THE CRYSTAL AND MOLECULAR STRUCTURE OF THE NORMAL ALIPHATIC DICARBOXYLIC ACIDS

Thesis

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Doctor of Philosophy

in the
University of Glasgow

by
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Preface.

All of the work which is described in this thesis is being prepared as a series of papers, which are to be published in conjunction with Professor J. Monteath Robertson, F.R.S.

I wish to offer my sincere thanks to Professor Robertson for suggesting the problem for research, and for his constant assistance and encouragement throughout the work. My thanks are also due to Doctor G. Badger for his helpful criticism of aspects of the work relating to organic chemistry; and to Messrs. I.C.I. Ltd. for a scholarship held during part of the time.

J.D.M.

Glasgow,
September, 1948.

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Summary.

The crystal structures of succinic, adipic, sebacic and glutaric acids have been investigated fully by the two-dimensional X ray method.

Unusual variations in certain of the molecular dimensions have been observed, which may be considered to have significance, and a possible qualitative explanation for these variations is given in terms of resonance theory.

An attempt is also made to correlate the chemical and physical properties of these acids with their crystal and molecular structure.

The necessity for including the hydrogen atoms of a compound in the calculations of structure factors is demonstrated.

Introduction.

At various times since the advent of X ray structure analysis, a considerable amount of interest has been focussed on the structures of the normal aliphatic dicarboxylic acids. This series ,.indeed, presents an admirable subject for study by the X ray method, all the lower members of it at least producing very good, well formed crystals, much more satisfactory for examination than the crystals of the corresponding monocarboxylic acids.

A most unusual and puzzling feature of homologous series of normal aliphatic compounds in general, such as, for example, the mono- and di-carboxylic acids, the hydrocarbons, alcohols, ketones, diamines, etc, is the fact that the members of each series show a most interesting variation in physical properties, depending on whether they have an even or an odd number of carbon atoms in the molecule. This alternating effect on going up the series is shown to a greater or less extent by all of these compounds, but in none to the same degree as in the normal aliphatic dibasic acids.

By the late nineteen-twenties, the unit cells and space groups of most of the common members of the series had been determined, and from then on the structures of three of the acids, oxalic, succinic, and adipic, have been worked out by the Fourier method, and the bond lengths calculated.

A very great amount of physical and chemical data has been collected for this series, and numerous theories have been proposed at one time and another to account for the variation in properties of the even and odd members, but, for want of detailed knowledge of the structures, they have all remained speculatory.

At the present day, the broad outlines of X ray structure determination theory have become well established. Some of the limitations of the method have been realised, and many of the previously determined structures, which were carried out with incomplete data, would merit re-examination in the light of this knowledge. It appears probable that future advances in the subject will be made by the study of the variations of very precisely measured bond dimensions and angles, in relatively simple molecules, and the interpretation and correlation of these in terms of chemical theory.

From the point of view of X ray structure analysis, therefore, the study of a group of closely related compounds, such as the normal aliphatic dicarboxylic acids, simultaneously, has much to commend it.

Firstly, it should be possible to obtain a number of independent measurements of the bond lengths in aliphatic chains, and also, to shed some further light on the symmetry or disymmetry of the carbon - oxygen linkages in the carboxyl group.

Secondly, by the examination of the intermolecular distances in the crystals, it might be possible to find some systematic variation which would coincide with the known variations in properties.

A further impetus has been provided to the work on these acids by the industrial uses of some of them in the constitution of synthetic polyamide fibres. These fibres consist usually of adipic or sebacic acids combined with hexamethylene diamine in long chain polymers, the basic 'repeat unit' of which is an acid and amine residue linked end to end. The high mechanical strength of these fibres has led to their study in industry, and in this connection, an accurate knowledge of the structures of these acids might be of advantage.

Accordingly, the present work has been undertaken, and, to a certain extent, the objects set out with have been attained.

β-Succinic Acid.

Crystal Data. - β-succinic acid $C_4H_6O_4$. M.-116.0 m.pt.-185°C. D calc = 1.533 D found = 1.550 monoclinic prismatic.

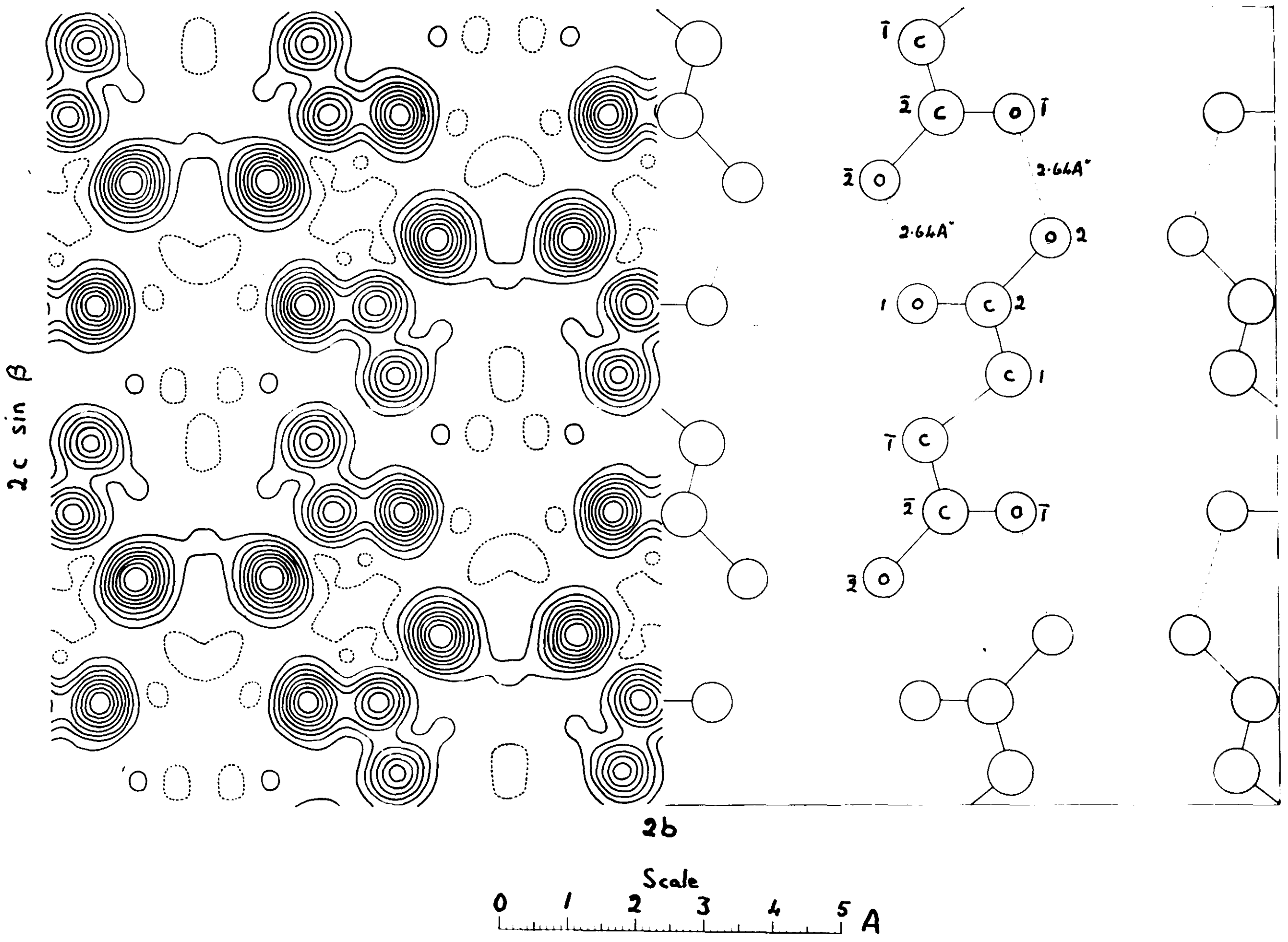
$a = 5.10 \pm 0.01$ Å; $b = 8.88 \pm 0.03$ Å; $c = 7.61 \pm 0.02$ A

$\beta = 133.6 \pm 0.3^\circ$

Absent spectra, h01 when h is odd, 0k0 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=250 $Å^3$ Absorption coefficient for X rays, (λ=1.54 A), μ=14.5 cms^{-1}. Total number of electrons per unit cell - F(000) - 124.

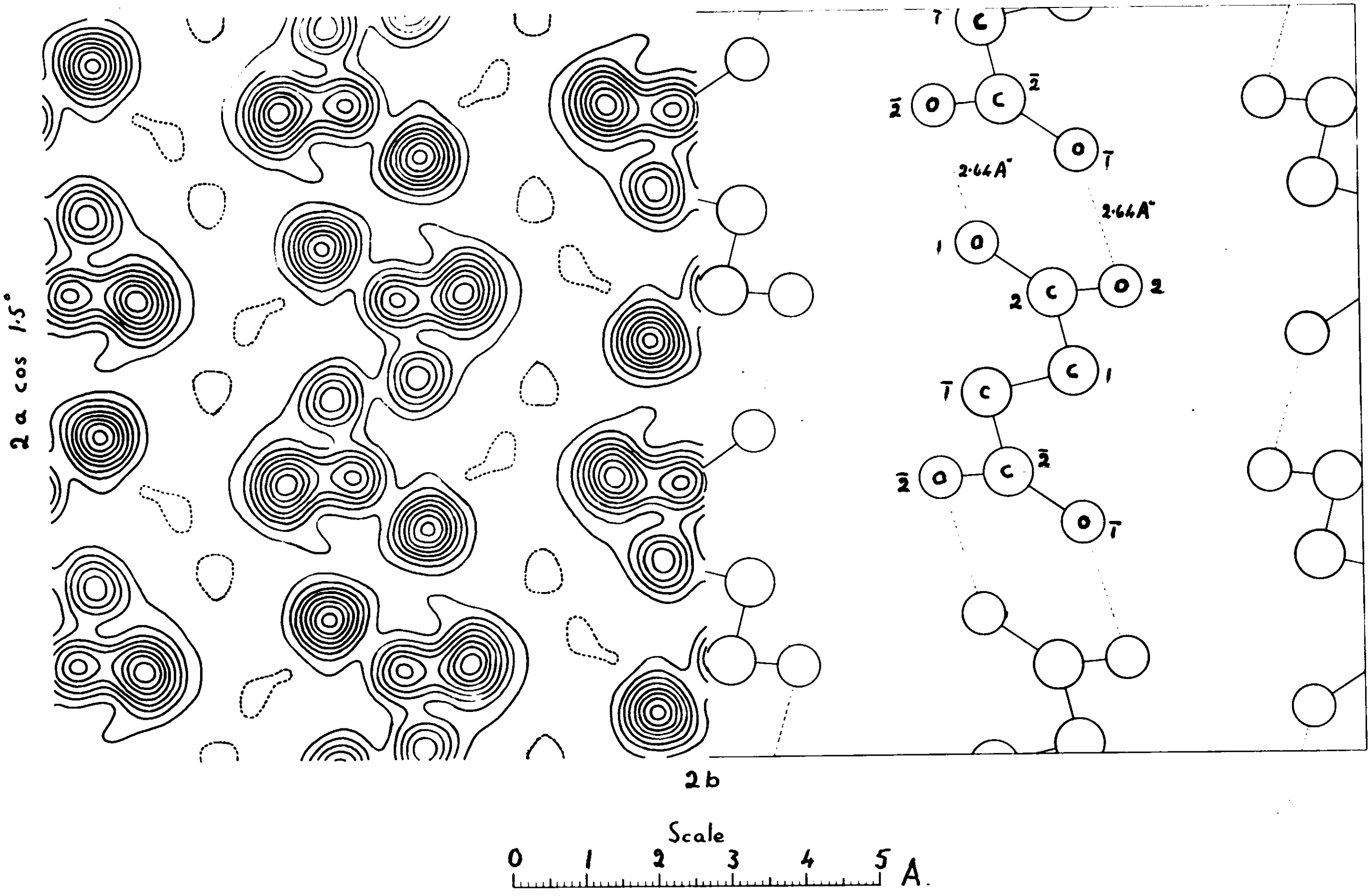
Crystal Habit. Crystallisation from water produces needles elongated along the c axis, which are so thin in the other dimensions as to be useless. Slow recrystallisation from dilute solutions in ethyl acetate, however, gives crystals with a tendency to elongation along the a axis, which are quite suitable for X ray work. Crystals so obtained are extremely brittle, and any attempt to cut them appears to shatter the crystal lattice, producing multiple X ray reflections, although microscopically the crystal appears quite sound. There is a very marked fibre cleavage in the direction of the c axis. The most common faces occurring are the

Figure 1.



