212. *The Crystal and Molecular Structure of Certain Dicarboxylic Acids. Part VII. β-Glutaric Acid.*

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Glutaric acid is the first truly representative member of the well-defined " odd " series of normal aliphatic dicarboxylic acids. A quantitative *X*-ray investigation of the crystal structure is described. The unit cell is doubled as compared with the " even " acids, and there is a space-group change from C_{2h}^5 to C_{2h}^6. The molecule displays a two-fold axis of symmetry instead of a centre. These changes, however, are essentially superficial, and there is a marked general resemblance in the molecular arrangements in the odd and the even series. In fine structure some significant changes are detected. The bond lengths are more closely normal in glutaric acid, and the slight alternating variations detected in the acids of the even series are absent. The carboxyl group also deviates further from the plane of chain carbon atoms. Another significant effect is found in the intermolecular-approach distances. The end-to-end hydrogen bridge connections between the carboxyl groups of adjoining molecules (2·69 A.) are almost the same as in the " even " structures, but the lateral connections (3·6 A. minimum) are much weaker. These facts probably account for some of the outstanding differences in physical properties shown by the acids of the odd and even series.

No precise structure determination has yet been reported for any of the normal aliphatic dicarboxylic acids with an odd number of carbon atoms in the chain, although lattice constants and space-group data for several members are available (Caspari, *J.*, 1928, 3235; 1929, 2709; Dupré la Tour, *Compt. rend.*, 1932, **194**, 622). It is a matter of considerable interest to determine the general arrangement of the molecules in this series, and also to discover whether the bond-length variations which have been detected in the carbon chains for succinic, adipic, and sebacic acids (Parts IV—VI) also occur in the acids of the odd series.

In the present paper we examine in detail the structure of β-glutaric acid (the crystal modification which is stable at ordinary temperatures). Glutaric acid is the first normal member of the well-defined odd series, as the data available for malonic acid (Gerstäcker, Moller, and Reis, *Z. Krist.*, 1927, **66**, 421) indicate a structure which may differ considerably from that of the higher members of the series.

Although the unit cell in glutaric acid is doubled as compared with the corresponding even acids, and there is a space-group change involving a molecular axis of symmetry instead of a centre, yet the main outlines of the structure which we have now determined are remarkably similar to those of the even acids. This may be seen very readily by comparing the *b* axis projections (Fig. 1) with the corresponding projection of the adipic acid structure (Part V). It would seem, therefore, that the symmetry and space-group changes which are necessarily encountered in passing from the even to the odd series of compounds are not sufficient in themselves to account for the very pronounced differences in physical properties shown by these series, although this has been suggested as an explanation (Muller, *Proc. Roy. Soc.*, 1929, *A*, **126**, 317). One is compelled to seek for a more fundamental cause, probably connected with the fine structure of the molecules themselves. In this connection our present results show a more regular carbon chain in the glutaric acid molecule, and an absence of the alternating bond-length variations which appear to be characteristic of the acids of the even series. There are also some significant differences in the intermolecular-approach distances which are described more fully below. It is likely that these two features of the structure are intimately connected.

