	− 9.75
3	7.10	− 6.62
4	4.83	− 4.16
5	3.08	− 1.97
6	6.47	+ 5.49
7	< 0.93	− 1.05

l	F_o	F_c
	1,13l	
1	2.57	− 2.38
2	1.45	− 1.38
3	1.64	− 2.10

l	F_o	F_c
	$\bar{1}$,13l	
1	10.37	− 9.74
2	< 1.03	+ 0.42
3	16.75	+ 16.01
4	4.42	+ 4.25

k	F_o	F_c
	0k0	
2	34.52	− 34.79
4	57.13 *	− 67.99
6	32.89	+ 34.73
8	11.91	+ 12.06
10	12.75	− 12.98
12	1.85	+ 2.07

l	F_o	F_c
	00l	
2	9.55	− 9.45
4	19.32	+ 19.60
6	5.44	− 4.65
8	32.89	− 35.49
10	11.91	+ 12.81
12	17.68	− 20.19
14	2.26	+ 2.72
16	2.26	+ 2.23

l	F_o	F_c
	01l	
1	4.72	− 4.80
2	23.54	− 25.89
3	16.02	+ 16.06
4	7.61	− 7.29
5	30.01	− 28.49
6	18.19	− 17.86
7	15.93	+ 16.68
8	4.62	− 4.07
9	< 2.06	+ 0.38
10	2.47	− 1.84
11	5.14	+ 4.74
12	3.39	− 3.69
13	5.65	+ 5.94

	F_o	F_c		F_o	F_c
14	4.72	+ 5.01	l	05l	
15	6.07	− 6.42			
16	1.12	+ 1.55	1	2.26	+ 2.45
			2	17.26	+ 17.85
l	02l		3	5.96	− 5.56
			4	5.04	+ 4.62
1	4.21	− 4.14	5	18.19	+ 17.29
2	1.85	− 1.61	6	16.54	+ 15.83
3	20.55	+ 21.13	7	3.50	− 2.90
4	8.13	− 8.68	8	< 2.15	+ 1.51
5	20.76	+ 21.14	9	< 2.26	+ 1.14
6	3.39	− 2.99	10	< 2.26	+ 0.84
7	12.43	+ 12.71	11	< 2.26	− 0.02
8	9.25	+ 9.26	12	< 2.06	+ 1.47
9	2.67	+ 2.39	13	3.08	− 2.91
10	< 2.15	− 1.00	14	6.17	− 6.36
11	9.86	− 10.53	15	1.54	+ 1.72
12	5.44	+ 5.37			
13	8.74	− 9.40	l	06l	
14	< 1.85	+ 0.10			
15	5.35	− 5.30	1	8.13	+ 7.77
			2	2.67	+ 2.51
l	03l		3	12.85	− 12.95
			4	9.55	+ 9.65
1	9.55	+ 9.59	5	11.40	− 10.34
2	3.18	+ 2.56	6	< 2.06	+ 0.60
3	16.86	− 15.46	7	10.18	− 9.81
4	16.23	− 15.87	8	16.96	− 17.34
5	24.76	+ 25.42	9	7.40	− 7.45
6	14.48	+ 13.76	10	< 2.26	− 0.18
7	21.58	− 22.30	11	7.29	+ 7.59
8	4.53	− 3.91	12	7.71	− 9.02
9	2.06	− 1.99	13	< 1.64	+ 0.93
10	< 2.15	+ 1.64	14	< 1.33	+ 0.61
11	6.68	− 6.60			
12	< 2.26	+ 0.76	l	07l	
13	7.10	− 7.49			
14	2.36	− 1.64	1	13.78	− 13.70
15	7.29	+ 8.01	2	15.32	− 15.19
			3	6.37	+ 5.66
l	04l		4	16.54	+ 16.66
			5	18.19	− 18.30
1	17.05	− 17.34	6	28.36	− 27.93
2	7.29	+ 7.45	7	13.15	+ 13.06
3	1.85	− 1.28	8	5.56	+ 5.01
4	8.64	− 8.44	9	3.18	+ 3.47
5	10.69	− 10.09	10	2.78	− 2.94
6	6.89	+ 6.26	11	3.50	+ 4.00
7	6.07	− 5.33	12	2.26	− 2.34
8	22.91	+ 23.91	13	6.89	+ 7.55
9	9.15	+ 8.15	14	5.35	+ 7.66
10	8.64	− 8.54			
11	2.57	− 1.73	l	08l	
12	11.72	+ 13.43			
13	8.22	+ 9.60	1	19.62	+ 20.28
14	2.57	− 2.70	2	2.78	− 2.66
15	1.33	+ 1.64	3	3.50	+ 3.40
			4	< 2.15	− 1.85