Projection along [a] axis. In all diagrams, each contour line represents a density increment of one electron per A^2, the one electron line being dotted.

Figure 2.



Projection of structure along [101] axis

(001), (010), (111), (110), and (011).

Further goniometric and optical data are given by Groth (1), and the crystal structure has been investigated by Yardley (2) and Dupré la Tour (3), who determined the lattice constants and space group. The structure has been further examined by Verweel and MacGillavry (4), an analysis involving the measurement of intensities from oscillation photographs, and leading to a determination of the atomic coordinates. The present work was carried out to verify these previous results, and if possible, obtain some refinement of their accuracy.

Analysis of the Structure.

The asymmetric unit in the crystal structure consists of one half molecule. In the work carried out by Verweel and Macgillavry (loc. cit.),,two projections of the structure were made, along the a and b axes. The a axis projection gave very good resolution of all the atoms, the b axis projection very poor resolution owing to the nearness of the atoms to one another in projection.

Using the previous workers' final coordinates for the first calculation of structure factors, a Fourier synthesis of the observed 0kl terms was carried out. Slight shifts in atomic positions were obtained, necessitating the change of sign of a number of reflections. The final projection of the structure along the a axis is given in Figure 1. From this, very accurate values of the y and z coordinates for all the atoms can be obtained.

Instead of using the projection along the b axis for the x coordinates, as aws done before, these were obtained from a projection along the $[101]$ diagonal, using the $hk\bar{h}$ structure factors. In this projection also, Figure 2, all the atoms are again resolved. These two projections together accurately define the structure.

Orientation, Coordinates and Dimensions.

The principal molecular axis (L) was taken as the line passing through the mid points of the three carbon-carbon bonds in the molecule. The four carbon atoms in the molecule are coplanar, so the second molecular axis (M) was chosen to lie in this plane at right angles to (L). (N) is at right angles to (L) and (M).

The angles which the molecular axes (L), (M), and (N) make with the crystallographic axes a, b, and c' (c' is the perpendicular to a and b), are given in Table 1 and express the orientation of the molecule. The coordinates of the atoms in the asymmetric unit

Table 1.

Orientation of the molecule in the crystal.

$\chi_L = 56.0^\circ$ $\cos\chi_L = 0.559$ $\chi_M = 60.4^\circ$ $\cos\chi_M = 0.494$

$\psi_L = 68.5^\circ$ $\cos\psi_L = 0.367$ $\psi_M = 150.2^\circ$ $\cos\psi_M = -0.867$

$\omega_L = 42.0^\circ$ $\cos\omega_L = 0.744$ $\omega_M = 86.8^\circ$ $\cos\omega_M = 0.056$

$\chi_N = 48.2^\circ$ $\cos\chi_N = 0.667$

$\psi_N = 70.3^\circ$ $\cos\psi_N = 0.337$

$\omega_N = 131.7^\circ$ $\cos\omega_N = -0.665$

Table 2.

Atom	x Å	y Å	z Å	x' Å	z' Å	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
C_1	0.276	0.592	0.602	0.140	0.436	19.5°	24.0°	28.5°
C_2	0.099	0.326	1.966	1.257	1.423	7.0°	13.2°	93.0°
O_1	-0.602	-0.703	1.976	1.965	1.431	-42.5°	-28.5°	93.5°
O_2	0.864	1.233	3.234	1.367	2.342	61.0°	50.0°	153.0°

Coordinates of atoms w.r.t. crystallographic axes.

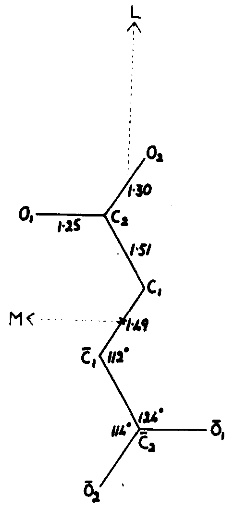
Table 3.

Coordinates of atoms w.r.t. molecular axes. (Å).

Atom	L	M	N
C_1	0.615	-0.420	0.002
C_2	1.878	0.404	-0.001
O_1	1.900	1.657	0.121
O_2	2.969	-0.268	-0.231

Figure 3.

Intramolecular distances.



Succinic Acid

Table 4.

Bond Lengths	Present work	Previous work	Bond Angles
$\bar{C}_1 - C_1$	- 1.49±0.02A°	1.52A°	$\bar{C}_1 - C_1 - C_2$:- 112°
$C_1 - C_2$	- 1.51 "	1.51A°	$C_1 - C_2 - O_1$:- 124°
$C_2 - O_1$	- 1.25 "	1.28A°	$C_1 - C_2 - O_2$:- 114°
$C_2 - O_2$	- 1.30 "	1.31A°	

with respect to the crystallographic axes are given in Table 2. All the other atoms in the unit cell can be obtained from these by the appropriate symmetry operations.

The molecular dimensions and bond lengths are given in Table 4, and shown diagrammatically in Figure 3. They do not differ so widely from the values found previously as might be expected from the difference in atomic coordinates. The good resolution obtained in both zones, however, makes their accuracy more to be trusted. Table 3 lists the coordinates of the atoms with respect to the molecular axes (L), (M), and (N).

All the carbon atoms in the molecule are coplanar, this plane passing through the centre of symmetry in the middle of the molecule. The carboxyl group $C_1C_2O_1O_2$ is also planar, but its plane is rotated through about 6° with respect to the plane of the carbons about the axis C_1C_2. The plane of the carboxyl group passes through the centre of symmetry between molecules along the c axis, and therefore also passes through the carboxyl group of the next molecule. Atoms C_1^{I}, C_2^{I}, C_2^{II}, C_1^{II} are collinear.

Intermolecular Distances.

The intermolecular distances are shown in Figure 4, and listed in Table 5. The closest approach between molecules is the hydrogen bridging between the oxygen atoms of adjacent carboxyl groups along the c axis.

Figure 4.

Intermolecular distances.

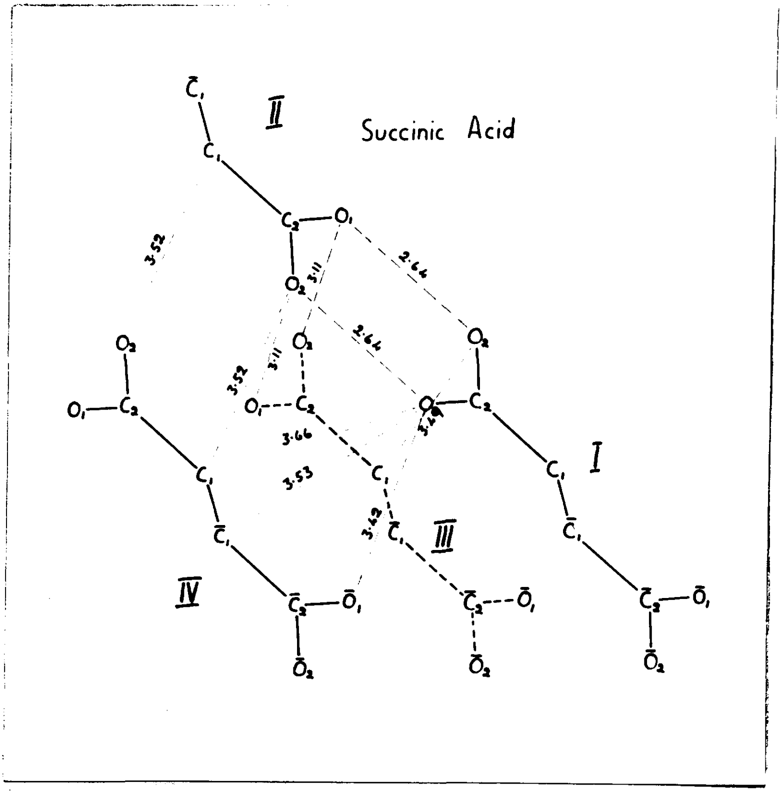


Table 5.

Bond	Length	Bond	Length
$O_1^{I}-O_2^{II}$	2.64±0.05 Å	$O_1^{I}-\bar{O}_1^{IV}$	3.42±0.05 Å
$O_2^{I}-O_1^{II}$	2.64 "	$O_2^{I}-C_1^{III}$	3.49 "
$O_2^{II}-O_1^{III}$	3.11 "	$O_2^{II}-C_1^{IV}$	3.52 "
$O_1^{II}-O_2^{III}$	3.11 "	$O_1^{I}-\bar{C}_1^{IV}$	3.53 "
$O_2^{I}-O_2^{III}$	3.23 "	$O_1^{I}-C_1^{IV}$	3.66 "

In comparison with the other acids q.v. the oxygen-oxygen distances in succinic acid are rather short, the molecules being packed together very compactly.

Experimental.

X ray Measurements.

The crystals used in this investigation were obtained by recrystallisation from ethyl acetate solutions.

Copper K radiation was used throughout, and rotation, oscillation and moving film photographs of the principal zones were taken. The axial lengths and space group found confirmed the previous workers' results.

The crystals used for the 0kl zone had cross-section normal to the a axis of 0.09 × 0.11 mm, and 0.45 × 0.52 mm. With these dimensions absorption of the X ray beam by the crystal specimen was minimised, and corrections for it were not made. All the crystalline specimens used were characterised by the high degree of perfection of the crystal faces, also by the sharp X ray reflections they produced. Accordingly, one crystal was dipped in liquid air, before use, to ensure that the lattice was of the true 'mosaic' type. The intensities from this crystal, however, did not differ appreciably from those found for the other specimens. Altogether 59 out of a possible 69 reflections were recorded, as compared with 46 in the previous work. For the $hk\bar{h}$ zone, a specimen 0.38 × 0.42 mm cross-section was used.

These crystals were completely immersed in the X ray beam, and the spectra recorded on series of moving films. The intensities were measured visually, and a range of intensity of 1500 to 1 was covered. The intensities for the two zones were correlated, and their structure factors calculated, by the usual methods, and are listed in Table 6 as F meas. No absolute measurements were made.

Fourier Analysis.

