210. *The Crystal and Molecular Structure of Certain Dicarboxylic Acids. Part V. Adipic Acid.*

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The crystal structure of adipic acid has been further refined by means of two projections and the use of very complete Fourier series. The measurements indicate an alternation of long and slightly shorter bonds over the entire length of the six-membered carbon chain, although these variations are barely greater than the possible experimental error. The arrangement of the molecules in the crystal is discussed and it is shown that, in addition to the end-to-end hydrogen bonding between the carboxyl groups of adjoining molecules, there is an unusually close lateral approach (3·3 A.) between an oxygen atom of one molecule and the second carbon atom in the chain of another molecule.

A QUANTITATIVE determination of the crystal structure of adipic acid has recently been carried out by MacGillavry (*Rec. Trav. chim.*, 1941, **60**, 605) with results which show interesting contractions in the carbon–carbon bond lengths in the saturated chain, the mean value being about 1·51 A. as compared with the accepted normal value of 1·54 A. In the present paper we have attempted a further refinement of this structure based on the use of more complete Fourier series. Our results are in excellent general agreement with those of MacGillavry, but we obtain a different distribution of bond length variations in the chain. We believe the pattern of variations now obtained is significant, and it will be further discussed in a later paper in connection with a theory of the alternating effects in homologous series of aliphatic compounds.

Crystal Data.—Adipic acid, $C_6H_{10}O_4$; *M*, 146·1; m. p. 153°; *d*, calc. 1·359, found 1·345. Monoclinic prismatic, $a = 10·07 \pm 0·03$, $b = 5·16 \pm 0·01$, $c = 10·03 \pm 0·03$ A., $\beta = 137·1° \pm 0·2°$. Absent spectra, (*h*0*l*) when *h* is odd, (0*k*0) when *k* is odd. Space group $C_{2h}^5(P2_1/a)$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell, 355 A.^{3}. Absorption coefficient for *X*-rays ($\lambda = 1·54$ A.) $\mu = 12·0$ cm.$^{-1}$. Total number of electrons per unit cell = F(000) = 156.

Well-formed crystals were obtained by slow evaporation of solutions in ethyl acetate. The crystals were frequently elongated in the direction of the *b* axis, the (001) and (100) faces being generally well developed; (110) and (011) also appear. There is pronounced cleavage on (010).

Further crystal data are given by Groth ("Chemische Krystallographie", 1919, **3**, 465), and Caspari (*J.*, 1928, 3235) has determined the lattice constants and space group in agreement with our data.

Analysis of the Structure.—The cell dimensions in adipic acid are considerably different from those of succinic acid (Part IV, preceding paper). In both cases the molecules are arranged end-to-end along the direction of the *c* axis, but the lateral arrangement of the chains is different in the two structures.

The adipic acid structure has been determined in detail by MacGillavry (*loc. cit.*) and it is not necessary to describe it again here. We are concerned with a further refinement of the parameters determined by MacGillavry. This was carried out by several successive Fourier syntheses giving projections of the structure along the *b* axis and along the [101] axis. In the final *b* axis projection 80 out of a possible 91 reflections (to the limit of copper radiation) were included, and in the [101] axis projection 58 out of a possible 63 reflections. These figures compare with totals of 58 and 35 terms in the corresponding series employed by MacGillavry.

Our final electron-density maps are shown in Figs. 1 and 2, from which it is clear that good resolution of most of the atoms is obtained. In the *b* axis projection (Fig. 1) one of the carboxyl oxygen atoms and one of the carbon atoms are obscured, and their positions cannot be determined with quite the same certainty as the others. Bulges on the one-electron line (dotted) near the central pair of carbon atoms in Fig. 1 appear to indicate the presence of hydrogen atoms, but this matter has not been further investigated in the present structure.

Orientation, Co-ordinates, and Dimensions.—The molecular axes are chosen as for succinic acid (Part IV), *L* passing through the mid points of the three central carbon–carbon bonds, and *M* lying in the plane of the four central carbon atoms (Fig. 3); *N* is perpendicular to *L* and *M*. The angles which these axes make with the *a* and *b* crystal axes and their perpendicular (*c*′) are given in Table I.