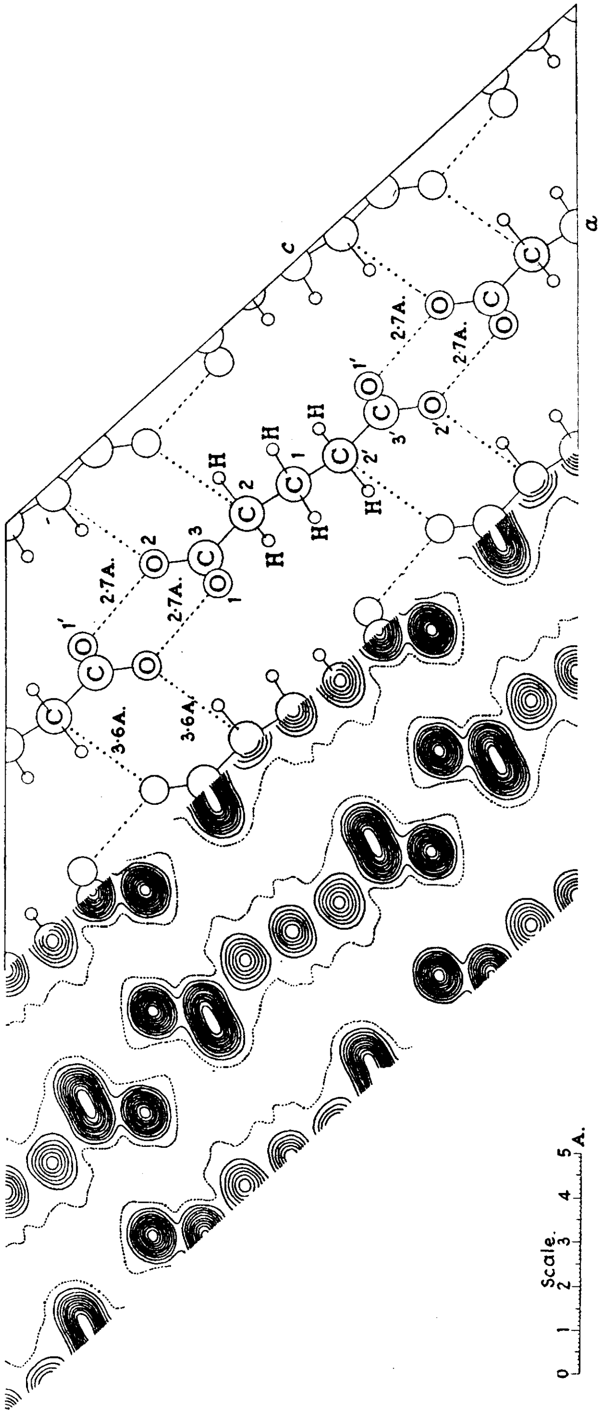
Crystal Data.—β-Glutaric acid, $C_5H_8O_4$; *M*, 132·1; m. p. 97·5°; *d*, calc. 1·388, found 1·400. Monoclinic prismatic, $a = 10{\cdot}06 \pm 0{\cdot}03$, $b = 4{\cdot}87 \pm 0{\cdot}01$, $c = 17{\cdot}40 \pm 0{\cdot}05$ A., $\beta = 132{\cdot}6° \pm 0{\cdot}4°$. Absent spectra, (hkl) when $h + k + l$ is odd, $(h0l)$ when either h or l is odd. Space group, C_s^4 (Ia) or C_{2h}^6 $(I2/a)$ (C_{2h}^6 assumed in this analysis). Four molecules per unit cell. Molecular symmetry, two-fold axis. Volume of the unit cell, 627 A.^{3}. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$ A.), $\mu = 13{\cdot}0$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 280.

Glutaric acid is very soluble in most of the common solvents except benzene. The most satisfactory method of obtaining crystal specimens suitable for *X*-ray work proved to be that of making concentrated solutions in ethyl alcohol, and allowing the alcohol to evaporate until the syrup solidified. This method gave large, soft, and sometimes well-formed crystals which were easily cut to suitable dimensions. The crystals generally showed well-developed (001) and (100) faces, with a tendency for elongation in the direction of the *b* axis. There is pronounced cleavage on (111). Further goniometric and optical data are given by Dupré la Tour (*loc. cit.*), who also investigated the crystal structure. Lattice constants and space group were determined, but no analysis of the atomic structure was made.