For the projection along the a axis, the electron density was computed at 450 points on the asymmetric unit, the b axis being divided into 60 parts of 0.148 Å and $c \sin\beta$ into 30 parts of 0.184 Å. The summations were carried out to three figure accuracy, and the results plotted on a scale of 5 cms/Å by graphical interpolation of the summation totals. The resulting contour map for the 0kl zone, showing one complete molecule, is given in Figure 5. The positions finally assigned to the atomic centres are marked by small crosses. The [101] projection was computed similarly, in this case the intervals being :- b, 60 parts of 0.148 Å; a cos 1° 33', 30 parts of 0.170 Å.

The structure factors calculated from the final structure are listed in Table 6 as F calc. The atomic scattering curve for adipic acid (page 30), was found to be fairly satisfactory for succinic acid, loading oxygen to carbon in the ratio 1.5 to 1.0 in the same manner. As the percentage of oxygen with respect to carbon becomes higher, the method of using a loaded carbon atomic scattering curve for oxygen becomes less satisfactory, and the discrepancies are hence somewhat higher. The discrepancies finally obtained are listed below.

Discrepancies between measured and calculated structure factors.

Zone	Morrison	Verweel and MacGillavry
0kl	22.5%	30.7%
hkh	21.7%	-
h0l	-	29.5%
Overall	22.0%	31.0%

In Figure 5 it can be seen that there are small peaks in the two electron level which occur approximately where the hydrogen atoms of the CH_2 group should appear. It is quite possible that these peaks are due to the hydrogen atoms, but until this has been confirmed by a full three dimensional synthesis, no attempt has been made to include them in calculations of the structure factors, or to make any calculation of the length of the C-H bond.

Figure 5.

Contour map of 0kl zone showing positions assigned to atoms.

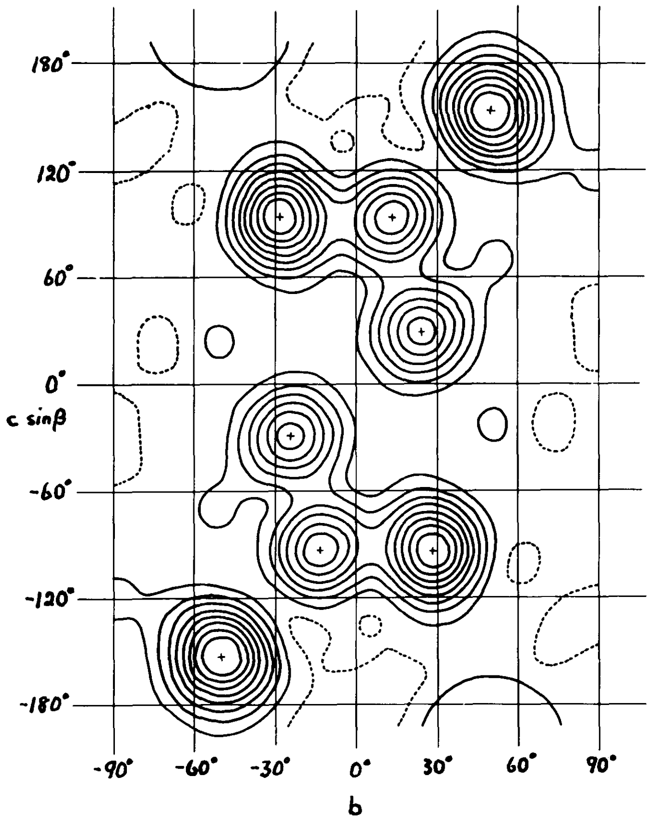


Table 6.
Measured and calculated structure factors.

hkl	sinθ	F meas	F calc
020	.173	24.0	34.0
040	.346	15.5	-16.0
060	.519	7.5	-9.0
080	.692	4.0	-3.5
0100	.865	3.5	-2.5
001	.140	6.0	-10.5
002	.280	10.5	-13.0
003	.419	<1.0	2.5
004	.559	9.0	9.0
005	.699	2.0	-1.5
006	.838	9.5	-7.5
007	.978	0.5	1.5
011	.165	5.0	4.0
021	.223	10.0	10.0
031	.295	1.5	-1.0
041	.373	10.0	12.0
051	.455	3.0	-1.5
061	.537	6.5	-8.5
071	.622	7.0	7.0
081	.706	6.5	-5.0
091	.791	6.5	5.5
0101	.876	<1.0	1.0
0111	.961	1.5	1.0
012	.292	7.0	-6.5
022	.329	14.5	-16.0
032	.381	4.5	3.0
042	.445	9.0	-7.0
052	.514	11.0	12.5
062	.590	6.5	6.5
072	.667	<1.5	1.0
082	.746	4.0	3.5
092	.828	4.0	-3.0
0102	.909	1.0	-0.5
0112	.992	<0.5	-0.5
013	.429	15.5	17.5
023	.454	2.0	3.0
033	.494	15.5	18.0
043	.544	2.0	1.0
053	.602	2.5	-2.5
063	.667	1.5	-1.5
073	.737	4.0	-3.5
083	.809	1.5	-1.0
093	.885	4.0	-1.5
0103	.961	<1.0	0.0
014	.565	4.5	-5.0
024	.586	8.0	9.0
034	.616	1.5	-0.0
044	.658	3.0	1.5
054	.707	8.0	6.0
064	.763	3.5	-2.5
074	.824	2.5	1.0
084	.889	1.5	-1.5
094	.958	2.0	-1.5
015	.704	2.0	1.5
025	.719	4.0	-3.5
035	.745	2.0	0.5
045	.780	2.5	-2.0
055	.822	<1.0	-1.0
065	.872	4.0	2.0
075	.924	2.5	1.5
085	.984	2.0	1.5
016	.844	<1.0	-0.0
026	.856	5.0	-3.0
036	.879	1.0	0.5
046	.907	1.5	1.5
056	.943	<1.0	0.5
066	.987	1.0	1.0
017	.983	<0.5	0.0
027	.995	<0.5	-0.0
$20\bar{2}$	.299	17.5	-18.0
$40\bar{4}$	.598	7.0	8.0
$60\bar{6}$	.886	3.5	-2.5
$11\bar{1}$	.173	2.0	-0.0
$21\bar{2}$	.311	8.0	9.5
$31\bar{3}$	.459	10.0	12.5
$41\bar{4}$	.606	2.0	2.0
$51\bar{5}$	.755	6.0	4.0
$61\bar{6}$	.889	<1.0	-0.5
$12\bar{1}$	.229	17.5	17.0
$22\bar{2}$	.347	1.0	1.0
$32\bar{3}$	.482	16.5	-18.5
$42\bar{4}$	.624	2.5	1.0
$52\bar{5}$	.770	7.5	7.0
$62\bar{6}$	.903	1.5	-0.5

hkl	sinθ	F	
		meas	calc
$13\bar{1}$	.299	2.5	3.5
$23\bar{2}$	.396	15.5	17.5
$33\bar{3}$	.518	<1.5	-0.0
$43\bar{4}$	.653	2.0	2.5
$53\bar{5}$	.793	3.0	1.5
$63\bar{6}$	.924	<1.0	-0.5
$14\bar{1}$	.378	7.0	-5.0
$24\bar{2}$	.457	4.5	6.0
$34\bar{3}$	.566	4.0	-4.0
$44\bar{4}$	.689	<1.5	-1.0
$54\bar{5}$	.744	4.5	4.5
$64\bar{6}$	.952	<1.0	1.0
$15\bar{1}$	.457	2.5	4.5
$26\bar{2}$	.524	9.5	9.0
$35\bar{3}$	.622	4.5	-0.0
$45\bar{4}$	.738	<1.5	0.5
$55\bar{5}$	.865	2.0	-1.5
$65\bar{6}$	.985	< .5	0.5
$16\bar{1}$	.541	2.0	-1.5
$26\bar{2}$	.599	7.0	-8.5
$36\bar{3}$	.686	1.5	1.0
$46\bar{4}$	.792	4.0	6.0
$56\bar{5}$	.914	3.0	0.5

hkl	sinθ	F	
		meas	calc
$17\bar{1}$	.424	<1.5	-0.0
$27\bar{2}$	.676	<1.5	-1.0
$37\bar{3}$	.753	4.0	-3.5
$47\bar{4}$	.850	<1.5	-0.5
$57\bar{5}$	.964	2.5	-2.0
$18\bar{1}$	.707	9.5	7.5
$28\bar{2}$	.753	6.0	-3.5
$38\bar{3}$	.825	3.0	-2.0
$48\bar{4}$	.915	1.0	1.0
$19\bar{1}$	.792	2.0	-1.0
$29\bar{2}$	.835	3.0	-2.5
$39\bar{3}$	.899	2.0	-1.0
$49\bar{4}$	.982	0.5	-0.5
$110\bar{1}$	.879	4.5	3.0
$210\bar{2}$	.915	1.5	1.5
$310\bar{3}$	.974	2.0	-0.5
$111\bar{1}$	.962	1.0	-0.5

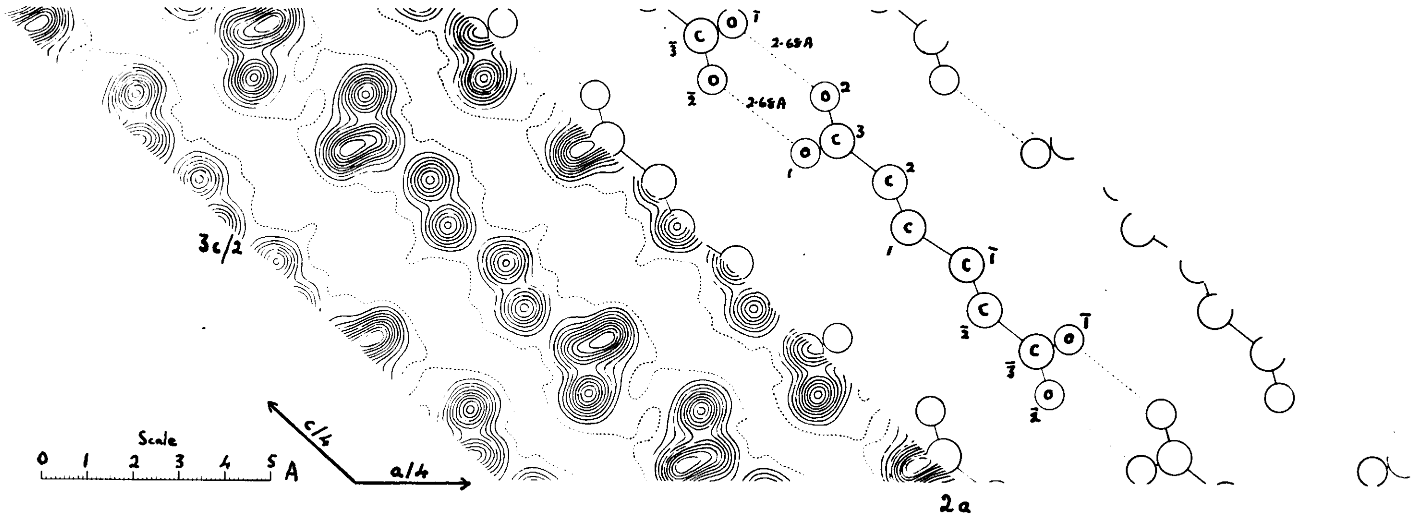
Adipic Acid.