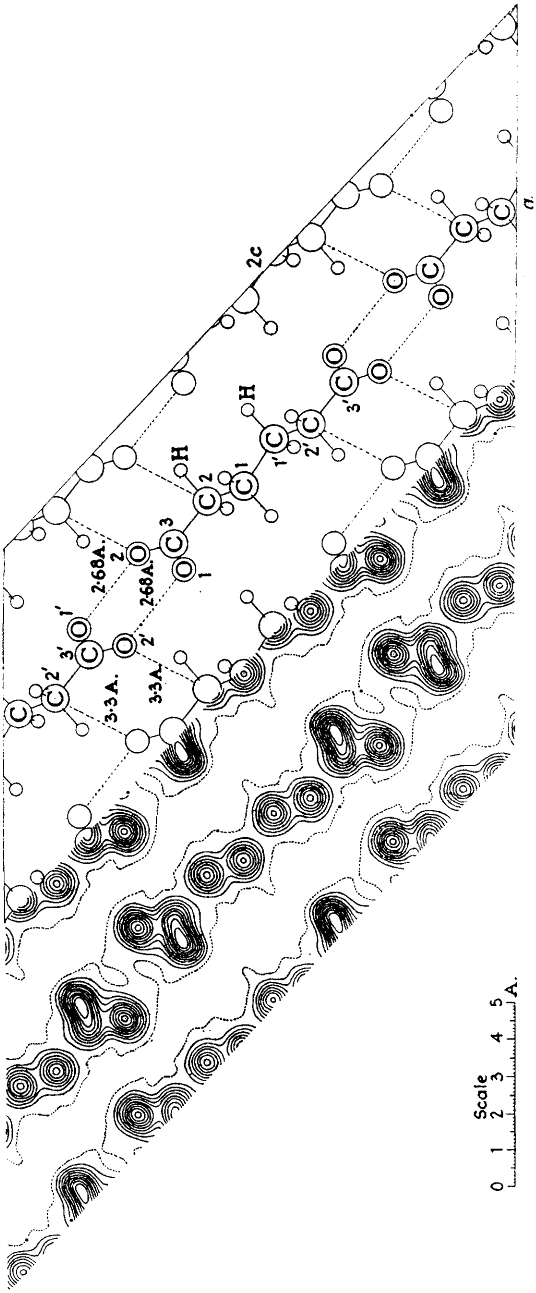
TABLE I.

Orientation of the molecule in the crystal.

$\chi_L = 48·5°$, $\cos\chi_L = 0·6633$	$\chi_M = 61·0°$, $\cos\chi_M = 0·4854$	$\chi_N = 55·3°$, $\cos\chi_N = 0·5699$
$\psi_L = 104·6°$, $\cos\psi_L = -0·2517$	$\psi_M = 30·5°$, $\cos\psi_M = 0·8616$	$\psi_N = 116·2°$, $\cos\psi_N = -0·4411$
$\omega_L = 45·2°$, $\cos\omega_L = 0·7047$	$\omega_M = 98·6°$, $\cos\omega_M = -0·1489$	$\omega_N = 133·9°$, $\cos\omega_N = -0·6936$

The estimated co-ordinates of the atoms in the asymmetric crystal unit (half the molecule) are listed in Table II, referred to the crystal axes. The co-ordinates referred to the molecular axes, *L, M,* and *N*, as defined above, are given in Table III.

FIG. 1.



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

The bond lengths and valency angles deduced from the co-ordinates are shown in Fig. 3. The figures are collected and compared with previous work in Table IV. The agreement on the whole is good, the greatest divergence being in the carboxyl group where the distances are in any case extremely difficult to determine with precision.