Analysis of the Structure.—The space group C_s^4 which is available in the hemihedral class of the monoclinic system would only require four asymmetric molecules in the unit cell. In this analysis we assume the space group of higher symmetry, C_{2h}^6, which requires eight asymmetric units to complete the symmetry. The justification for this choice ultimately rests on the success of the analysis as a whole. On this basis (C_{2h}^6) it is necessary to assume a two-fold axis of symmetry, parallel to the *b* crystal axis, passing through the central carbon atom of the molecule. The molecular model which we assume in accordance with the chemical evidence (Fig. 3) can have this symmetry, and its possible orientation in the crystal is considerably limited (Table I). The analysis of the structure is thereby simplified. The length of the *c* axis (17·4 A.) indicates quite clearly that two molecules must lie end to end within this translation, and they will presumably be connected by hydrogen bridges across the carboxyl groups, as in the other members of the series. In the present case, however, these two molecules will be related by the glide plane *c* instead of by a pure translation as in the case of the even acids.

On the basis of these considerations it proved a matter of no great difficulty to postulate a trial structure which yielded a fair measure of agreement between the observed and the calculated structure factors. The co-ordinates were then refined by carrying out successive double Fourier syntheses giving projections of the structure along the *a* and *b* axes. The final projections are shown in Figs. 1 and 2, and from these maps most of the atomic co-ordinates can be obtained with considerable accuracy.

Fig. 1.



Projection of glutaric acid structure along the b *axis on* (010). *Contour scale : one electron per* A.^{2} *per line, one-electron line dotted.*

A synthesis giving a projection of the structure along the [101] axis was also carried out, but the resolution was not satisfactory and it is not reproduced.

Orientation, Co-ordinates, and Dimensions.—The principal molecular axis, *L*, is chosen as the straight line joining the mid-points of the two central carbon–carbon bonds in the molecule

(Fig. 3). The second molecular axis M is the two-fold symmetry axis passing through the central carbon atom, and it is necessarily parallel to the b crystal axis. It must lie at right angles to L, in the plane of the three central carbon atoms. N is perpendicular to L and M. The orientation of the molecule in the crystal is then given by the angles in Table I, the same notation being used as in the previous papers.

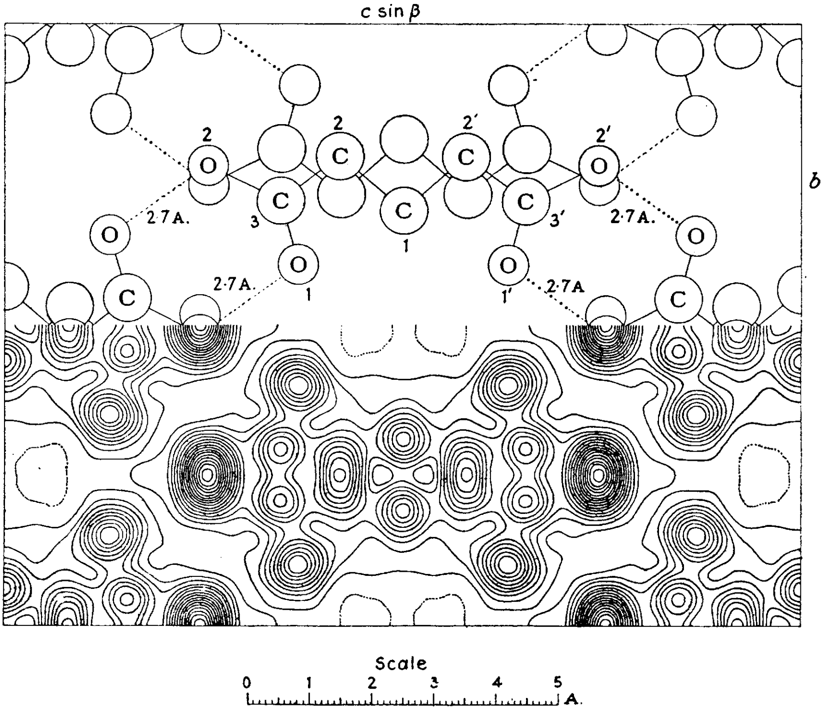
TABLE I.

Orientation of the molecule in the crystal.