Crystal Data. - adipic acid $C_6H_{10}O_4$. M.= 146.1
m.pt.-153°C. D calc = 1.359 D found = 1.345
monoclinic prismatic.
a = 10.07±0.03 Å; b = 5.16±0.01 Å; c = 10.03±0.03 Å;
β = 137.1±0.2°
Absent spectra, h01 when h is odd, 0k0 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 Å^3
Absorption coefficient for X rays, (λ=1.54 Å)., μ = 12.0 cms^{-1}.
Total number of electrons per unit cell - F(000) - 156.

Crystal Habit.

Satisfactory well formed crystals were obtained by slow evaporation of dilute solutions in ethyl acetate. They frequently showed elongation into needles along the b axis, the (001) and (100) faces being generally very well developed, also the (110) and (011). There is pronounced cleavage on (010).

Further goniometric and optical crystal data are given by Groth (5), and the crystal structure has been investigated by Caspari (6), who determined the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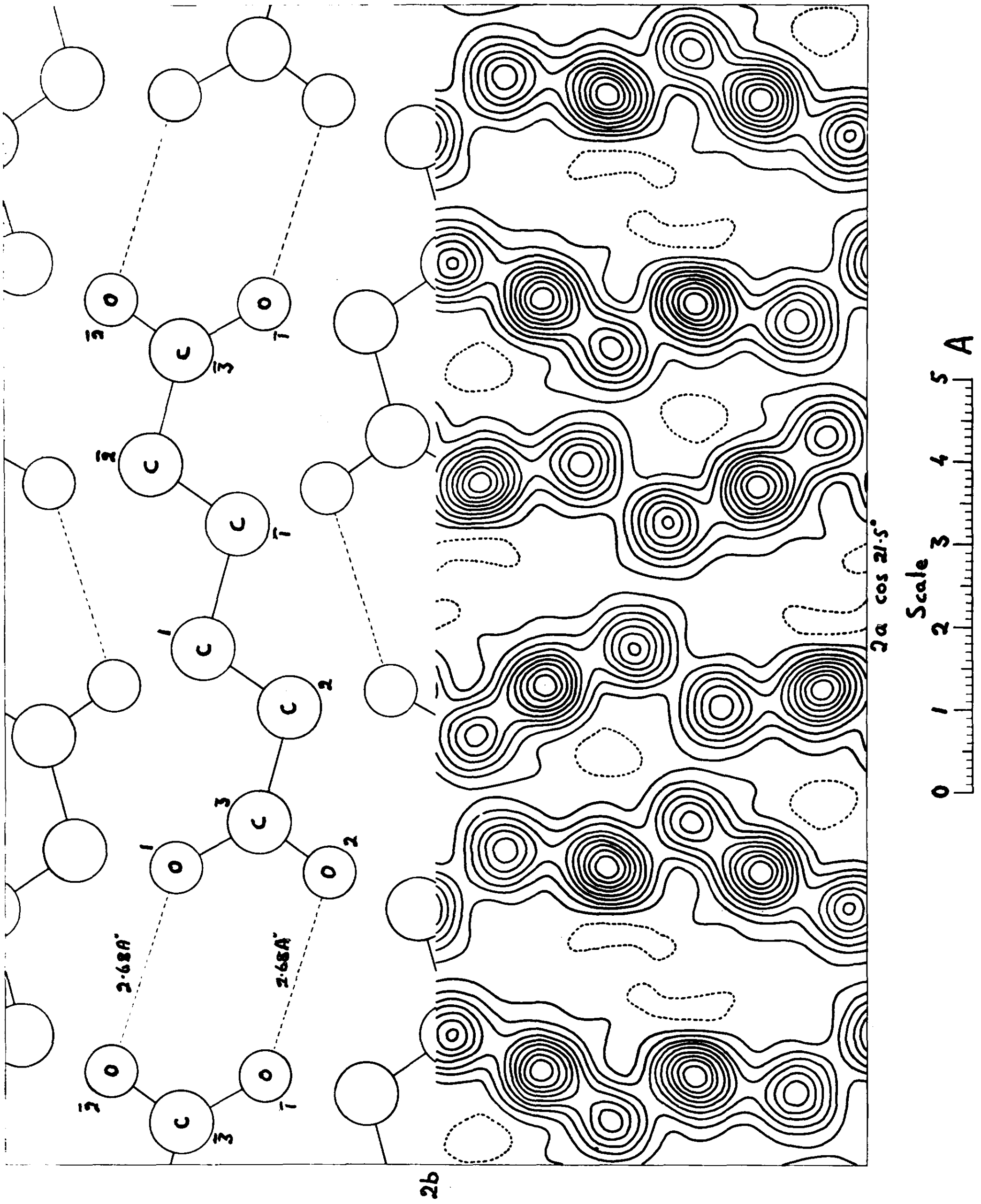
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2b

lattice constants and space group. A further examination of the structure has been carried out by MacGillavry (7), involving the measurement of reflections, and leading to a determination of the atomic parameters. The object of the present study was to obtain some refinement of the atomic structure proposed by MacGillavry.

Analysis of the Structure.

The asymmetric unit in the crystal structure consists of one half molecule. The coordinates of the final structure obtained by MacGillavry were used for the first calculation of structure factors, and by successive Fourier syntheses of the observed structure amplitudes quite a considerable refinement of these coordinates was obtained. The final projection of the structure on the (010) plane is shown in Figure 6, and from this accurate values of the x and z coordinates for all the atoms except C_3 and O_1 are obtained. The y coordinates were also refined by projection along the $[10\bar{1}]$ axis, using the $hk\bar{h}$ structure factors. In this projection, Figure 7, all the atoms are resolved. These two projections together precisely define the structure.

Orientation, Coordinates and Dimensions.

The principal molecular axis (L), was taken as the straight line through the mid points of the central three carbon - carbon bonds in the molecule. The four central carbon atoms in the molecule are coplanar within experimental error (± 0.02 Å), so the second molecular axis (M) was chosen to lie in this plane, at right angles to (L). (N) is the axis at right angles to (L) and (M).

The angles which these molecular axes make with the crystallographic axes a, b and c' (c' is the perpendicular to a and b), are given in Table 7, and express the orientation of the molecule.

The coordinates of the atoms in the asymmetric unit with respect to the crystallographic axes are given in Table 8. The other half of the molecule and the remaining molecule can be derived from these coordinates by the usual symmetry operations and translations applicable to the space group $P2_1/a$.

The molecular dimensions and bond lengths were calculated from these coordinates, and the results are shown in Figure 8 and listed in Table 10. The differences between the present and the previously found values are in one or two cases rather large.

The coordinates of the atoms with respect to the molecular axes (L), (M) and (N) are listed in Table 9.

Table 7.

Orientation of the molecule in the crystal.

$\chi_L = 48.5^\circ$	$\cos\chi_L = 0.663$	$\chi_M = 61.0^\circ$	$\cos\chi_M = 0.485$
$\psi_L = 104.6^\circ$	$\cos\psi_L = -0.252$	$\psi_M = 30.5^\circ$	$\cos\psi_M = 0.862$
$\omega_L = 45.2^\circ$	$\cos\omega_L = 0.705$	$\omega_M = 98.6^\circ$	$\cos\omega_M = -0.149$

$\chi_N = 55.3^\circ$ $\cos\chi_N = 0.570$

$\psi_N = 116.2^\circ$ $\cos\psi_N = -0.441$

$\omega_N = 133.9^\circ$ $\cos\omega_N = -0.694$

Table 8.

Coordinates of atoms w.r.t. crystallographic axes.

Atom	x Å	y Å	z Å	x'Å	z'Å	2πx/a	2πy/b	2πz/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°	37.7°	105.5°
O_2	1.025	-1.296	4.730	2.438	3.220	36.7°	-90.5°	170.0°

Table 9.

Coordinates of atoms w.r.t. molecular axes (Å).

Atom	L	M	N
C_1	0.644	0.427	0.000
C_2	1.866	-0.427	-0.000
C_3	3.175	0.336	-0.136
O_1	3.128	1.564	0.008
O_2	2.215	-0.411	-0.272

Figure 8.

Intramolecular distances.

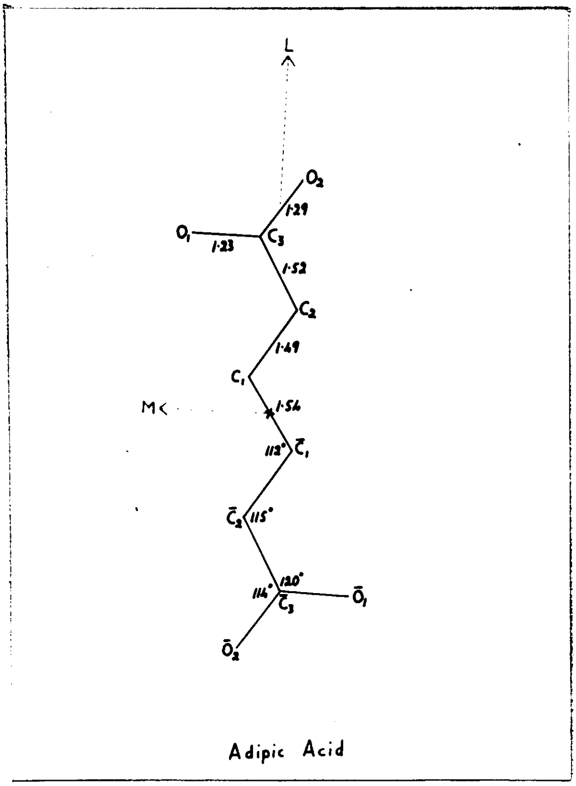


Table 10.

Bond lengths		Present work		Previous work	Bond angles Present work
$\bar{C}_1 - C_1$	=	1.54±0.02Å		1.51Å	$\bar{C}_1 - C_1 - C_2$:- 112°
$C_1 - C_2$	=	1.49	"	1.52Å	$C_1 - C_2 - C_3$:- 115°
$C_2 - C_3$	=	1.52	"	1.49Å	$C_2 - C_3 - O_1$:- 120°
$C_3 - O_1$	=	1.23	"	1.28Å	$C_2 - C_3 - O_2$:- 114°
$C_3 - O_2$	=	1.29	"	1.38Å	

All the carbon atoms of the methylene chain are coplanar, this plane passing through the centre of the molecule. $C_3^{\overline{I}}$ is twisted out of this plane, however, and $C_2^{\overline{I}}$, $C_3^{\overline{I}}$, $O_1^{\overline{I}}$, $O_2^{\overline{I}}$ all lie approximately on a plane tilted at $C_2^{\overline{I}}$ by about 6° to the plane of the carbon chain. This plane through the carboxyl group passes through the centre of symmetry between this molecule and the next up the c axis, and therefore also passes through $O_1^{\overline{II}}$, $O_2^{\overline{II}}$, $C_3^{\overline{II}}$, $C_2^{\overline{II}}$ of that molecule. Atoms $C_2^{\overline{I}}$, $C_3^{\overline{I}}$, $C_3^{\overline{II}}$, $C_2^{\overline{II}}$ are collinear.

Intermolecular distances.