Our measurements indicate a distinct alternation of long and slightly shorter bonds over the

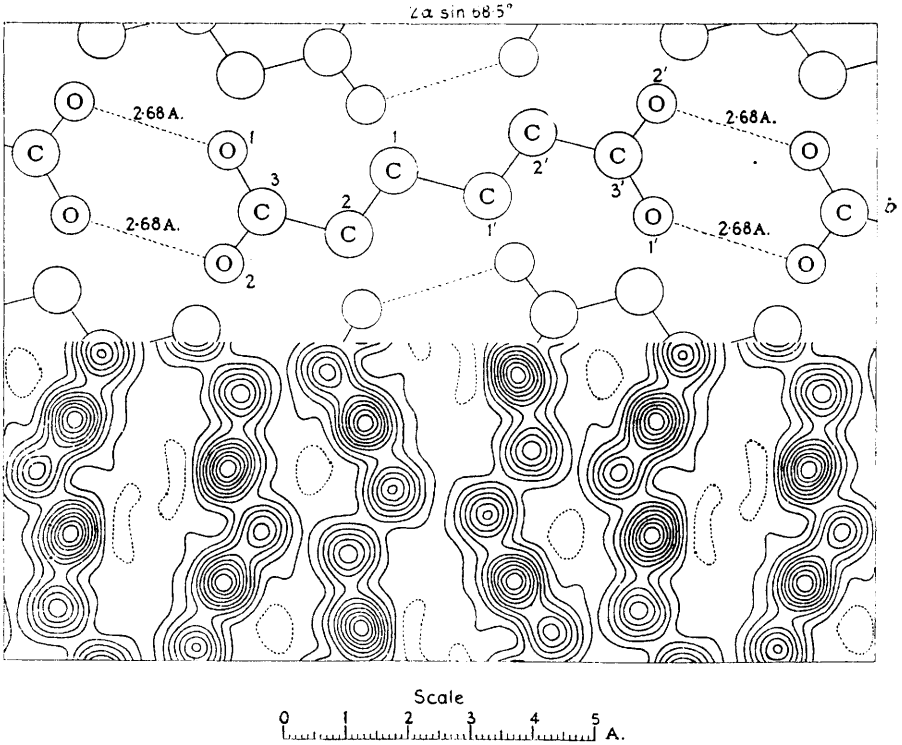
TABLE II.

Co-ordinates. Centre of symmetry as origin.

x, y, z refer to monoclinic crystal axes; x', y, z' refer to orthogonal axes a, b, and 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)	−0·215	0·206	0·573	0·634	0·390	− 7·7°	14·3°	21·5°
C(2)	0·453	−0·838	2·027	1·032	1·380	16·0	−58·5	72·6
C(3)	0·269	−0·448	3·355	2·188	2·284	9·6	−31·5	120·0
O(1)	−0·715	0·540	2·945	2·872	2·006	−25·7	37·5	105·5
O(2)	1·025	−1·296	4·730	2·438	3·220	36·7	−90·5	170·0

FIG. 2.



Projection of adipic acid structure along [101] *axis. Contour scale as in Fig.* 1.

TABLE III.

Co-ordinates referred to molecular axes L, M, *and* N. (*Origin at centre of symmetry.*)

Atom.	L, A.	M, A.	N, A.
C(1)	0·644	0·427	0·000
C(2)	1·868	−0·427	0·000
C(3)	3·175	0·336	−0·138
O(1)	3·183	1·561	0·008
O(2)	4·213	−0·414	−0·272

TABLE IV.

Molecular dimensions.

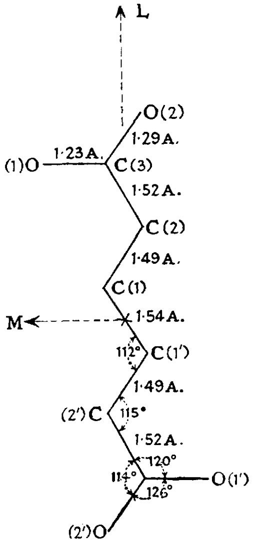
Present work.	Previous work.*	Present work.	Previous work.*
C(1′)–C(1) = 1·54 ± 0·02 A.	1·51 A.	C(1′)–C(1)–C(2) = 112°	112°
C(1)–C(2) = 1·49 ,,	1·52	C(1)–C(2)–C(3) = 115	114
C(2)–C(3) = 1·52 ± 0·03	1·49	C(2)–C(3)–O(1) = 120	122
C(3)–O(1) = 1·23 ± 0·04	1·28	C(2)–C(3)–O(2) = 114	114
C(3)–O(2) = 1·29 ,,	1·38	O(1)–C(3)–O(2) = 126	124

* MacGillavry (*loc. cit.*).

entire length of the six-carbon saturated chain. The variations are not much greater than the possible experimental error, but they are confirmed to some extent by our other measurements in this series.

