164. *The Crystal and Molecular Structures of Tiglic and Angelic Acids. Part I. Tiglic Acid.*

By A. L. PORTE and J. MONTEATH ROBERTSON.

X-Ray analysis shows that tiglic acid crystals are triclinic, space-group C_i-$P\bar{1}$, with two molecules of $C_5H_8O_2$ per unit cell. The use of molecular Fourier transforms leads to a fairly direct determination of the structure and shows that the acid is 2-methyl-*trans*-but-2-enoic acid, confirming the accepted chemical formula. The atoms are clearly resolved on the electron-density projections and the molecule is planar except for the hydrogen atoms and the methyl group attached to the β-carbon atom, which is 0·1 Å above the mean plane. This displacement, and a small distortion of the bond angles, relieves the intramolecular overcrowding.

EXTENSIVE study has recently been made [1] of the preparation and properties of the 2-methylalk-2-enoic acids, R·CH₂·CH:CMe·CO₂H. The simplest members of the series, tiglic and angelic acids (R = H), have long been known, but the geometric configurations assigned to them are based on rather indirect evidence. The present work was therefore undertaken to attempt an unambiguous determination of the position of all the atoms in space by the method of *X*-ray crystal analysis.

[1] Cason, Allinger, and Williams, *J. Org. Chem.*, 1953, **18**, 842; Cason, Allinger, and Allen, *ibid.*, 1953, **18**, 857; Cason and Ralm, *ibid.*, 1954, **19**, 1836; Ställberg-Stenhagen, *Arkiv Kemi*, 1954, **6**, 537.

Chemical evidence indicates that tiglic acid is 2-methyl-*trans*-but-2-enoic acid (I), and angelic acid is believed to be the corresponding *cis*-acid (II). The evidence for these configurations is based on the work of Sudborough and Davies [2] on the rates of esterification

$$\begin{array}{cc} CH_3—CH & CH_3—CH \\ \| & \| \\ CH_3—C—CO_2H & HO_2C—C—CH_3 \\ (I) & (II) \end{array}$$
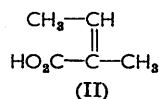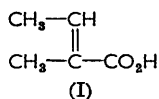
of the acids; of von Auwers and Wissebach [3] on a comparison of the physical properties of the two acids with those of the two crotonic acids of known configuration; of Pfeiffer [4] on the dibromo-derivatives of tiglic and angelic acid; and on that of Dreiding and Pratt [5] who obtained angelic acid by the carboxylation of *trans*-but-2-enyl-lithium.

The combination of all this evidence may be regarded as conclusive, but the method of X-ray analysis provides a more direct approach and in addition gives a complete picture of the geometry of the molecules. In particular, as these molecules may be expected to be nearly planar, the method of the molecular Fourier transform [6] may be applied to the problem. The question of configuration then reduces to that of finding which of the two possible transforms fits each reciprocal lattice.

The results described below lead to a very direct and accurate determination of the structure of tiglic acid as the *trans*-isomer. For angelic acid, described in the following paper, there are difficulties due to an abnormally high temperature factor and possible disorder. The two-dimensional methods employed, while not sufficient to yield accurate molecular dimensions, enable us to confirm the *cis*-configuration for this acid.

Crystal Data.—Tiglic acid, $C_5H_8O_2$; M, 100·1, m. p. 64·5°; d, calc. 1·164, found, 1·163. Triclinic, $a = 7·70 \pm 0·02$; $b = 5·23 \pm 0·02$; $c = 7·42 \pm 0·02$ Å. $\alpha = 96·6° \pm 0·5°$, $\beta = 86·5° \pm 0·5°$, $\gamma = 106° \pm 0·5°$. No systematic absences. Space-group, C_1^1–P1 or C_i^1–P$\bar{1}$ (complete analysis confirms P$\bar{1}$). Two molecules per unit cell. No molecular symmetry required. Volume of unit cell = 285·6 Å³. Absorption coefficient for X-rays ($\gamma = 1·542$ Å) $\mu = 8·56$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 108.