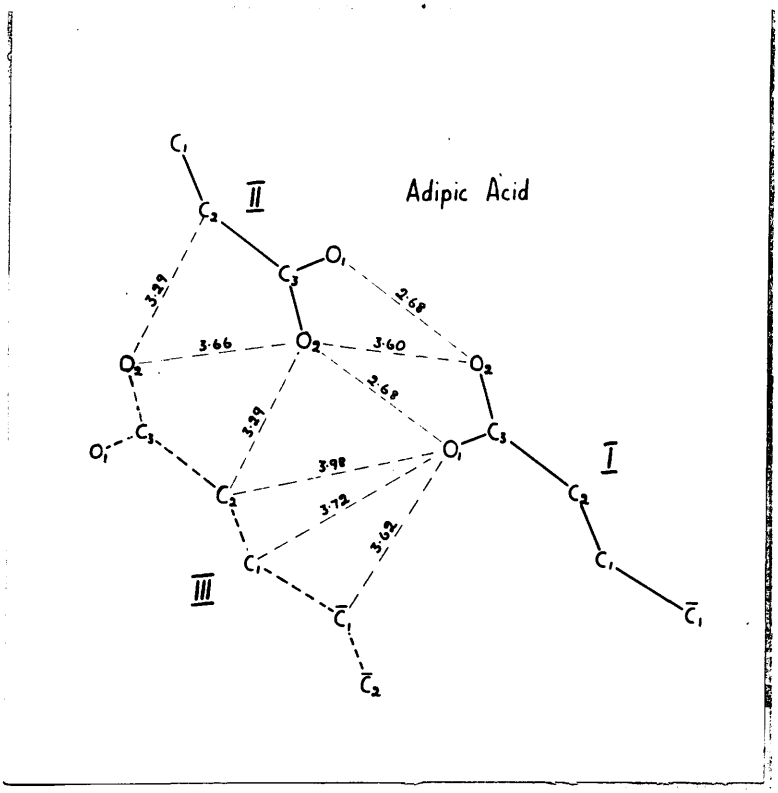
The closest approach between adjacent molecules is the hydrogen bridging between the oxygens of adjacent carboxyl groups along the c axis. The various distances are shown in Figure 9 and Table 11.

Table 11.

Bond	Distance	Bond	Distance
$O_1^{\overline{I}} - O_2^{\overline{II}}$	= 2.68±0.05Å	$O_2^{\overline{II}} - O_2^{\overline{III}}$	= 3.66±0.05A
$C_2^{\overline{III}} - O_2^{\overline{II}}$	= 3.29 "	$C_1^{\overline{III}} - O_1^{\overline{I}}$	= 3.72 "
$O_2^{\overline{I}} - O_2^{\overline{II}}$	= 3.60 "	$C_2^{\overline{III}} - O_2^{\overline{II}}$	= 3.94 "
$C_1^{\overline{III}} - O_1^{\overline{I}}$	= 3.62	$C_2^{\overline{III}} - O_1^{\overline{I}}$	= 3.98 "

Figure 9.

Intermolecular distances.



Experimental.

X ray Measurements.

Suitable small crystals for X ray intensity measurements were easily obtained by crystallisation from ethyl acetate solutions.

Copper Kα radiation was used throughout, and rotation, oscillation and moving film photographs of the principal zones were taken.

The axial lengths and space group were first checked, and were found to agree with those in the previous work.

The principal crystal used for the h0l zone had cross-section normal to the b axis of 0.77 × 0.43 mm. Absorption corrections were made, but were found to make little difference save to one or two planes. For the strongest reflections a smaller crystal, cross-section 0.11 × 0.16 mm was used. 80 out of a possible 91 planes were recorded, as compared with the 58 observed by MacGillavry.

For the $hk\bar{h}$ zone, a specimen 0.47 × 0.55 mm cross-section was used, and for the hk0 zone one 0.41 × 0.58 mm.

These crystals were completely immersed in the X ray beam, and the spectra recorded on series of moving films. For measurement of intensities in all cases the multiple film technique of Robertson (8) was used, the total range of intensities covered being about 12,000 to 1. The sets of intensities for the different zones were correlated by means of their common axial reflections. Their structure factors were calculated from the intensities by the usual formulae applicable to mosaic type crystals, and are listed in Table 12 as F meas. Absolute measurements were not carried out, and the scale of the F values was obtained on an absolute basis by correlation with the values finally calculated from the atomic positions found.

Fourier Analysis.

The final structure proposed by MacGillavry was used as a basis for the first calculation of structure factors, and two dimensional Fourier syntheses were carried out.

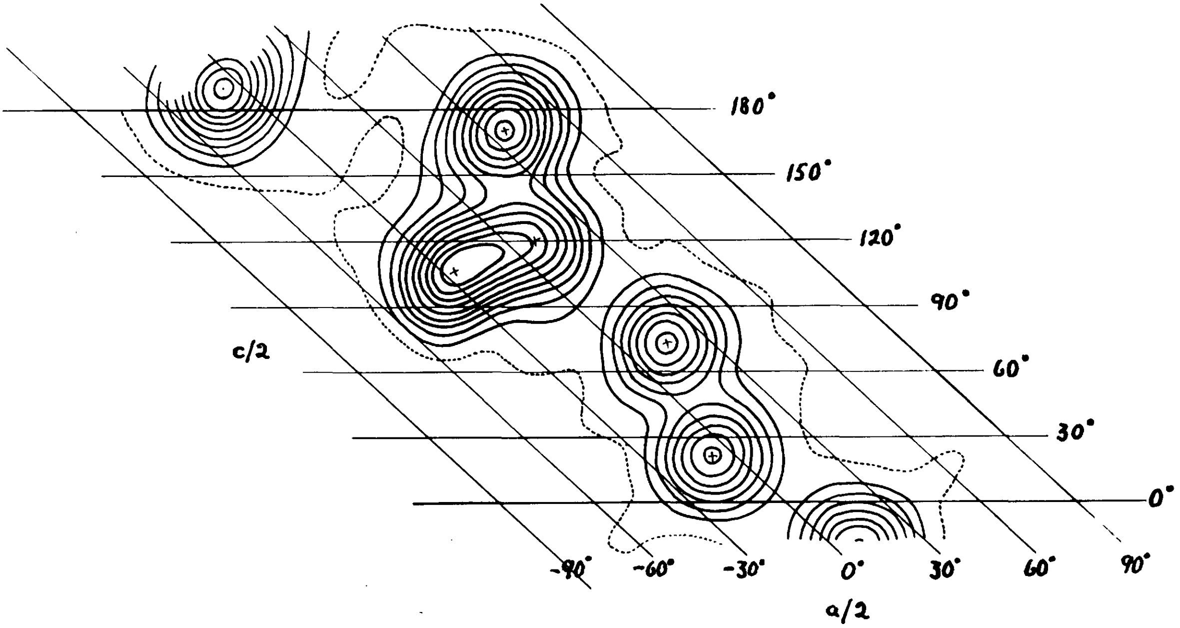
For the projection along the b axis, the electron density was computed at 900 points on the asymmetric unit, the a and c axes each being divided into 60 parts, giving intervals of 0.168 Å along the a axis, and 0.167 Å along the c. The summations were carried out by means of the three figure stencil method of Robertson (9), and the positions of the contour lines plotted on a scale of 5 cms/Å by graphical interpolation of the summation totals. The resulting contour map for the h01 zone is shown in Figure 10, one quarter of the unit cell being given. The final atomic positions are marked by small crosses.

The projection along [101] was computed similarly, in this case the intervals being :- b, 30 parts of 0.172Å and a cos 21° 29', 60 parts of 0.156Å.

From the final coordinates, Table 8, all the structure factors were recalculated, the results being given in Table 12. A new composite scattering curve was derived to give optimum discrepancy between F meas and

Figure 10.

Asymmetric unit, showing positions assigned to atoms.



F calc, the oxygen atoms being loaded with respect to carbon by the usual factor of 1.5 to 1.0.

New Atomic Scattering Curve for adipic acid.

sinθ (λ=1.54Å)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f_c	100	75	60	49	38	29	19	13	8.4	4.7

The discrepancies finally obtained, expressed as percentages, are :-

Zone	% discrepancy	
	Morrison	MacGillavry
h0l	15.5%	27.7%
hkh	16.7%	22.4%
Overall	17.4%	24.7%

Table 12.
Measured and calculated structure factors.

hkl	sinθ	F meas	F calc	hkl	sinθ	F meas	F calc
200	.212	67.5	62.0	603	.948	2.5	1.5
400	.423	6.0	5.0	602	.848	2.5	0.5
600	.634	1.5	-4.5	601	.756	< 1.5	3.5
800	.845	<1.0	1.5	$60\bar{1}$	.590	11.5	12.5
				$60\bar{2}$	.525	2.0	3.0
001	.113	20.0	-22.0	$60\bar{3}$	.478	1.5	-2.0
002	.225	7.0	-7.0	$60\bar{4}$	.458	21.0	-22.5
003	.337	6.5	5.5	$60\bar{5}$	.463	5.5	-6.0
004	.449	17.0	16.0	$60\bar{6}$	.495	8.5	9.5
005	.562	13.0	-13.0	$60\bar{7}$	.548	12.5	-11.5
006	.674	6.0	5.5	$60\bar{8}$	.616	7.0	-7.5
007	.787	4.0	-3.0	$60\bar{9}$	.695	3.5	-2.0
008	.899	4.5	-3.5	$60\overline{10}$	.790	<1.0	1.0
				$60\overline{11}$	.883	3.5	-3.0
207	.965	2.0	-2.5	$60\overline{12}$	.975	4.5	4.0
206	.855	1.0	1.0				
205	.743	2.5	-4.0	801	.979	1.5	-1.5
204	.633	11.5	13.5	$80\bar{1}$	.813	3.0	3.5
203	.525	3.0	1.0	$80\bar{2}$	.740	1.5	4.5
202	.418	11.0	-8.0	$80\bar{3}$	.683	6.0	-10.0
201	.317	3.0	2.0	$80\bar{4}$	.639	< 1.5	0.5
$20\bar{1}$	.160	2.0	-3.0	$80\bar{5}$	.611	11.0	-11.5
$20\bar{2}$	.164	12.5	-15.0	$80\bar{6}$	.608	2.5	3.0
$20\bar{3}$	.233	25.5	28.5	$80\bar{7}$	.621	7.0	-8.0
$20\bar{4}$	.329	21.0	-19.0	$80\bar{8}$	.656	4.5	4.0
$20\bar{5}$	.434	6.0	-7.0	$80\bar{9}$	.710	8.5	-7.0
$20\bar{6}$	.539	8.0	7.0	$80\overline{10}$	.790	<1.0	0.0
$20\bar{7}$	.646	< 1.5	0.5	$80\overline{11}$	.850	1.5	-1.0
$20\bar{8}$	.756	15.5	-14.5	$80\overline{12}$	.935	7.0	4.0
$20\bar{9}$	.868	2.5	2.5				
$20\overline{10}$	.980	<0.5	0.5	$100\bar{2}$	.960	1.0	0.5
				$100\bar{3}$	.894	1.5	-4.0
405	.944	1.0	1.5	$100\bar{4}$	.836	< 1.0	2.5
404	.838	2.5	2.5	$100\bar{5}$	.796	8.0	-6.5
403	.735	6.0	4.0	$100\bar{6}$	.770	4.0	-4.0
402	.631	3.5	-5.0	$100\bar{7}$	.758	4.0	2.0
401	.538	11.0	12.0	$100\bar{8}$	.763	1.0	2.0
$40\bar{1}$	.371	19.5	19.5	$100\bar{9}$	.784	5.0	-4.0
$40\bar{2}$	.320	9.0	-11.0	$100\overline{10}$	.821	2.5	-2.0
$40\bar{3}$	.303	25.0	26.5	$100\overline{11}$	.870	4.5	3.0
$40\bar{4}$	.329	47.0	-46.0	$100\overline{12}$	.935	3.0	1.0
$40\bar{5}$	.390	3.5	3.5				
$40\bar{6}$	.468	7.0	7.0	$120\bar{6}$	.960	2.5	-4.0
$40\bar{7}$	.556	3.5	-2.0	$120\bar{7}$	.930	3.5	3.5
$40\bar{8}$	.655	22.5	-19.5	$120\bar{8}$	.915	1.5	-1.0
$40\bar{9}$	.758	4.0	4.0	$120\bar{9}$	.914	1.0	-0.5
$40\overline{10}$	.864	<1.0	-0.0	$120\overline{10}$	.925	<1.0	-1.0
$40\overline{11}$	.975	2.0	-1.0	$120\overline{11}$	.960	2.5	2.5
				$120\overline{12}$	.988	< 0.5	-1.0