With regard to the geometry of the molecule, the four central carbon atoms are necessarily coplanar with the centre of symmetry. The terminal carbon atom, however, with the oxygens of the carboxyl group, lie on another plane which is tilted by about 6° to the plane of the carbon chain. This plane through the carboxyl group includes the centre of symmetry between adjacent molecules along the *c* axis and passes through the carboxyl group of the next molecule.

FIG. 3.



Dimensions of the adipic acid molecule.

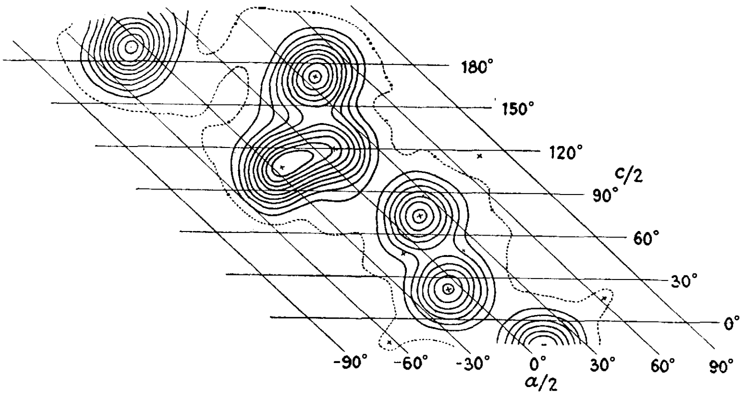
Intermolecular Distances.—The significant intermolecular approach distances are marked by dotted lines in the drawings which accompany the contour maps in Figs. 1 and 2. These and other distances less than 4 A. are collected in Table V.

The most important linkages are the hydrogen bridges of length about 2·68 A. which connect the carboxyl groups of adjoining molecules in the *c* axis direction. These appear to be slightly longer than the corresponding bridges in succinic acid (2·64 A.) and very distinctly longer than some of the bridges in oxalic acid dihydrate (Part I, Dunitz and Robertson, *J.*, 1947, 142). Another interesting approach is that between the carboxyl oxygen O(2) and the carbon atom C(2) of the reflected molecule one translation further along the *c* axis. The order of this approach distance would appear to indicate some very weak and unusual type of hydrogen bridge involving a carbon atom. All the other approach distances are greater than 3·6 A. and would not therefore seem to have any special significance.

EXPERIMENTAL.

X-Ray Measurements.—All the *X*-ray work was carried out with copper *K*-α radiation (λ = 1·54 A.) and photographic methods. The cell dimensions, space group, etc., were checked by rotation and oscillation photographs, while moving-film methods were employed exclusively for the intensity work. The principal crystal specimen used for the (*h*0*l*) zone had cross-section normal to the *b* axis 0·77 mm × 0·43 mm. Approximate absorption corrections were applied, but were found to make little

FIG. 4.



Asymmetric crystal unit, showing positions assigned to atoms.

TABLE V.

Intermolecular distances (A.).*

O(1*A*) . . . O(2*C*)	= 2·68 ± 0·05		O(2*C*) . . . O(2*B*)	= 3·66 ± 0·05	
O(2*B*) . . . C(2*C*)	= 3·29	,,	C(1*B*) . . . O(1*A*)	= 3·72	,,
O(2*A*) . . . O(2*C*)	= 3·60	,,	C(2*B*) . . . O(2*C*)	= 3·94	,,
C(1'*B*) . . . O(1*A*)	= 3·62	,,	C(2*B*) . . . O(1*A*)	= 3·98	,,

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

TABLE VI.