Thick needles developed along the b axis were obtained by slow crystallization from light petroleum. The crystals are extremely volatile and were sealed in gelatine capsules during the experiments.

Structure Analysis.—The projection of the structure along the short b axis (5·23 Å) was first studied. In the corresponding (h0l) zone 109 reflections were observed with Cu radiation out of a possible 151, and there appeared to be a good chance of resolving all the atoms clearly.

There are two molecules in the unit cell and it was assumed that these might exist as a centrosymmetric dimer, with hydrogen bonding between the carboxyl groups. This arrangement is very common among monocarboxylic organic acids. A simplified planar model was therefore set up, as shown at the bottom of Fig. 1, in which all the bond lengths were taken as 1·4 Å and the hydrogen bonds as 2·8 Å. On the basis of this centrosymmetric structure the Fourier transform

$$T (X^*, Y^*) = 2\sum \omega \cos 2\pi (X^*\xi + Y^*\eta)$$

was evaluated and is plotted in Fig. 1. In this expression ω is a weighting factor corresponding to the number of electrons associated with each atom.

The reciprocal net of the (h0l) structure factors was found to fit this transform, and the orientations of the a* and c* axes which give the best fit are shown in the diagram. The corresponding planar model for the *cis*-isomer leads to a transform (Fig. 1 of the following

[2] Sudborough and Davies, *J.*, 1909, **95**, 976.
[3] von Auwers and Wissebach, *Ber.*, 1923, **56**, 715.
[4] Pfeiffer, *Z. phys. Chem.*, 1904, **48**, 40.
[5] Dreiding and Pratt, *J. Amer. Chem. Soc.*, 1954, **76**, 1902.
[6] Knott, *Proc. Phys. Soc.*, 1940, **52**, 229; Klug, *Acta Cryst.*, 1950, **3**, 176.

paper) which is similar in some respects. However, all attempts to fit the tiglic acid reciprocal net to this transform led to serious discrepancies and consequently there is no doubt that tiglic acid is in fact 2-methyl-*trans*-but-2-enoic acid.

By using the phase angles derived from the transform with the fit shown in Fig. 1 the electron density as projected on (010) was now computed by summing the appropriate double Fourier series. This gave a map in which all the carbon and oxygen atoms were clearly resolved. Structure factors calculated from the co-ordinates obtained from this map resulted in an average discrepancy (R) of 21% for the ($h0l$) zone at this stage, showing that a good approximation to the true structure had already been obtained. Application of successive difference syntheses then resulted in a final discrepancy of 11·1% for this zone, and the final electron-density map is shown in Fig. 2.

The final difference map obtained in this refinement still showed small peaks on atoms C(3) and C(4) and evidence of considerable anisotropic thermal motion, especially in the region
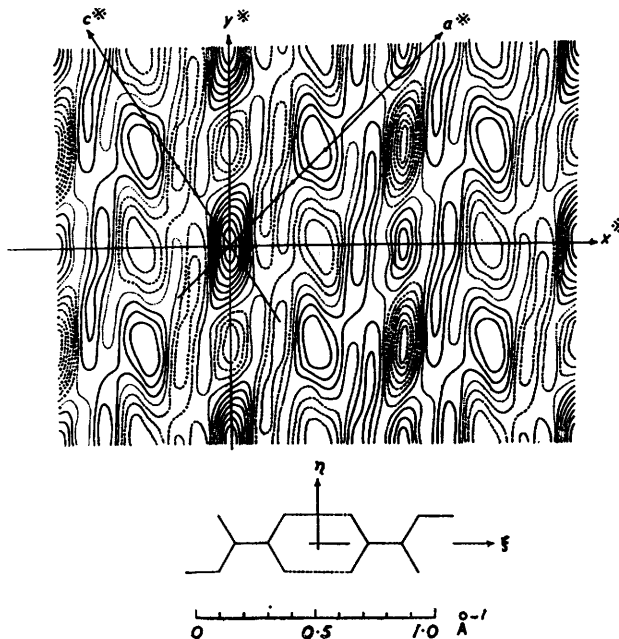

FIG. 1. *Fourier transform of idealised dimer of tiglic acid with the* a * *and* c * *reciprocal axes superimposed.*

of the oxygen atoms. No attempt was made to evaluate the anisotropic temperature factors. The mean values obtained for the Debye factors (B) for the principal projections are shown in Table 1. Those obtained from the ($0kl$) zone were not as thoroughly investigated and are less accurate. The general trend in these factors, however, indicates that the atoms furthest from the centre have the largest thermal motion, especially the terminal atoms which are bonded to only one carbon atom.