		F	
hkl	sinθ	meas	calc
020	.299	5.5	-3.5
040	.597	2.0	-2.5
060	.896	1.5	-3.0
20$\bar{2}$	.164	11.0	-15.5
40$\bar{4}$	.329	43.5	-46.0
60$\bar{6}$	.495	8.5	10.0
80$\bar{8}$	.656	4.5	4.5
100$\overline{10}$	.821	2.0	-2.0
120$\overline{12}$	.988	0.5	-1.0
11$\bar{1}$	.171	3.0	1.0
12$\bar{1}$	.310	3.5	3.5
13$\bar{1}$	.457	4.0	4.5
14$\bar{1}$	.606	4.0	-4.0
15$\bar{1}$	.753	4.5	4.5
16$\bar{1}$	.903	1.0	-0.0
21$\bar{2}$	.223	5.5	-5.0
22$\bar{2}$	.342	4.5	4.0
23$\bar{2}$	.480	12.5	14.0
24$\bar{2}$	.620	5.0	5.0
25$\bar{2}$	.766	7.5	-9.0
26$\bar{2}$	.913	0.5	1.0
31$\bar{3}$	.290	16.5	16.5
32$\bar{3}$	.388	14.5	-16.0
33$\bar{3}$	.513	2.0	3.0
34$\bar{3}$	.647	7.0	-7.0
35$\bar{3}$	.788	5.0	-5.5
36$\bar{3}$	.933	1.5	-0.5
41$\bar{4}$	.363	7.5	4.5
42$\bar{4}$	.446	9.0	10.0
43$\bar{4}$	.557	3.0	-1.5
44$\bar{4}$	.683	0.5	-0.5
45$\bar{4}$	.816	1.0	0.5
46$\bar{4}$	.958	<0.5	1.5
51$\bar{5}$	.439	9.0	-7.0
52$\bar{5}$	.504	1.5	0.0
53$\bar{5}$	.609	3.0	-4.5
54$\bar{5}$	.726	2.5	2.5
55$\bar{5}$	.853	<0.5	0.0
56$\bar{5}$	.988	<0.5	-1.0
61$\bar{6}$	.516	1.5	-1.0
62$\bar{6}$	.578	7.0	-6.5
63$\bar{6}$	.667	14.0	-14.0
64$\bar{6}$	.778	5.5	-4.0
65$\bar{6}$	.895	1.0	2.0

		F	
hkl	sinθ	meas	calc
71$\bar{7}$	.596	6.0	-5.5
72$\bar{7}$	.650	8.0	7.5
73$\bar{7}$	.731	3.0	-3.0
74$\bar{7}$	.831	1.5	1.5
75$\bar{7}$	.944	<0.5	1.0
81$\bar{8}$	.675	5.5	5.0
82$\bar{8}$	.724	5.5	-6.0
83$\bar{8}$	.797	4.0	4.5
84$\bar{8}$	.890	1.0	1.0
85$\bar{8}$	.995	0.0	-0.5
91$\bar{9}$	.759	3.0	-2.0
92$\bar{9}$	.800	3.0	-3.0
93$\bar{9}$	.867	0.5	1.5
94$\bar{9}$	.955	1.5	-1.0
101$\overline{10}$	.839	1.0	-1.5
102$\overline{10}$	.879	3.5	2.0
103$\overline{10}$	.940	5.5	3.5
111$\overline{11}$	.919	1.5	1.5
112$\overline{11}$	.955	<0.5	0.0
110	.184	60.5	54.5
120	.317	19.5	13.5
130	.461	7.5	7.0
140	.606	2.0	2.0
150	.754	4.0	-4.5
160	.902	<2.0	-0.5
210	.259	42.5	39.5
220	.366	6.0	7.5
230	.496	4.0	1.5
240	.634	5.0	-4.5
250	.775	2.5	3.0
260	.921	<1.5	-1.5
310	.350	19.5	25.5
320	.434	22.5	24.5
330	.549	<2.0	-1.5
340	.676	4.0	3.5
350	.810	3.0	-1.5
360	.950	<1.5	-1.0
410	.447	20.0	25.5
420	.516	9.0	14.5
430	.615	7.5	6.5
440	.731	4.5	-3.5
450	.857	<2.0	1.0
460	.991	<1.0	1.0

		F	
hkl	Sinθ	meas	calc
510	.548	4.5	4.5
520	.606	9.5	14.0
530	.692	<2.5	2.0
540	.796	2.0	3.0
550	.914	<1.5	1.0
610	.650	4.5	3.5
620	.699	4.5	5.5
630	.777	5.5	7.0
640	.870	<2.0	0.0
650	.978	<1.0	-1.0

		F	
hkl	sinθ	meas	calc
710	.753	<2.5	-1.0
720	.796	5.0	4.5
730	.864	<2.0	0.5
740	.949	<1.5	0.5
810	.857	<2.0	-0.5
820	.896	<2.0	-0.0
830	.955	<1.5	2.5
910	.960	<1.0	-0.5
920	.995	<1.0	0.5

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Sebacic Acid.

Crystal Data. - sebacic acid $C_{10}H_{18}O_4$. M.=202.1
m.pt.-134°C. D calc = 1.226 D found =1.231
monoclinic prismatic.
a = 10.10±0.03 Å; b = 5.00±0.01 Å; c = 15.1±0.05 Å;
β = 133.8±0.3°
Absent spectra, h0l when h is odd, 0k0 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=548 $Å^3$
Absorption coefficient for X rays, (λ=1.54 Å), μ=9.08 cms^{-1}.
Total number of electrons per unit cell - F(000) - 220.

Crystal Habit.

From most solvents recrystallisation gives rise to crystals which are so thin upon (001) as to be useless for X ray work. With care, and slow recrystallisation from amyl acetate, however, crystalline fragments can sometimes be obtained which can be cut to give suitable specimens. Crystals so obtained show usually only the (001) and (100) faces, no end faces being definitely identifiable. There is a marked cleavage on (001) and (100).

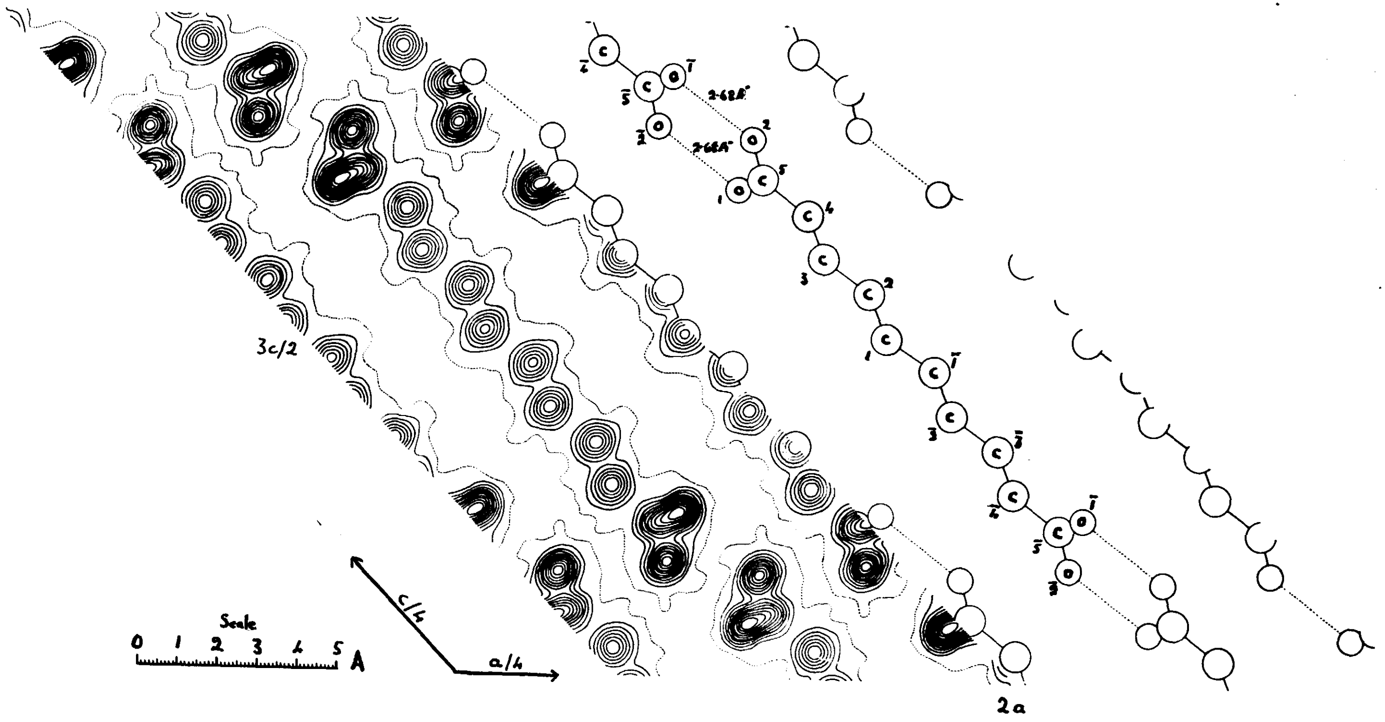
Further goniometric and optical data are given by Caspari (6), who has also investigated the crystal structure. His X ray work was carried out by means of rotation and oscillation photographs on glass quarter plates, and leads to a determination of the space group. He suggests probable arrangements for the molecules in the crystal, but the work does not lead to the determination of any atomic positions.

Analysis of the Structure.

The asymmetric unit in the crystal structure consists of one half molecule. The dimensions of the a and b axes are almost identical with those of adipic acid q.v., so it is reasonable to suppose that the molecular arrangement in the two acids will be similar, the additional four carbon atoms in the chain of sebacic acid being accommodated by the increased c axis, and almost parallel to it. The similarity of the b axes in the two acids also indicates that the tilt of the molecule to the (010) plane should be approximately the same.