Measured and calculated values of the structure factor.

hkl.	$\sin\theta$ (λ = 1·54).	F, meas.	F, calc.
200	0·212	67·5	+62·0
400	0·423	6·0	+ 5·0
600	0·634	1·5	− 4·5
800	0·845	<1·0	+ 1·5
001	0·113	20·0	−22·0
002	0·225	7·0	− 7·0
003	0·337	6·5	+ 5·5
004	0·449	17·0	+16·0
005	0·562	13·0	−13·0
006	0·674	6·0	+ 5·5
007	0·787	4·0	− 3·0
008	0·899	4·5	− 3·5
207	0·965	2·0	− 2·5
206	0·855	1·0	+ 1·0
205	0·743	2·5	− 4·0
204	0·633	11·5	+13·5
203	0·525	3·0	+ 1·0
202	0·418	11·0	− 8·0
201	0·317	3·0	+ 2·0
$20\bar{1}$	0·160	2·0	− 3·0
$20\bar{2}$	0·164	12·5	−15·0
$20\bar{3}$	0·233	25·5	+28·5
$20\bar{4}$	0·329	21·0	−19·0
$20\bar{5}$	0·434	6·0	− 7·0
$20\bar{6}$	0·539	8·0	+ 7·0
$20\bar{7}$	0·646	<1·5	+ 0·5
$20\bar{8}$	0·756	15·5	−14·5
$20\bar{9}$	0·868	2·5	+ 2·5
$2,0,\overline{10}$	0·980	<0·5	+ 0·5
405	0·944	1·0	+ 1·5
404	0·838	2·5	+ 2·5
403	0·735	6·0	+ 4·0
402	0·631	3·5	− 5·0
401	0·538	11·0	+12·0
$40\bar{1}$	0·371	19·5	+19·5
$40\bar{2}$	0·320	9·0	−11·0
$40\bar{3}$	0·303	25·0	+26·5
$40\bar{4}$	0·329	47·0	−46·0
$40\bar{5}$	0·390	3·5	+ 3·5
$40\bar{6}$	0·468	7·0	+ 7·0
$40\bar{7}$	0·556	3·5	− 2·0
$40\bar{8}$	0·655	22·5	−19·5
$40\bar{9}$	0·758	4·0	+ 4·0
$4,0,\overline{10}$	0·864	<1·0	− 0·0
$4,0,\overline{11}$	0·975	2·0	− 1·0
603	0·948	2·5	+ 1·5
602	0·848	2·5	+ 0·5
601	0·756	<1·5	+ 3·5
$60\bar{1}$	0·590	11·5	+12·5
$60\bar{2}$	0·525	2·0	+ 3·0
$60\bar{3}$	0·478	1·5	− 2·0
$60\bar{4}$	0·458	21·0	−22·5
$60\bar{5}$	0·463	5·5	− 6·0
$60\bar{6}$	0·495	8·5	+ 9·5
$60\bar{7}$	0·548	12·5	−11·5
$60\bar{8}$	0·616	7·0	− 7·5
$60\bar{9}$	0·695	3·5	− 2·0
$6,0,\overline{10}$	0·790	<1·0	+ 1·0
$6,0,\overline{11}$	0·883	3·5	− 3·0
$6,0,\overline{12}$	0·975	4·5	+ 4·0
801	0·979	1·5	− 1·5
$80\bar{1}$	0·813	3·0	+ 3·5
$80\bar{2}$	0·740	1·5	+ 4·5
$80\bar{3}$	0·683	6·0	−10·0
$80\bar{4}$	0·639	<1·5	+ 0·5
$80\bar{5}$	0·611	11·0	−11·5
$80\bar{6}$	0·608	2·5	+ 3·0
$80\bar{7}$	0·621	7·0	− 8·0
$80\bar{8}$	0·656	4·5	+ 4·0
$80\bar{9}$	0·710	8·5	− 7·0
$8,0,\overline{10}$	0·790	<1·0	+ 0·0
$8,0,\overline{11}$	0·850	1·5	− 1·0
$8,0,\overline{12}$	0·935	7·0	+ 4·0
$10,0,\bar{2}$	0·960	1·0	+ 0·5
$10,0,\bar{3}$	0·894	1·5	− 4·0
$10,0,\bar{4}$	0·836	<1·0	+ 2·5
$10,0,\bar{5}$	0·796	8·0	− 6·5
$10,0,\bar{6}$	0·770	4·0	− 4·0
$10,0,\bar{7}$	0·758	4·0	+ 2·0
$10,0,\bar{8}$	0·763	1·0	+ 2·0
$10,0,\bar{9}$	0·784	5·0	− 4·0
$10,0,\overline{10}$	0·821	2·5	− 2·0
$10,0,\overline{11}$	0·870	4·5	+ 3·0
10,0,12	0·935	3·0	+ 1·0
$12,0,\bar{6}$	0·960	2·5	− 4·0
$12,0,\bar{7}$	0·930	3·5	+ 3·5
$12,0,\bar{8}$	0·915	1·5	− 1·0
$12,0,\bar{9}$	0·914	1·0	− 0·5
$12,0,\overline{10}$	0·925	<1·0	− 1·0
$12,0,\overline{11}$	0·960	2·5	+ 2·5
$12,0,\overline{12}$	0·988	<0·5	− 1·0
020	0·299	5·5	− 3·5
040	0·597	2·0	− 2·5
060	0·896	1·5	− 3·0
$11\bar{1}$	0·171	3·0	+ 1·0
$12\bar{1}$	0·310	3·5	+ 3·5
$13\bar{1}$	0·457	4·0	+ 4·5
$14\bar{1}$	0·606	4·0	− 4·0
$15\bar{1}$	0·753	4·5	+ 4·5
$16\bar{1}$	0·903	1·0	− 0·0
$21\bar{2}$	0·223	5·5	− 5·0
$22\bar{2}$	0·342	4·5	+ 4·0
$23\bar{2}$	0·480	12·5	+14·0
$24\bar{2}$	0·620	5·0	+ 8·0
$25\bar{2}$	0·766	7·5	− 9·0
$26\bar{2}$	0·913	0·5	+ 1·0
$31\bar{3}$	0·290	16·5	+16·5
$32\bar{3}$	0·388	14·5	−16·0
$33\bar{3}$	0·513	2·0	+ 3·0
$34\bar{3}$	0·647	7·0	− 7·0
$35\bar{3}$	0·788	5·0	− 5·5
$36\bar{3}$	0·933	1·5	− 0·5
$41\bar{4}$	0·363	7·5	+ 4·5
$42\bar{4}$	0·446	9·0	+10·0
$43\bar{4}$	0·557	3·0	− 1·5
$44\bar{4}$	0·683	0·5	− 0·5
$45\bar{4}$	0·816	1·0	+ 0·5
$46\bar{4}$	0·958	<0·5	+ 1·5