TABLE 1. *Values of* $B \times 10^{16}$ *cm.*^{2}

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	O(6)	O(7)
($h0l$) zone	5·1	4·8	4·2	4·4	4·8	5·1	5·1
($0kl$) zone	6·2	5·1	4·0	3·8	5·8	5·1	5·1

Fig. 3 shows a difference synthesis in which the theoretical carbon and oxygen atoms each with their appropriate isotropic thermal motion have been subtracted from the observed electron distribution. The significant peaks are now due to the hydrogen atoms. There is naturally little resolution of individual atoms in this map, but although it is not possible to say exactly where a given hydrogen atom is situated, the expected number of

atoms in each neighbourhood is present. The electron density of the hydrogen atom of the carboxyl group, which is responsible for the hydrogen bonding between the molecules of the dimer, is very much smeared out, as would be expected from the electrovalent character of the bond. However, the map indicates clearly a peak of 0·6 e Å⁻² much nearer to O(6) than to O(7). The hydrogen bond is therefore asymmetric, and the hydrogen atom concerned is bonded to O(6). It also appears to be situated slightly off the line joining the hydrogen-bonded oxygens.

Projections of the structure along the *a* and *c* axes are shown in Figs. 4 and 5. These were prepared in the same manner as for the *b*-axis projection, but in the case of these zones the refinement process was not carried quite as far. In the (0*kl*) zone 73 reflections were observed out of a possible 97 and after refinement the discrepancy was reduced to 13·4%. Most of the atoms are very clearly resolved in this map (Fig. 4) but there is some

FIG. 2. *Electron density projection drawn on a plane normal to the* b *axis for the tiglic acid dimer.*
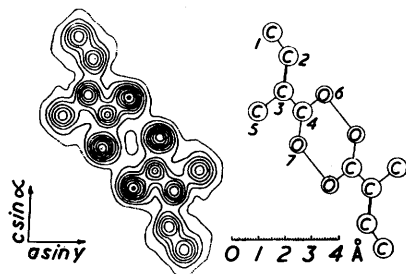
(Contour interval 1 e Å⁻² with the one-electron line dotted.)

FIG. 3. *Difference synthesis for* b-*axis projection showing electron distribution due to hydrogen atoms only.*
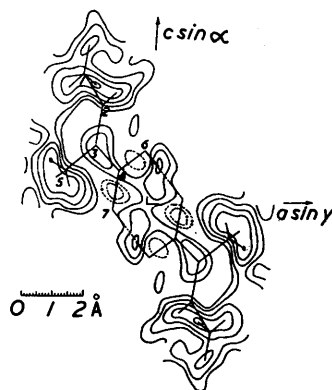
(Contour interval 0·2 e Å⁻². Negative contours dotted.)

overlap with adjoining dimers. In the projection drawn perpendicular to the *c* axis (Fig. 5) there is no resolution of individual atoms, but the map demonstrates clearly the arrangement of the molecules in the unit cell. In particular it shows the origin of the very pronounced cleavage plane, (2̄10), which is characteristic of these crystals. For this projection 60 structure factors were employed and the final discrepancy was 15·1%.