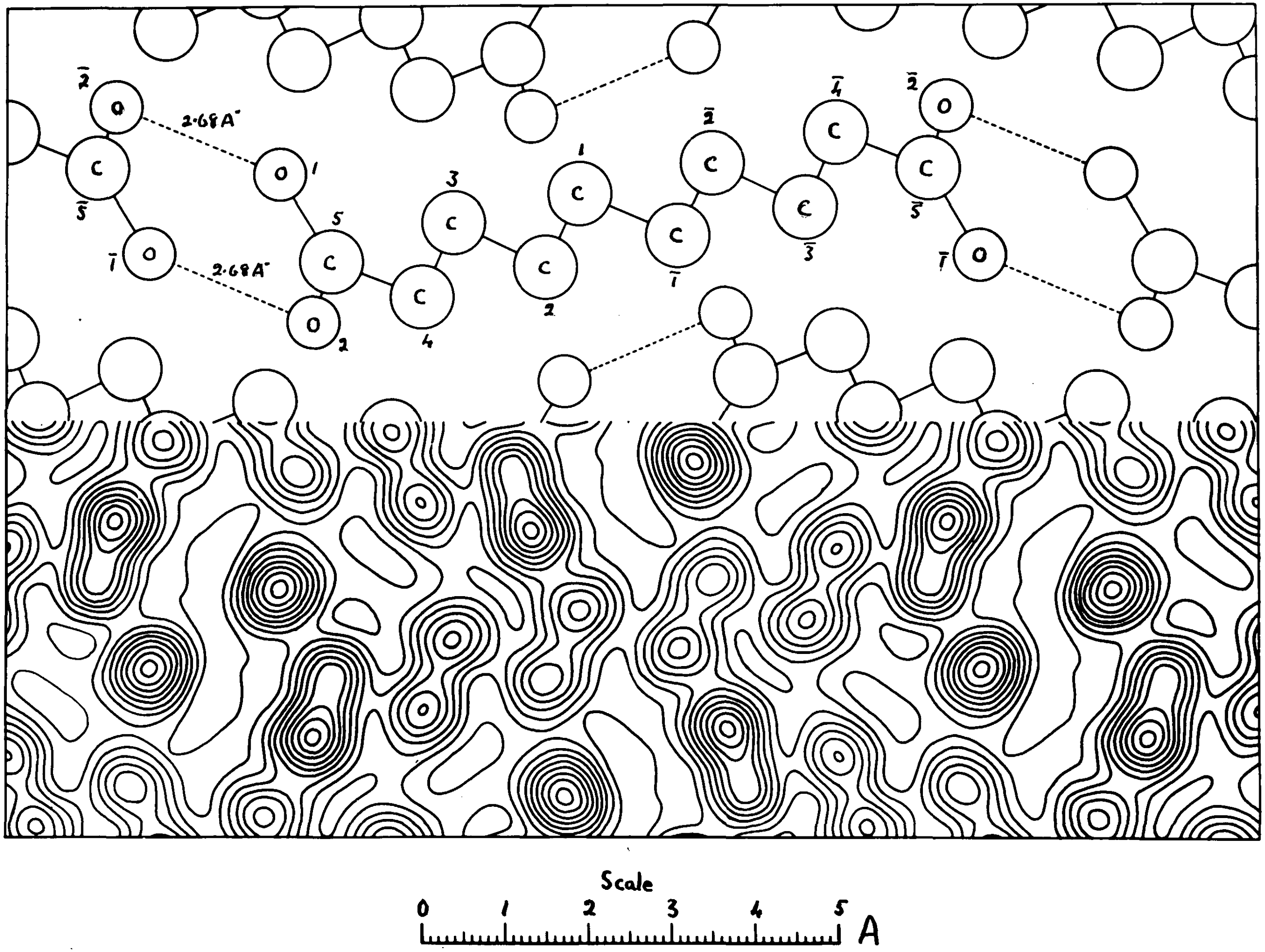
From a consideration of these facts, and an examination of the planes of outstanding intensity, notably the (200), (006), $(40\bar{6})$, $(40\overline{12})$, $(20\bar{6})$ and $(20\overline{12})$, it was possible to find by trial, a structure which gave fair agreement between calculated and measured structure factors. In this structure the whole molecule was assumed to be planar. The

Figure 11.



Projection of structure on (010) plane

Figure 12.



Projection of structure along [101] diagonal axis.

The coordinates of this were then refined by successive Fourier syntheses, giving projections of the structure on the (010) plane. The final projection is shown in Figure 11, and from it accurate values of the x and z coordinates for all the atoms except C_5 and O_1 are obtained.

The y coordinates were then also obtained by trial, and checked by another Fourier projection made along the [101] axis using the $hk\bar{h}$ structure factors. This is shown in Figure 12. All the atoms are resolved except C_5, the position of which is again uncertain. The information given by this projection is not of such high accuracy, owing to the fact that the atoms are very crowded in projection, causing the peaks to be somewhat spread out. Nevertheless, the two projections together give a fairly precise picture of the whole molecular structure.

Orientation, Coordinates and Dimensions.

The mid points of the seven central carbon - carbon bonds in the molecule are found to lie in a straight line. This line was accordingly chosen as the principal molecular axis (L). Within experimental error (±0.03 Å) the central eight carbon atoms are coplanar, so the second molecular axis (M) was chosen to lie in this plane, at right angles to (L). (N) is

Table 13.

Orientation of the molecule in the crystal.

$\chi_L = 50.3^\circ$ $\cos\chi_L = 0.639$ $\chi_M = 63.3^\circ$ $\cos\chi_M = 0.449$

$\psi_L = 98.2^\circ$ $\cos\psi_L = -0.142$ $\psi_M = 29.9^\circ$ $\cos\psi_M = 0.867$

$\omega_L = 40.9^\circ$ $\cos\omega_L = 0.756$ $\omega_M = 102.6^\circ$ $\cos\omega_M = -0.218$

$\chi_N = 51.5^\circ$ $\cos\chi_N = 0.623$

$\psi_N = 118.6^\circ$ $\cos\psi_N = -0.478$

$\omega_N = 128.2^\circ$ $\cos\omega_N = -0.619$

Table 14.

Coordinates of atoms w.r.t. crystallographic axes

Atom	x Å	y Å	z Å	x'Å	z'Å	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
C_1	-0.221	0.270	0.553	0.604	0.399	-7.9°	19.4°	13.2°
C_2	0.387	-0.630	2.088	1.059	1.507	13.8°	-45.4°	49.8°
C_3	0.036	-0.094	3.252	2.217	2.346	1.3°	-6.8°	77.5°
C_4	0.650	-1.000	4.757	2.646	3.433	23.2°	-72.0°	113.4°
C_5	0.353	-0.570	5.978	3.789	4.313	12.6°	-41.0°	142.5°
O_1	-0.501	0.480	5.623	4.396	4.057	-17.9°	34.6°	134.1°
O_2	1.040	-1.320	7.348	4.050	5.302	37.2°	-95.0°	175.2°

Table 15.

Coordinates of atoms w.r.t. molecular axes. (A).

Atom	L	M	N
C_1	0.650	0.418	0.001
C_2	1.907	-0.397	0.030
C_3	3.184	0.405	-0.023
C_4	4.431	-0.423	0.008
C_5	5.769	0.270	-0.031
O_1	5.816	1.508	0.004
O_2	6.789	-0.476	-0.119

the axis at right angles to (L) and (M).

The orientation of the molecule can be expressed by the angles which these molecular axes (L), (M) and (N) make with the crystallographic axes a, b, and c'. These angles are given in Table 13. The coordinates of the atoms in the asymmetric unit with respect to the crystallographic axes are collected in Table 14. The coordinates of all the other atoms in the unit cell can be derived from these by the usual symmetry operations for the space group. The molecular dimensions and bond lengths calculated from these coordinates are shown in Figure 13. and listed in Table 16.

Table 16.

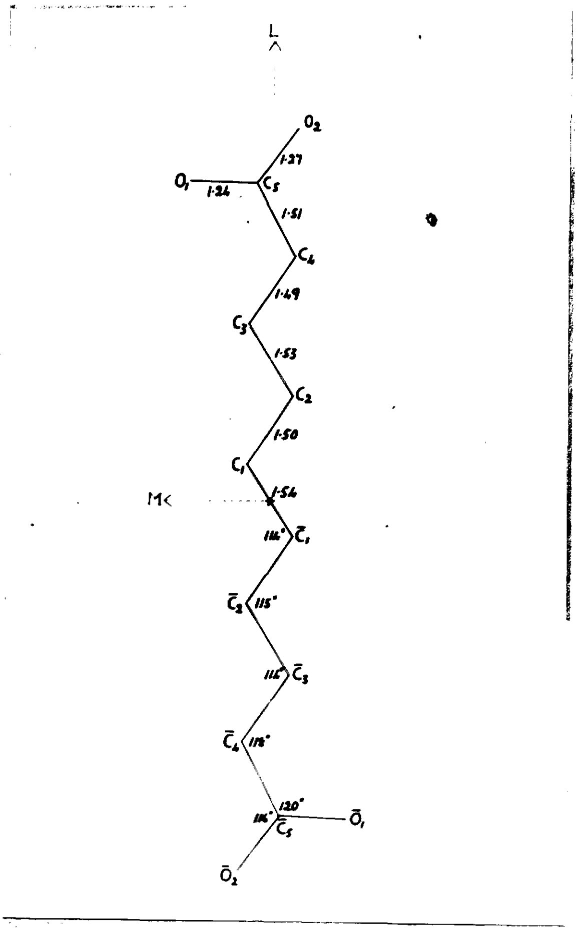
Bond	Length	Bond Angles
$\bar{C}_1 - C_1$	= 1.54±0.02 Å	$\bar{C}_1 - C_1 - C_2$:- 114°
$C_1 - C_2$	= 1.50 "	$C_1 - C_2 - C_3$:- 115°
$C_2 - C_3$	= 1.53 "	$C_2 - C_3 - C_4$:- 114°
$C_3 - C_4$	- 1.49 "	$C_3 - C_4 - C_5$:- 118°
$C_4 - C_5$	= 1.51 "	$C_4 - C_5 - O_1$:- 120°
$C_5 - O_1$	= 1.24 "	$C_4 - C_5 - O_2$:- 116°
$C_5 - O_2$	= 1.27 "	

For convenience the coordinates of the atoms may be expressed with respect to the molecular axes (L), (M), and (N). These coordinates are listed in Table 15.

Atoms C_1, C_2, C_3, C_4 are coplanar, and this plane passes through the centre of symmetry in the middle of the molecule. C_5 is twisted out of this plane, and C_4, C_5, O_1, and O_2 all lie on a plane tilted at C_4 by approximately 3° to the plane of the carbon chain. This new plane passes through the centre of symmetry between this molecule and the next along the c axis, and therefore also contains $C_4^{\overline{II}}$, $C_5^{\overline{II}}$, $O_1^{\overline{II}}$, $O_2^{\overline{II}}$ of that molecule. Atoms $C_4^{\overline{I}}$, $C_5^{\overline{I}}$, $C_5^{\overline{II}}$, $C_4^{\overline{II}}$ are collinear.

Figure 13.

Intramolecular distances.



Intermolecular Distances.

The closest approach between adjacent molecules occurs along the c axis, where hydrogen bridges of 2.68 A are formed between the oxygen atoms of adjacent carboxyl groups. The various distances are shown in Figure 14 and Table 17. The values given are the closest distances between the pairs of atoms. Distances not given are greater than 4.0 A.

Figure 14.

Diagram showing intermolecular distances.