$\chi_L = 57{\cdot}7°$, $\cos\chi_L = 0{\cdot}5343$	$\chi_M = 90°$, $\cos\chi_M = 0{\cdot}0000$	$\chi_N = 32{\cdot}3°$, $\cos\chi_N = 0{\cdot}8455$
$\psi_L = 90{\cdot}0°$, $\cos\psi_L = 0{\cdot}0000$	$\psi_M = 0°$, $\cos\psi_M = 1{\cdot}0000$	$\psi_N = 90{\cdot}0°$, $\cos\psi_N = 0{\cdot}0000$
$\omega_L = 32{\cdot}3°$, $\cos\omega_L = 0{\cdot}8455$	$\omega_M = 90°$, $\cos\omega_M = 0{\cdot}0000$	$\omega_N = 122{\cdot}3°$, $\cos\omega_N = -0{\cdot}5343$

The co-ordinates of the atoms with reference to the molecular axes, L, M, and N, as defined above, are given in Table III, from which the dimensions may be compared with those of the other acids in this series.

FIG. 2.



Projection of glutaric acid structure along the a *axis. Contour scale as in Fig.* 1.

The co-ordinates with respect to the crystallographic axes are given in Table II. In this space group (C_{2h}^6) it is usually most convenient to refer the origin of co-ordinates to a centre of symmetry. The centre chosen in this case lies between the molecules, at $a/4$ from the centre of a molecule (Fig. 1). In the projection shown in Fig. 1 there is an apparent centre of symmetry at the centre of the molecule, which is viewed along the two-fold axis. This is not a true centre of symmetry but it gives the structure an appearance very similar to that of adipic acid and sebacic acid (Parts V and VI). In the projection shown in Fig. 2 there is also an apparent centre of symmetry at the intersection of the glide plane and the two-fold axis, but again this is only a centre when viewed in projection. The co-ordinates in Table II are therefore referred to the true centre of symmetry as origin, and the figures consequently differ rather widely from those of the even acids, which are referred to true centres of symmetry at the centres of the molecules.

In Table III, however, the co-ordinates are referred to the intersection of the molecular axes as origin, and this point lies at ($-0{\cdot}250a$, $0{\cdot}031b$, 0) with respect to the crystallographic origin. These co-ordinates are comparable with the corresponding figures given for the other acids.

The bond lengths and valency angles deduced for the glutaric acid molecule are shown in Fig. 3, and the figures are collected in Table IV.

TABLE II.

Co-ordinates. Centre of symmetry as origin.

x, *y*, *z*, refer to the monoclinic crystal axes, and *x′*, *y*, *z′*, to the orthogonal axes *a*, *b*, and their perpendicular *c′*.

Atom (cf. Fig. 3).	*x*, A.	*y*, A.	*z*, A.	*x′*, A.	*z′*, A.	$\frac{2\pi x}{a}$.	$\frac{2\pi y}{b}$.	$\frac{2\pi z}{c}$.
C(1)	−2·515	0·593	0·000	2·515	0·000	− 90·0°	43·8°	0·0°
C(2)	−2·216	−0·288	1·138	3·181	1·053	− 79·3	−21·2	29·7
C(3)	−2·347	0·419	2·682	4·162	1·980	− 84·0	31·0	55·5
O(1)	−3·172	1·474	2·296	4·722	1·694	−113·5	109·0	47·5
O(2)	−1·447	−0·149	4·253	4·325	3·139	− 51·8	−11·0	88·0

TABLE III.

Co-ordinates referred to molecular axes L, M, *and* N.

Atom.	*L*, A.	*M*, A.	*N*, A.	Atom.	*L*, A.	*M*, A.	*N*, A.
C(1)	0·000	0·441	0·000	O(1)	2·612	1·322	0·961
C(2)	1·246	−0·441	0·000	O(2)	3·622	−0·302	−0·146
C(3)	2·554	0·267	0·335				

TABLE IV.

Molecular dimensions.