Co-ordinates, Molecular Dimensions, and Orientation.—The final co-ordinates are given in Table 2; *x*, *y*, *z* are expressed as fractions of the axial lengths, and *X*, *Y*, *Z* in Ångström units, referred to the triclinic crystal axes. *X'*, *Y'*, *Z'*, also in Ångström units, are referred to rectangular axes with *OX'* coincident with *Oa* and the plane *X'OY'* coincident with (001). The transformation relations in terms of the triclinic angles α, β, and γ are then

$$X' = X + Y \cos \gamma + Z \cos \beta$$
$$Y' = Y \sin \gamma + Z (\cos \alpha - \cos \beta \cos \gamma)/(\sin \gamma)$$
$$Z' = Z \operatorname{cosec} \gamma (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{\frac{1}{2}}$$

Two independent estimates of *z* were obtained from the *a* axis and *b* axis projections (Figs. 4 and 2). The average deviation was 0·008 Å, which may be taken as an indication of the accuracy to be expected. The mean value is quoted in Table 2. The bond lengths and bond angles derived from these co-ordinates are shown in Fig. 6.

The molecule is found to be planar within the limits of probable error except for the

hydrogen atoms and the methyl group C(1) which lies 0·1 Å above the mean plane.   The equation of the mean plane through atoms 2, 3, 4, 5, 6, and 7, is

$$0·8907X' - 0·4348Y' - 0·1324Z' - 3·4373 = 0$$

and the distances of the various atoms from this plane are given in Table 3.   The orientation of the molecule in the crystal is defined by this plane and by giving the angle between the bond C(3)–C(4) and the *c* crystal axis, which is 52·8°.

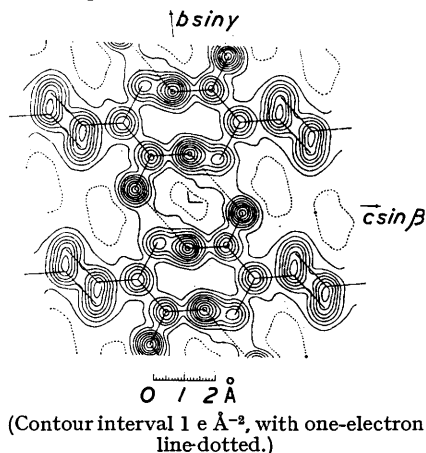FIG. 4.   *Electron-density projection on a plane normal to the a axis.*

(Contour interval 1 e Å^{-2}, with one-electron line-dotted.)

FIG. 5.   *Electron-density projection on a plane normal to the c axis.*

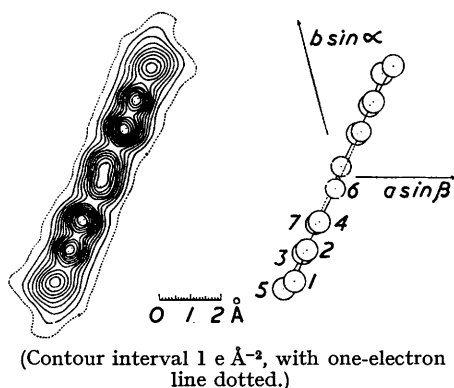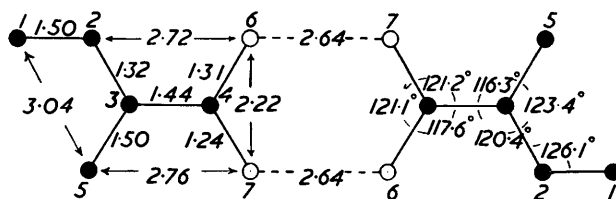(Contour interval 1 e Å^{-2}, with one-electron line dotted.)

FIG. 6.   *Bond lengths (Å) and bond angles in tiglic acid.*

Accuracy.—Application of the statistical methods described by Cruickshank [7] showed the standard deviations of the atomic co-ordinates of C(1) and C(5) to be 0·012 Å; of C(2),

TABLE 2.   *Co-ordinates.*

Atom	x	y	z	X	Y	Z	X'	Y'	Z'
C(1)	0·7000	0·3254	0·5557	5·3900	1·7018	4·1233	5·1725	1·2153	4·0957
C(2)	0·7863	0·5333	0·4298	6·0545	2·7892	3·1891	5·4803	2·3560	3·1677
C(3)	0·7667	0·5095	0·2523	5·9036	2·6647	1·8721	5·2834	2·3706	1·8596
C(4)	0·8707	0·7155	0·1450	6·7044	3·7421	1·0759	5·7387	3·4876	1·0687
C(5)	0·6440	0·2710	0·1506	4·9588	1·4173	1·1175	4·6364	1·2485	1·1100
O(6)	0·9773	0·9290	0·2310	7·5252	4·8587	1·7140	6·2907	4·4959	1·7025
O(7)	0·8530	0·6980	−0·0217	6·5681	3·6505	−0·1610	5·5522	3·5256	−0·1599