	F_o	F_c			F_o	F_c
5	13.78	+ 13.77	6		< 1.33	+ 1.05
6	5.23	− 5.34	7		9.55	+ 9.42
7	12.54	+ 12.43				
8	5.44	− 5.39	l		$0,13l$	
9	7.50	− 7.71				
10	2.26	+ 2.77	1		9.76	− 9.58
11	4.11	+ 4.43	2		3.69	− 3.45
12	2.47	− 2.34	3		3.08	− 3.14
13	7.40	− 8.58	4		5.86	+ 6.03
l		$09l$	h		$h00$	
1	7.92	+ 8.14	1		26.30	+ 30.30
2	3.18	− 2.33	2		4.21	− 3.40
3	3.18	+ 2.89	3		9.46	+ 8.39
4	7.29	− 6.70	4		< 3.60	+ 0.92
5	3.90	− 3.88	5		4.42	+ 5.45
6	< 2.26	− 0.50				
7	4.21	− 4.02	l		$20l$	
8	< 2.06	− 1.31				
9	2.47	− 3.00	2		32.47	− 36.07
10	< 1.75	+ 1.18	4		22.70	+ 22.42
11	2.26	− 2.04	6		6.07	− 5.89
12	1.75	+ 2.17	8		20.14	+ 19.33
			10		16.86	+ 14.66
l		$0,10l$	12		6.99	− 5.78
			14		4.93	+ 5.21
1	13.15	− 13.68				
2	4.62	− 4.60	l		$\bar{2}0l$	
3	7.10	+ 7.41				
4	2.15	− 2.32	2		12.94	− 13.09
5	< 2.15	− 0.51	4		26.30	− 31.25
6	2.99	+ 3.13	6		15.00	+ 15.78
7	< 1.96	− 0.63	8		9.97	− 9.74
8	9.67	+ 10.68	10		17.05	+ 17.34
9	7.40	+ 8.54	12		5.35	+ 4.77
10	4.11	+ 4.12	14		3.50	− 3.43
11	5.75	− 7.03				
			l		$30l$	
l		$0,11l$				
			2		19.11	− 19.19
1	4.93	+ 5.34	4		5.44	− 5.22
2	10.89	+ 11.76	6		< 3.69	− 0.61
3	< 2.06	+ 0.14	8		6.58	− 6.38
4	9.46	− 9.89	10		12.24	+ 10.92
5	5.75	+ 6.23				
6	19.53	+ 20.13	l		$\bar{3}0l$	
7	< 1.64	− 1.70				
8	5.23	− 4.74	2		10.07	− 9.98
9	2.99	− 3.03	4		5.23	+ 5.77
			6		< 3.60	+ 3.20
l		$0,12l$	8		< 3.69	− 2.44
			10		9.76	+ 9.31
1	12.54	− 12.08	12		< 3.08	− 3.44
2	< 1.85	− 0.05	14		< 1.96	+ 0.23
3	3.90	− 3.84				
4	3.18	+ 2.55				
5	9.15	− 8.51				

l	F_o	F_c		F_o	F_c
		$40l$	4	< 3.60	+ 0.82
			6	< 3.50	+ 1.62
2	< 3.50	+ 0.97	8	< 3.18	− 3.57
4	< 3.29	− 3.39	10	< 2.57	− 2.40
6	7.80	− 7.14			
8	< 2.15	+ 0.51			
			l		$\bar{5}0l$
l		$\bar{4}0l$			
			2	< 2.15	− 0.08
2	10.49	+ 10.29	4	< 2.06	− 1.53