TABLE VI.—*continued.*

hkl.	sin θ (λ = 1·54).	F, meas.	F, calc.
$51\bar{5}$	0·439	9·0	− 7·0
$52\bar{5}$	0·504	1·5	− 0·0
$53\bar{5}$	0·609	3·0	− 4·5
$54\bar{5}$	0·726	2·5	+ 2·5
$55\bar{5}$	0·853	<0·5	+ 0·0
$56\bar{5}$	0·988	<0·5	− 1·0
$61\bar{6}$	0·516	1·5	− 1·0
$62\bar{6}$	0·578	7·0	− 6·5
$63\bar{6}$	0·667	14·0	−14·0
$64\bar{6}$	0·778	5·5	− 4·0
$65\bar{6}$	0·895	1·0	+ 2·0
$71\bar{7}$	0·596	6·0	− 5·5
$72\bar{7}$	0·650	8·0	+ 7·5
$73\bar{7}$	0·731	3·0	− 3·0
$74\bar{7}$	0·831	1·5	+ 1·5
$75\bar{7}$	0·944	<0·5	+ 1·0
$81\bar{8}$	0·675	5·5	+ 5·0
$82\bar{8}$	0·724	5·5	− 6·0
$83\bar{8}$	0·797	4·0	+ 4·5
$84\bar{8}$	0·890	1·0	+ 1·0
$85\bar{8}$	0·995	<1·0	− 0·5
$91\bar{9}$	0·759	3·0	− 2·0
$92\bar{9}$	0·800	3·0	− 3·0
$93\bar{9}$	0·867	0·5	+ 1·5
$94\bar{9}$	0·955	1·5	− 1·0
$10,1,\overline{10}$	0·839	1·0	− 1·5
$10,2,\overline{10}$	0·879	3·5	+ 2·0
$10,3,\overline{10}$	0·940	5·5	+ 3·5
$11,1,\overline{11}$	0·919	1·5	+ 1·5
$11,2,\overline{11}$	0·955	<0·5	+ 0·0
110	0·184	60·5	+54·5
120	0·317	19·5	+13·5
130	0·461	7·5	+ 7·0
140	0·606	2·0	+ 2·0
150	0·754	4·0	− 4·5
160	0·902	<2·0	− 0·5