TABLE 3.   *Distances of atoms from mean molecular plane.*

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	O(6)	O(7)
d (Å).....................	+0·098	0	−0·008	+0·016	+0·003	−0·014	−0·004

C(3), and C(4) to be 0·009 Å, and those of the oxygen atoms to be 0·007 Å, in both the *a*- and *b*-axis projections.   From these results the standard deviation of the bond lengths

[7] Cruickshank, *Acta Cryst.*, 1949, **2**, 65; 1954, **7**, 519.

is found to vary from 0·012 Å for the carbon–oxygen bonds to 0·015 Å for the bond C(1)–C(2). The standard deviation of the bond angles is about 0·8°. The standard deviation of the projected electron density is 0·14 e Å^{-2} for the *b*-axis projection and 0·3 e Å^{-2} for the *a*-axis projection.

Non-bonded Distances and Molecular Arrangement.—The arrangement of the molecules in the crystal and the intermolecular approach distances are shown in Figs. 7 and 8. The closest approach occurs between the oxygen atoms of the carboxyl groups where the hydrogen bond distance is 2·64 Å, a value which is normal for this type of structure.
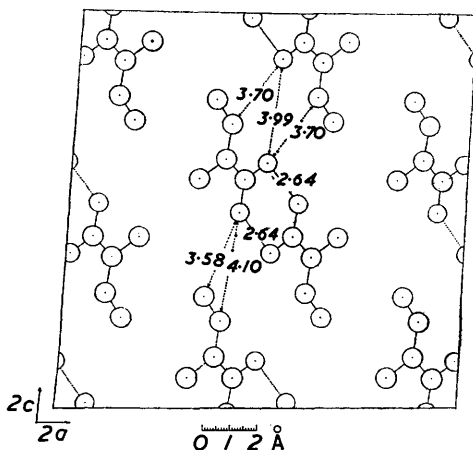

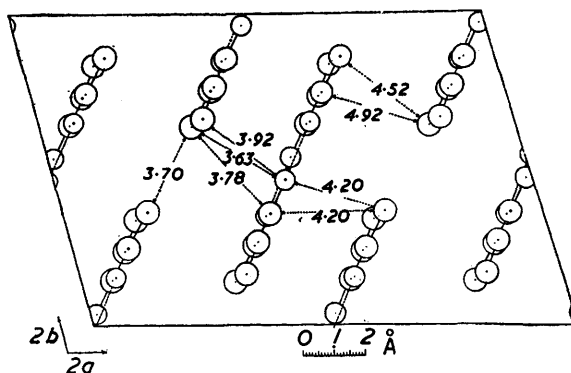FIG. 7. *Arrangement of the molecules on the* (010) *plane.*

FIG. 8. *Arrangement of the molecules on the* (001) *plane.*

Between the carbon atoms the minimum approach distance, 3·70 Å, occurs in the cleavage plane between methyl groups related by a centre of symmetry, although somewhat shorter distances occur between some of the carbon and oxygen atoms. These van der Waals distances are in general of the expected order. The methyl group approach is shorter than the corresponding distances in durene and in hexamethylbenzene, but similar to those found in 2 : 3 : 5 : 6-tetramethylpyrazine and in DL-alanine. As Levy and Corey [8] have stated, when the longer non-bonded methyl–methyl distances are involved it is probable that the rotations of the methyl groups are independent of each other. With shorter distances, as in the present example, the rotations, if any, will tend to synchronise until eventually the carbon–hydrogen bonds act as cogs in rotating wheels.

Whether or not this idea applies to methyl groups in neighbouring molecules, it must be true for methyl groups belonging to the same tiglic acid molecule, if these are rotating.