senting the mean square displacements projected on to the plane of the molecule, is given in Fig. 7.
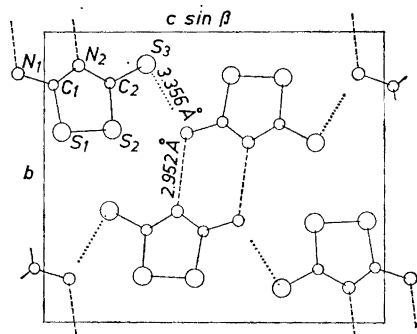
Fig. 6. The arrangement of molecules in the unit cell as seen along the a axis. Dashed lines indicate the N—H···N hydrogen bonds, and dotted lines indicate the N—H···S hydrogen bonds to molecules in unit cells above and below.
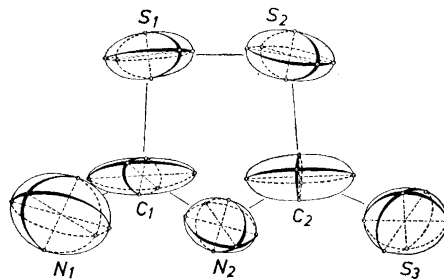
Fig. 7. The mean square vibrational displacements in principal axes directions, projected onto the least squares plane of the molecule.

A detailed discussion of the thermal vibration is hardly warranted in view of the small number of reflections with $h > 1$ in the material. Therefore no correction in bond lengths for rigid body vibrations has been undertaken. However, the derived thermal vibrations in xanthan hydride and rhodan hydrate [17] are in general much the same, and a qualitative account of the thermal vibrations in the crystal structure of xanthan hydride may therefore be of interest.

According to Table 8 the nitrogen and sulphur atoms are vibrating more in a direction normal to the plane than in the plane of the molecule, and the carbon atoms are vibrating more in the plane, approximately in the C—C direction. Fig. 7 indicates that the molecule as a whole has some translational vibration in the C—C direction, and probably also some librational vibration about an axis parallel to this direction through the center of gravity of the molecule.

REFERENCES

1. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
2. Kehl, W. L. and Jeffrey, G. A. *Acta Cryst.* **11** (1958) 813.
3. Jeffrey, G. A. and Shiono, R. *Acta Cryst.* **12** (1959) 447.
4. Hordvik, A. *Acta Chem. Scand.* **14** (1960) 1218.
5. Hordvik, A. *Acta Chem. Scand.* **15** (1961) 1186.
6. Foss, O. *Acta Chem. Scand.* **10** (1956) 871.
7. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
8. Tomiie, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
9. Viervoll, H. and Ögrim, O. *Acta Cryst.* **2** (1949) 277.
10. Wilson, A. J. C. *Nature* **150** (1942) 152.
11. Zachariasen, W. H. *Acta Cryst.* **5** (1952) 68.
12. Cochran, W. and Woolfson, M. M. *Acta Cryst.* **8** (1955) 1.
13. Hantsch, A. and Wolvekamp, M. *Ann.* **331** (1904) 265.
14. Rossmann, M. G., Jacobsen, R. A., Hirshfeld, F. L. and Lipscomb, W. N. *Acta Cryst.* **12** (1959) 530.
15. Pepinsky, R., Robertson, J. M. and Speakman, J. C. (Ed.) *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Pergamon Press, Oxford 1961, p. 42.
16. Hirshfeld, F. L. *Instruction for use of the least square program for WEIZAC.* The Weizmann Institute of Science, Rehovoth, Israel.
17. Hordvik, A. *To be published.*
18. Darlow, S. F. *Acta Cryst.* **13** (1960) 383.
19. Pauling, L. *The Nature of the Chemical Bond,* 3rd Ed., Cornell University Press, Ithaca, New York 1960.
20. Bak, B., Hansen-Nygaard, L. and Rastrup-Andersen, J. *J. Mol. Spectry.* **2** (1958) 361.
21. Bergson, G. *Arkiv Kemi* **19** (1962) 181.