C(1)–C(2) = 1·53 ± 0·02 A.
C(2)–C(3) = 1·53 ± 0·03
C(3)–O(1) = 1·23 ,,
C(3)–O(2) = 1·30 ,,

C(2′)–C(1)–C(2) = 109°
C(1)–C(2)–C(3) = 115
C(2)–C(3)–O(1) = 123
C(2)–C(3)–O(2) = 115
O(1)–C(3)–O(2) = 122

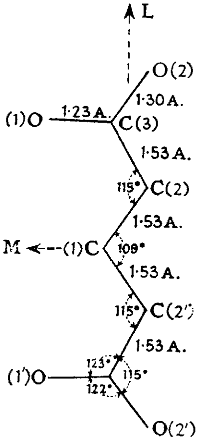
Within the experimental limits the carbon–carbon bonds lengths appear to be normal, and there is no evidence for alternating long and short bonds of the type that have been reported for all the acids of the " even " series. This observation is of considerable theoretical interest but too much weight should probably not be attached to it until it can be confirmed either by a more detailed (three-dimensional) investigation of this acid, or by similar observations on, further members of the " odd " series.

There are, however, two other ways in which the glutaric acid structure differs considerably from that of the members of the " even " series. The first concerns the geometry of the molecule in the crystal, and the second the intermolecular-approach distances.

With regard to the geometry of the molecule it is found that the planes of the carboxyl groups are inclined at about 32° to the plane of the three central carbon atoms of the chain. This compares with a corresponding deviation in sebacic acid of only about 3°, and in adipic acid of about 6°. Most of the 32° inclination in glutaric acid is due to rotation of the carboxyl group about the C(2)–C(3) bond, but the atom C(3) is also raised above the plane of the three central atoms by 0·33 A., indicating a rotation about the C(1)–C(2) bond of about 14°.

Intermolecular Distances.—The more important approach distances between the molecules are indicated by dotted lines on the right hand part of Fig. 1, and the distances which are less than 4 A. are collected in Table V. The closest approaches are again found in the pair of strong hydrogen bridges which connect adjoining carboxyl groups. The distance here, 2·69 A., is closely similar to that found in all the other aliphatic acids examined.

FIG. 3.



Dimensions of the glutaric acid molecule.

The lateral connections of the glutaric acid molecules, however, are strikingly different in one respect. There is no other distance less than 3·59 A. The unusual bond of about 3·3 A., which exists in adipic and sebacic acid between one of the carboxyl oxygen atoms and the second carbon atom in the chain of an adjoining molecule, has disappeared and is replaced by an approach of 3·59 A., which can only have significance as a relatively weak van der Waals attraction.

TABLE V.

Intermolecular distances (A.).*

O(1*A*) . . . O(2*C*)	= 2·69 ± 0·05	O(1*A*) . . . C(2*B*)	= 3·74 ± 0·05
O(2*A*) . . . O(1*C*)	= 2·69 ,,	O(2*C*) . . . C(2*B*′)	= 3·77 ,,
O(2*C*) . . . C(2*B*)	= 3·59 ,,	O(2*C*) . . . O(2*B*)	= 3·71 ,,
O(1*A*) . . . C(2′*B*)	= 3·69 ,,	O(1*A*) . . . C(1*B*)	= 3·89 ,,

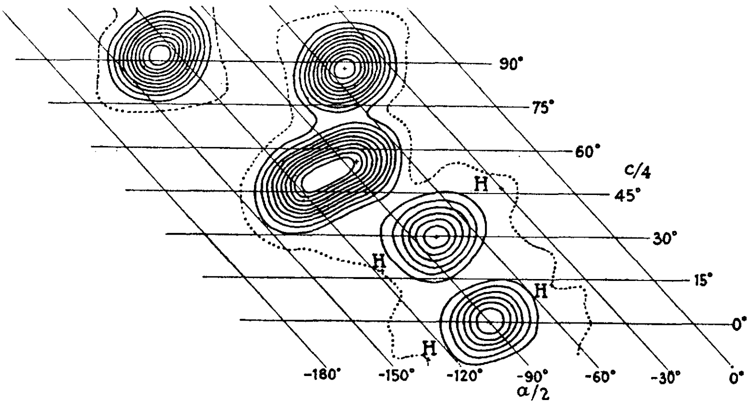
* *A* = standard molecule; *B* = reflected molecule; *C* = molecule one translation along *c* axis.