[8] Levy and Corey, *J. Amer. Chem. Soc.*, 1941, **63**, 2095.

The intramolecular distance in this case is only 3·04 Å (Fig. 6) and so it follows immediately that the hydrogen atoms of these methyl groups must have a staggered configuration. Independent rotation would mean a hydrogen atom approach of about 1·8 Å or less, which is far below what is required by the van der Waals radii.

Discussion.—From Table 3 it is clear that the molecule is planar to within the limits of error except for the methyl group, C(1), which lies 0·1 Å above the plane. This is a significant departure from the plane, being about eight times the estimated standard deviation. A strictly coplanar model with bond angles of 120° would bring the methyl groups C(1) and C(5) to within 2·8 Å of one another. The distortion which allows this distance to be increased to the observed value of 3·04 Å involves an increase of the angle C(1)C(2)C(3) to 126° and a smaller increase of the angle C(2)C(3)C(5) to 123°. The overcrowding is also relieved by a rotation about the double bond C(2)=C(3) of about 4° which raises C(1) above the molecular plane by 0·1 Å. These distortions involve C(1) rather than C(5) because the latter atom is already very close to O(7), the intramolecular distance here being only 2·76 Å.

Another feature of the stereochemistry concerns the structure of the dimer. The mean molecular plane does not pass exactly through the centre of symmetry of the dimer, but is found to be at a distance of 0·05 Å from this symmetry centre. Thus the planes of the two halves of the dimer are displaced from each other by 0·1 Å. Thus indicates some departure of the O–H bond from the molecular plane, but although this hydrogen atom can be seen in the difference synthesis map (Fig. 2) it is not possible to determine its position with certainty.

The formal double bonds C(2)=C(3) and C(4)=O(7) are conjugated, and one would therefore expect some shortening of the intermediate bond C(3)–C(4). The observed shortening from a pure single sp^2 bond length of 1·50 Å is 0·06 Å and this is significant, being about five times the estimated standard deviation. According to the well-established curve correlating bond orders and bond lengths [9] the formal single bond C(3)–C(4) should therefore have a mobile bond order of about 0·5. Hence both the
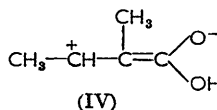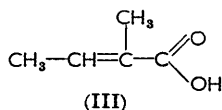
structures (III) and (IV) as well as those involving resonance within the carboxyl group must make appreciable contributions to the normal state of the tiglic acid molecule. A consequence of the polar structure is that nucleophilic reagents should attack the molecule at the β-position of the butenoic acid chain, and such reactions are known.[10]

In butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, the formal single bond has been assigned a mobile bond order of 0·447.[11] Because of the enhanced electronegativity of oxygen it would be expected that the corresponding bond in $>$C=Ċ–Ċ=O structures should have a slightly greater mobile bond order. This appears to be borne out by our results, but the accuracy is not sufficient to be conclusive.

EXPERIMENTAL

Cu-K_α radiation, $\lambda = 1·542$ Å, was used in all the X-ray measurements. The reflections were recorded on rotation, oscillation, and moving-film photographs, and the intensities were estimated visually, use being made of the multiple-film technique and calibration wedges. Cell dimensions and triclinic angles were determined from rotation and equatorial layer-line

[9] Goodwin and Vand, *J.*, 1955, 1687.
[10] Buckles, Mock, and Locatell, *Chem. Rev.*, 1955, **55**, 659.

moving-film photographs, the angles by triangulation from diagonal translation measurements and also by measurement of the reciprocal angles from the equatorial photographs. In a preliminary account of this structure [12] less accurate values for the angles were given, and the angle γ was incorrectly given as the supplement of the angle now used (106°).