hkl.	sin θ (λ = 1·54 A.)	F, meas.	F, calc.
210	0·259	42·5	+39·5
220	0·366	6·0	+ 7·5
230	0·496	4·0	+ 1·5
240	0·634	5·0	− 4·5
250	0·775	2·5	+ 3·0
260	0·921	<1·5	− 1·5
310	0·350	19·5	+25·5
320	0·434	22·5	+24·5
330	0·549	<2·0	− 1·5
340	0·676	4·0	+ 3·5
350	0·810	3·0	− 1·5
360	0·950	<1·5	− 1·0
410	0·447	20·0	+25·5
420	0·516	9·0	+14·5
430	0·615	7·5	+ 6·5
440	0·731	4·5	− 3·5
450	0·857	<2·0	+ 1·0
460	0·991	<1·0	+ 1·0
510	0·548	4·5	+ 4·5
520	0·606	9·5	+14·0
530	0·692	<2·5	+ 2·0
540	0·796	2·0	+ 3·0
550	0·914	<1·5	+ 1·0
610	0·650	4·5	+ 3·5
620	0·699	4·5	+ 5·5
630	0·777	5·5	+ 7·0
640	0·870	<2·0	+ 0·0
650	0·978	<1·0	− 1·0
710	0·753	<2·5	− 1·0
720	0·796	5·0	+ 4·5
730	0·864	<2·0	+ 0·5
740	0·949	<1·5	+ 0·5
810	0·857	<2·0	− 0·5
820	0·896	<2·0	− 0·0
830	0·955	<1·5	+ 2·5
910	0·960	<1·0	− 0·5
920	0·995	<1·0	+ 0·5

difference save for one or two planes. For the strongest reflections a small crystal, cross-section 0·11 mm. × 0·16 mm., was used. For the (*hk*$\bar{h}$) zone a specimen of cross-section 0·47 mm. × 0·55 mm. was used, and for the (*hk*0) zone, one of 0·41 mm. × 0·58 mm. The multiple-film technique was used to correlate visual estimates of intensities over a total range of about 12,000 to 1, and the sets of intensities for the different zones were correlated by means of their common axial reflections. The structure factors were derived by the usual formulæ for mosaic-type crystals and the results are listed in Table VI. The absolute scale was derived by correlation with the F values calculated from the final co-ordinates.

Fourier Analysis.—In the projection along the *b* axis the electron density was computed at 900 points on the asymmetric unit, the axial subdivisions being $a/60$ = 0·168 A. and $c/60$ = 0·167 A. The usual three figure methods were employed. The positions finally assigned to the atoms in the asymmetric unit are shown in Fig. 4, which is superimposed on the co-ordinate net-work.

For the [101] axis projection the axial sub-divisions were $b/30$ = 0·172 A., and a cos 21·5°/60 = 0·156 A.

From the final co-ordinates the structure factors were recalculated, making use of the composite scattering curve given in Part IV. This curve was originally derived from the adipic acid work, and is not really very suitable for succinic acid. As before, the oxygen contributions were weighted relatively to the carbon contributions in the ratio of 1·5 to 1·0. The results are shown in Table VI. The mean discrepancies between the calculated and observed structure factors, expressed in the usual manner (see Part IV), are 15·5% for the (*h*0*l*) zone, and 16·7% for the *hk*$\bar{h}$) zone.

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[*Received, September 27th,* 1948.]