This difference in structure is no doubt responsible for some of the outstanding physical properties of the glutaric acid crystals, such as their relatively low melting point and soft texture. It is probably one of the fundamental points of difference between the acids of the odd and even series.

EXPERIMENTAL.

X-*Ray Measurements.*—Copper *K*-α radiation (λ = 1·54 A.) was used throughout the investigation. Rotation and oscillation photographs were taken for the preliminary measurements, but all the intensity records were made on a special type of moving-film camera adapted for easy manipulation of the film packs required for the multiple-film technique, and with screens capable of fine adjustment to cut down the background to a minimum (Robertson, *J. Sci. Instr.*, in the press).

FIG. 4.



Asymmetric crystal unit in the b *axis projection.*

For the ($h0l$) zone the principal crystal specimen was cut to a cross-section of 0·14 mm. × 0·25 mm. normal to the *b* axis. For the weaker reflections a larger specimen (0·28 mm. × 0·50 mm.) was employed. Relative absorption corrections were not applied. In all, a total of 80 out of a possible 86 reflections were recorded. For the ($0kl$) and ($hk\bar{h}$) zones specimens of similar size were used. All the crystals were completely immersed in the *X*-ray beam. The total range of intensities recorded was about 10,000 to 1.

The structure factors were calculated by the usual theory for mosaic-type crystals, and are given in Table VI under " F, meas." The absolute scale was obtained by correlation between the measured values and the values finally calculated from the co-ordinates.

Fourier Analysis and Calculations.—The structure was first determined by trial and then refined by successive Fourier syntheses. For the projections along the *b* axis the axial subdivisions were $a/60$ = 0·167 A. and $c/60$ = 0·290 A., and for those along the *a* axis, $b/30$ = 0·167 A. and $a \sin \beta/60$ = 0·214 A. The usual three-figure methods were employed. The positions finally assigned to the atoms, imposed on the co-ordinate network, are marked in Fig. 4.

The structure factors were recalculated from the final co-ordinates and the results are shown in Table VI. No allowance was made for the hydrogen atoms in this structure although there is some evidence of their effects in the electron-density maps, and in the discrepancies found in the calculations for some of the large spacing planes. A single composite atomic scattering curve was used, with the following *f* values:

$\sin\theta(\lambda = 1{\cdot}54)$	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
$f_{(c)}$	100	81	62	45	33	25	19	15	10	6·3

The figures differ slightly from those used for adipic and sebacic acids. It is to be expected that a slightly different average temperature factor will apply. On the basis of this curve the oxygen contributions were weighted relative to the carbon contributions in the ratio of 1·5 to 1·0. The average discrepancies finally obtained in the structure factor calculations, expressed in the usual way, were 18·5% for the ($h0l$) planes, 14·5% for the ($0kl$) planes, and 18·6% overall.

TABLE VI.

Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54 A.)	F, meas.	F, calc.
200	0·208	96·5	−115·5
400	0·416	9·5	+ 10·0
600	0·624	2·0	+ 4·5
800	0·832	5·0	+ 2·5
002	0·119	28·0	− 37·5
004	0·238	20·0	− 19·5
006	0·357	15·5	− 13·5
008	0·476	41·5	+ 39·0
0,0,10	0·595	22·0	− 20·5
0,0,12	0·714	18·0	+ 15·5
0,0,14	0·833	7·5	+ 5·5
0,0,16	0·952	3·5	+ 4·0
020	0·312	30·5	+ 32·5
040	0·624	3·0	+ 3·5
060	0·936	3·5	− 0·5
2,0,14	0·995	<0·5	− 0·0
2,0,12	0·875	9·0	− 6·5
2,0,10	0·758	3·5	− 1·0
208	0·640	20·0	− 19·5
206	0·524	11·0	+ 11·0
204	0·413	24·0	+ 24·0
202	0·304	15·0	− 15·5
20$\bar{2}$	0·155	6·5	+ 9·5
20$\bar{4}$	0·185	30·0	+ 38·0
20$\bar{6}$	0·270	42·0	− 42·0
20$\bar{8}$	0·374	10·0	− 9·0
2,0 $\overline{10}$	0·486	23·5	+ 22·5
2,0,$\overline{12}$	0·599	15·0	− 11·5
2,0,$\overline{14}$	0·717	29·0	− 28·5
2,0,$\overline{16}$	0·833	7·5	+ 4·0
2,0,$\overline{18}$	0·957	3·5	+ 2·5
4,0,10	0·935	4·5	+ 8·0
408	0·822	4·5	− 2·5
406	0·711	6·0	+ 3·0
404	0·603	19·5	− 21·0
402	0·504	24·0	+ 29·0
40$\bar{2}$	0·346	25·0	+ 30·0
40$\bar{4}$	0·309	29·0	− 29·0
40$\bar{6}$	0·317	71·5	+ 70·5
40$\bar{8}$	0·368	45·5	− 38·0
4,0,$\overline{10}$	0·444	10·0	− 8·5
4,0,$\overline{12}$	0·537	14·5	+ 8·0
4,0,$\overline{14}$	0·639	49·0	+ 44·5
4,0,$\overline{16}$	0·744	21·5	− 16·5
4,0,$\overline{18}$	0·861	1·5	+ 0·5
4,0,$\overline{20}$	0·974	1·5	+ 0·5
606	0·909	4·0	− 3·0
604	0·807	2·5	+ 3·5
602	0·712	5·0	− 8·0
60$\bar{2}$	0·548	21·0	− 21·5
60$\bar{4}$	0·493	<1·5	− 8·5
60$\bar{6}$	0·462	24·5	− 24·5
60$\bar{8}$	0·463	28·0	+ 25·5
6,0,$\overline{10}$	0·493	12·0	+ 7·5
6,0,$\overline{12}$	0·551	25·0	− 20·5
6,0,$\overline{14}$	0·623	26·5	− 28·0
6,0,$\overline{16}$	0·707	11·5	+ 8·5
6,0,$\overline{18}$	0·808	<2·0	0·0
6,0,$\overline{20}$	0·910	10·5	− 6·0
802	0·918	4·5	− 6·5
80$\bar{2}$	0·755	7·5	+ 9·0
80$\bar{4}$	0·690	11·0	+ 22·0
80$\bar{6}$	0·643	8·0	− 10·5
80$\bar{8}$	0·615	6·5	+ 4·0
8,0,$\overline{10}$	0·612	14·0	− 14·5
8,0,$\overline{12}$	0·633	22·0	+ 23·0
8,0,$\overline{14}$	0·672	2·0	− 1·0
8,0,$\overline{16}$	0·729	13·0	+ 10·5
8,0,$\overline{18}$	0·804	2·5	− 1·5
8,0,$\overline{20}$	0·888	15·0	+ 9·5
8,0,$\overline{22}$	0·981	13·0	− 5·0
10,0,$\bar{2}$	0·959	3·0	− 4·0
10,0,$\bar{4}$	0·891	1·5	− 8·0
10,0,$\bar{6}$	0·835	5·5	+ 9·0
10,0,$\bar{8}$	0·793	7·0	− 9·5
10,0,$\overline{10}$	0·769	5·5	+ 4·0
10,0,$\overline{12}$	0·763	3·0	− 3·5
10,0,$\overline{14}$	0·775	2·0	+ 2·0
10,0,$\overline{16}$	0·805	12·5	− 12·5
10,0,$\overline{18}$	0·854	1·5	− 3·5
10,0,$\overline{20}$	0·915	5·0	− 2·5
10,0,$\overline{22}$	0·988	<1·0	+ 3·0
12,0,$\bar{8}$	0·982	1·0	+ 2·0
12,0,$\overline{10}$	0·945	<1·0	+ 2·5
12,0,$\overline{12}$	0·922	6·0	− 7·5
12,0,$\overline{14}$	0·914	6·0	+ 5·0
12,0,$\overline{16}$	0·922	5·0	+ 5·0
12,0,$\overline{18}$	0·946	3·5	+ 4·5
12,0,$\overline{20}$	0·985	<1·0	+ 5·0
011	0·168	50·0	+47·5
013	0·239	5·0	− 6·0
015	0·336	3·5	+ 3·0
017	0·445	10·5	− 6·5
019	0·558	4·5	− 1·0
0,1,11	0·671	5·0	+ 6·0
0,1,13	0·789	15·0	+15·0
0,1,15	0·904	4·5	− 3·0
022	0·335	30·5	−22·0
024	0·394	34·5	+33·0
026	0·475	27·0	−25·0
028	0·569	<3·5	− 1·0
0,2,10	0·672	7·5	− 7·5
0,2,12	0·779	17·5	+18·5
0,2,14	0·890	3·0	− 4·5
031	0·473	11·0	+ 9·5
033	0·502	17·5	−17·0
035	0·555	13·0	−11·5
037	0·626	<4·0	+ 1·5
039	0·711	<4·0	+ 3·5
0,3,11	0·804	6·0	− 9·0
0,3,13	0·903	<3·0	− 1·5
042	0·636	7·5	−13·0
044	0·668	<4·0	+ 4·5
046	0·718	13·5	−12·5
048	0·785	<3·5	+ 5·0
0,4,10	0·863	<3·0	− 4·5
0,4,12	0·948	<2·5	− 1·0
051	0·781	11·5	−13·5
053	0·799	8·0	+ 8·5
055	0·834	<3·5	+ 4·0
057	0·883	7·5	− 8·0
059	0·945	<2·5	− 0·0
062	0·943	<2·5	− 1·5
064	0·965	<2·0	+ 2·0