TABLE 4. *Observed and calculated structure factors.*

Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c
000	—	108.0	021	11.1	−11.7	05$\bar{1}$	3.8	−3.0	207	1.8	−1.8	50$\bar{5}$	3.1	−3.5	2$\bar{3}$0	1.1	−4.7
001	6.3	7.3	022	7.6	−6.6	05$\bar{3}$	2.0	1.6	208	1.2	1.0	50$\bar{6}$	2.8	−2.0	240	1.4	2.2
002	1.1	0.5	023	5.4	−5.2	05$\bar{4}$	0.8	−0.8	301	4.1	−4.5	601	6.5	7.1	250	3.0	2.9
003	10.3	−11.8	024	8.5	7.9	055	1.8	−1.9	302	5.9	−5.7	604	2.1	−1.9	2$\bar{6}$0	2.4	−3.0
004	9.0	9.4	025	1.2	1.4	061	1.1	0.7	303	7.4	−7.2	605	5.2	4.5	310	5.8	4.4
005	6.5	6.4	026	3.4	−2.8	06$\bar{1}$	0.7	−0.3	304	2.9	−3.5	606	1.5	0.9	320	2.0	2.3
006	1.6	−1.2	027	2.6	−2.0	06$\bar{3}$	1.2	1.2	305	5.2	−4.7	60$\bar{1}$	1.8	−1.1	330	1.8	1.6
007	4.2	4.0	02$\bar{1}$	16.1	−16.8	101	35.5	34.6	306	3.4	−2.7	60$\bar{2}$	3.7	2.8	3$\bar{1}$0	22.5	21.3
008	1.2	1.5	02$\bar{2}$	16.4	−19.8	102	4.5	4.6	307	1.7	−0.5	60$\bar{4}$	1.0	1.8	3$\bar{2}$0	3.0	0.8
009	1.2	0.8	02$\bar{3}$	7.8	8.6	103	3.4	−3.9	30$\bar{1}$	7.6	−9.4	60$\bar{5}$	1.9	−2.2	410	5.2	6.5
010	16.8	−18.0	02$\bar{4}$	1.9	1.8	104	2.3	2.2	30$\bar{2}$	14.4	−15.5	706	1.3	1.6	420	5.3	4.4
020	5.6	−7.2	02$\bar{6}$	10.7	−10.5	105	1.3	0.9	30$\bar{3}$	8.9	−8.9	70$\bar{1}$	2.5	1.8	430	4.3	−4.6
030	5.9	5.8	02$\bar{7}$	2.4	−1.9	106	3.3	−3.3	30$\bar{4}$	2.2	2.1	70$\bar{2}$	1.0	1.4	4$\bar{1}$0	6.6	−6.0
040	5.9	5.5	031	10.9	11.4	107	3.4	−3.3	30$\bar{5}$	3.0	2.5	802	0.9	−1.0	4$\bar{2}$0	20.5	25.7
050	5.9	−5.9	032	4.6	5.1	108	1.6	1.9	30$\bar{7}$	1.7	−2.0	803	2.6	−1.6	4$\bar{3}$0	3.2	−2.7
100	21.0	21.9	033	2.7	−1.9	109	1.1	1.1	401	13.3	−12.5	805	1.0	−0.8	4$\bar{6}$0	1.4	1.5
200	17.3	−16.9	034	2.1	−1.6	10$\bar{1}$	12.9	−11.8	402	2.9	−2.9	80$\bar{1}$	2.7	2.6	510	2.4	2.2
300	0.6	0.7	035	4.2	3.5	10$\bar{2}$	16.5	−16.4	403	3.9	−5.1	80$\bar{2}$	1.7	−1.6	520	2.6	1.8
500	3.9	2.7	036	3.8	3.4	10$\bar{3}$	7.9	8.2	404	10.7	8.5	903	0.4	−0.7	530	4.3	−3.2
600	2.5	3.4	03$\bar{1}$	1.4	−0.9	10$\bar{4}$	13.5	12.9	406	3.7	−3.1	90$\bar{1}$	1.0	−1.5	5$\bar{1}$0	2.7	−0.2
800	1.6	1.7	03$\bar{2}$	5.5	5.2	10$\bar{5}$	6.1	6.5	407	2.9	−1.6	90$\bar{2}$	0.4	−1.0	5$\bar{2}$0	10.1	10.7
011	14.0	15.8	03$\bar{3}$	1.8	2.1	10$\bar{6}$	1.8	1.3	40$\bar{1}$	9.1	−11.5	110	5.9	4.8	610	2.8	2.8
012	17.1	−20.6	03$\bar{4}$	0.8	0.6	10$\bar{7}$	2.5	2.0	40$\bar{2}$	14.4	−14.2	120	6.4	6.5	620	2.1	−2.4
013	4.1	−3.2	03$\bar{5}$	2.9	−2.7	201	16.2	16.1	40$\bar{3}$	3.3	3.3	130	1.5	3.3	6$\bar{2}$0	2.3	−1.9
014	7.5	−5.7	03$\bar{6}$	1.0	1.6	202	20.7	−22.7	40$\bar{4}$	1.0	1.6	150	3.2	−2.4	6$\bar{3}$0	5.8	7.8
016	2.3	−1.7	037	1.2	1.1	203	3.3	−3.0	40$\bar{5}$	2.1	2.1	1$\bar{1}$0	7.7	7.1	6$\bar{4}$0	2.4	−1.1
017	5.2	−4.1	041	4.1	3.8	204	7.8	−5.5	40$\bar{6}$	6.3	−6.2	1$\bar{2}$0	1.5	3.1	710	2.1	1.4
018	0.6	−0.8	043	3.8	−2.6	206	3.0	−1.3	501	1.6	1.7	1$\bar{3}$0	1.8	3.2	720	2.6	−2.1
01$\bar{1}$	2.3	3.1	044	1.6	−1.4	207	5.4	−5.0	502	8.5	−7.7	1$\bar{6}$0	1.3	−1.2	730	1.1	0.8
01$\bar{2}$	1.7	−2.9	04$\bar{2}$	1.4	−1.7	20$\bar{1}$	5.2	6.2	503	3.5	−3.0	210	4.9	−4.5	7$\bar{1}$0	1.5	1.2
01$\bar{3}$	1.8	−1.2	04$\bar{3}$	1.6	1.0	20$\bar{2}$	4.4	−5.3	504	4.5	3.6	220	7.6	8.7	7$\bar{2}$0	1.9	−0.9
01$\bar{4}$	9.2	8.3	04$\bar{4}$	1.6	1.6	20$\bar{3}$	1.2	2.0	505	6.7	6.7	230	7.1	5.3	7$\bar{3}$0	3.0	4.4
01$\bar{5}$	1.4	−1.2	04$\bar{6}$	0.6	0.6	20$\bar{4}$	6.6	7.1	507	1.2	−1.3	240	5.8	−5.7	8$\bar{4}$0	1.1	2.2
01$\bar{6}$	4.2	4.0	047	2.3	2.4	205	0.9	−1.4	50$\bar{1}$	2.2	−2.2	2$\bar{1}$0	67.7	70.6	9$\bar{4}$0	0.6	1.6
01$\bar{7}$	2.3	−1.8	048	2.2	1.6	20$\bar{6}$	3.4	3.3	50$\bar{3}$	3.0	3.3	2$\bar{2}$0	7.5	−7.4			
01$\bar{8}$	2.1	1.4	054	1.1	−1.1												

The observed structure factors, F_o, were evaluated by the usual mosaic crystal formulæ and the calculated values F_c were obtained from the co-ordinates and the temperature-corrected scattering factors based on the calculation of McWeeny.[13]

Table 4 contains all the measured structure factors. Those too weak to be estimated have been omitted, but in these cases the calculated values were in general found to be of the expected order. The reliability index covering only the actually observed structure factors, $100\sum(|F_o| - |F_c|)/\sum|F_o|$, has the following values: $(0kl)$ zone, 13.4%; $(h0l)$ zone, 11.1%; $(hk0)$ zone, 15.1%; overall, allowing for multiplicity of axial reflections, 13.0%.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, GLASGOW.

[11] Coulson, " Valence," p. 254, Clarendon Press, Oxford, 1952.
[12] Porte and Robertson, *Nature*, 1955, **176**, 1116.
[13] McWeeny, *Acta Cryst.*, 1951, **4**, 513.