TABLE VI—*continued.*

hkl.	sin θ (λ = 1·54 A.).	F, meas.	F, calc.	*hkl.*	sin θ (λ = 1·54 A.).	F, meas.	F, calc.
$12\bar{1}$	0·323	12·0	− 5·0	$24\bar{2}$	0·641	5·5	+ 6·5
$22\bar{2}$	0·348	22·0	−24·5	$34\bar{3}$	0·664	10·0	+12·5
$32\bar{3}$	0·389	19·5	−12·0	$44\bar{4}$	0·695	2·5	− 7·0
$42\bar{4}$	0·439	27·5	−27·5	$54\bar{5}$	0·733	9·0	+11·0
$52\bar{5}$	0·496	8·0	− 7·5	$64\bar{6}$	0·776	5·0	+ 1·0
$62\bar{6}$	0·560	2·5	− 1·0	$74\bar{7}$	0·824	2·0	+ 3·0
$72\bar{7}$	0·623	16·5	−18·0	$84\bar{8}$	0·876	2·5	− 2·0
$82\bar{8}$	0·691	9·5	+14·5	$94\bar{9}$	0·931	4·5	+ 3·5
$92\bar{9}$	0·759	8·0	+ 7·5	$10,4,\bar{1}\bar{0}$	0·990	<1·0	+ 1·0
$10,2,\bar{1}\bar{0}$	0·831	10·0	+15·0				
$11,2,\bar{1}\bar{1}$	0·902	<1·5	− 1·0	$16\bar{1}$	0·940	9·0	− 6·5
$12,2,\bar{1}\bar{2}$	0·974	<1·0	− 2·5	$26\bar{2}$	0·950	2·0	+ 2·5
				$36\bar{3}$	0·966	<1·0	− 2·5
$14\bar{1}$	0·628	5·0	− 5·0	$46\bar{4}$	0·987	<1·0	+ 0·5

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