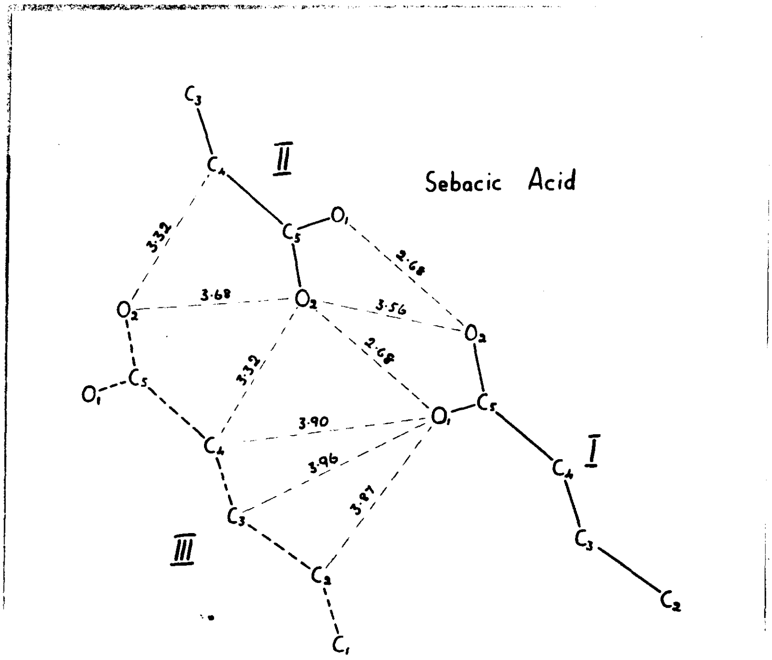


Table 17.

Bond		Distance	Bond		Distance
$O_1^{\bar{I}} - O_2^{\bar{II}}$	=	2.68±0.05A°	$O_2^{\bar{II}} - C_4^{\bar{III}'}$	=	3.78±0.05A°
$O_2^{\bar{I}} - O_1^{\bar{II}}$	=	2.68 "	$O_1^{\bar{I}} - C_2^{\bar{III}}$	=	3.87 "
$O_2^{\bar{II}} - C_4^{\bar{III}}$	=	3.32 "	$O_1^{\bar{I}} - C_4^{\bar{III}}$	=	3.90 "
$O_2^{\bar{I}} - O_2^{\bar{II}}$	=	3.56 "	$O_1^{\bar{I}} - C_3^{\bar{III}}$	=	3.96 "
$O_2^{\bar{II}} - O_2^{\bar{III}}$	=	3.68 "			

Experimental.

X ray Measurements.

Small crystals of suitable dimensions for X ray work were cut from larger fragments with a razor blade. Copper K radiation was used throughout, and rotation, oscillation and moving film photographs of the principal zones were taken.

For the h0l zone, the principal crystal used had cross-section normal to the b axis of 0.30 × 0.11 mm. Absorption corrections were not made, as they were found to make no significant difference to the intensities found. To extend the range of intensities a crystal 1.20 × 0.62 mm was used. The intensities for this, without correction, were found to be in good agreement for the weaker reflections, with those obtained from smaller specimens. Combining these results, 141 out of a possible 145 reflections were recorded. For the hk$\bar{h}$ zone, a specimen 0.55 × 0.45 mm cross-section was employed, and for the 0kl one 0.28 × 0.25 mm.

These crystals were completely immersed in the X ray beam, and the spectra recorded on series of moving films. For measurement of intensities the multiple film technique was used, the total range of intensities recorded being of the order of 25,000 to 1. The sets of intensities for the different zones were correlated by means of their common axial reflections. Their structure factors were calculated from the intensities by the usual formulae, and are listed in Table 19 as F meas. Absolute measurements were not made, and the scale of the F values was obtained on an absolute basis by correlation with the values finally calculated from the atomic positions found.

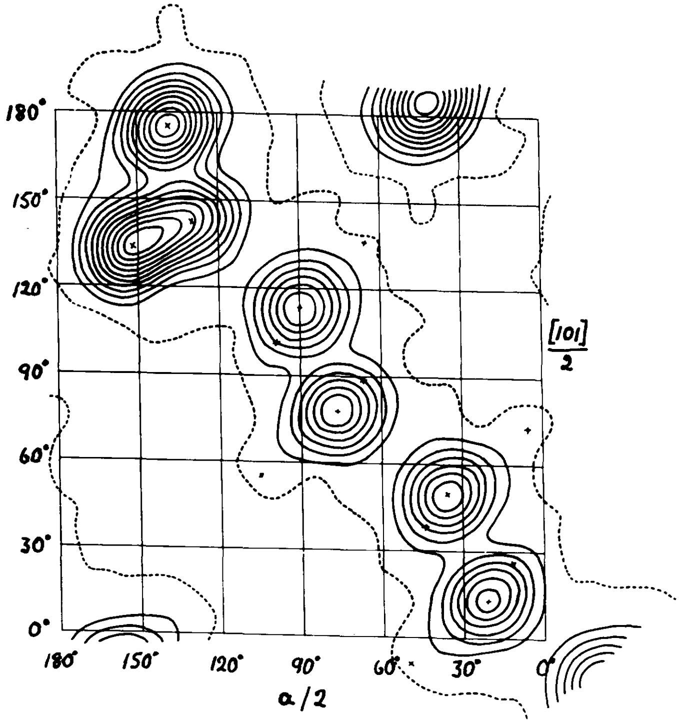
Fourier Analysis.

The structure was first determined by trial, then refined by successive two dimensional Fourier syntheses, giving projections normal to the b axis and the [101] axis.

For the projection along the b axis, the electron density was computed at 900 points on the asymmetric unit, the a and c axes each being divided into 60 parts, giving intervals of 0.168 A along the a axis and 0.252 A° along the c axis. The summations were carried out to three figure accuracy, and the positions of the contour lines plotted in the usual manner. The resulting contour map for the h0l zone is shown in Figure 15, the asymmetric unit being given. The positions assigned to the atoms are marked by small crosses.

Figure 15.

Asymmetric unit, h0l zone.



The projection along the [101] axis was computed similarly; in this case the b axis being divided into 30 parts (intervals of 0.167 Å), and a cos 2.1° into 60 parts (intervals of 0.168 Å).

From the final coordinates, Table 14, all the structure factors were recalculated, the results being given in Table 19. For the earlier calculation of structure factors the composite atomic scattering curve for carbon and oxygen used for benzoquinone (10), loading the oxygen atoms with respect to the carbons by a factor of 1.5 to 1.0 was applied, but, in the final calculations, a new scattering curve was derived and used which gave rather better agreement between F meas and F calc.

Sebacic acid atomic scattering curve.

sinθ (λ'=1.54Å)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f_c	100	85	62	44	33	25	18	13	8.8	5.5

The discrepancies finally obtained, expressed as percentages, are :-

h0l	16.7%
hkh	13.2%
All reflections	15.7%

It is interesting to note that the discrepancy between F meas and F calc for planes of low sinθ value is in one or two cases strikingly bad. Taking a number of planes of $\xi < 0.35$

Plane	F meas	F calc
001	33.5	-47.7
201	11.5	4.1
202	3.0	-0.2
203	13.5	15.3

the disagreement is as shown.

In sebacic acid the percentage of hydrogen atoms is relatively high, and no account is taken of these in calculating the structure factors. For planes of low sinθ value, i.e. of wide spacing, the contributions of the hydrogen atoms to the coherent scattering may reach appreciable levels. Accordingly, coordinates were assigned to the hydrogen atoms attached to the carbon chain, assuming a C-H distance of 1.09 A° and 109° between the two C-H bonds of each carbon.

Table 18.

Coordinates of hydrogen atoms w.r.t. crystallographic axes.

Atom	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
H_1	-59°	30°	-9°
H_2	14°	88°	26°
H_3	-6°	-112°	38°
H_4	66°	-55°	72°
H_5	-50°	3°	55°
H_6	22°	61°	89°
H_7	1°	-140°	101°
H_8	75°	-82°	136°

These positions are indicated in Figure 15 by small crosses, and are consistent with the variations in the one and two electron contour lines. On recalculation of the structure factors, including the contribution of the hydrogen atoms, and using the experimentally determined carbon scattering curve weighted for hydrogen in the ratio 1:6, a marked improvement was seen in the discrepancy for planes of low sinθ value; for planes of sinθ value greater than about 0.4 it appeared to lead only to random fluctuations in the F values. Accordingly, the hydrogens were assigned an atomic scattering curve which fell off to zero more rapidly than carbon.

Atomic scattering curve for hydrogen. (including temp. factor)

sinθ (λ=1.54A°)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f_H	100	83	58	36	20	8.7	2.9	0	0	0

The F values for all planes of sinθ value < 0.4 are listed in Table 20 with and without correction for the hydrogen contribution. For these planes without correction for the hydrogens the percentage discrepancy is 13.8%, with correction this falls to 8.4%. For sinθ values >0.4 the contributions of the hydrogen atoms appear to be too small to materially affect the F values. The coordinates of the carbon atoms were now varied, to see whether their positions might have been perturbed by the hydrogens, but within experimental error this was not found to be the case.

The effect of the hydrogen contribution to the planes of low sinθ value has been reported before, (11), but this would seem to be the first case where it is shown to such a marked degree.

Table 19

Measured and calculated structure factors.

		F	
hkl	sinθ	meas	calc
200	.212	94.0	99.5
400	1423	15.5	18.0
600	.635	1.0	-1.5
800	.846	1.5	-1.0
001	.070	33.5	-47.5
002	.141	11.0	17.0
003	.212	4.0	4.5
004	.282	9.5	-9.5
005	.353	8.0	7.0
006	.423	18.5	16.5
007	.494	15.0	-14.0
008	.564	13.5	14.0
009	.635	8.5	-8.5
0010	.705	5.0	5.0
0011	.776	10.0	-9.5
0012	.846	5.0	-5.5
0013	.917	2.0	1.5
0014	.987	0.5	0.0
020	.308	2.0	1.5
040	.616	<2.5	-2.0
060	.924	2.0	-3.0
2011	.938	4.0	-4.5
2010	.868	1.0	-0.0
209	.798	<1.0	-1.5
208	.728	4.0	6.0
207	.659	8.0	-10.0
206	.588	10.5	15.5
205	.521	8.5	8.5
204	.455	7.5	-6.5
203	.388	9.0	8.5
202	.323	2.5	-2.0
201	.263	18.5	-17.5
$20\bar{1}$	.171	11.5	4.0
$20\bar{2}$	.154	3.0	-0.0
$20\bar{3}$	.168	13.5	15.5
$20\bar{4}$	.206	23.5	-28.5
$20\bar{5}$	.259	25.5	26.0
$20\bar{6}$	.319	19.5	-19.0
$20\bar{7}$	.383	<0.5	0.0
$20\bar{8}$	.448	9.5	8.0
$20\bar{9}$	.514	10.5	-9.0
$20\overline{10}$	.584	7.0	4.5
$20\overline{11}$	.653	8.0	-7.5
$20\overline{12}$	.720	21.5	-19.5
$20\overline{13}$	.789	9.5	8.5
$20\overline{14}$	.858	4.5	-4.0
$20\overline{15}$	.928	1.5	1.0
409	.978	1.5	1.5
408	.910	1.0	-0.5
407	.845	1.0	-1.0
406	.780	2.0	4.0
405	.715	10.0	11.0
404	.653	4.0	-4.0
403	.589	6.0	8.5
402	.530	9.5	-11.0
401	.478	5.0	6.5
$40\bar{1}$	.380	26.0	29.0
$40\bar{2}$	.344	9.0	-8.0
$40\bar{3}$	.319	10.0	11.5
$40\bar{4}$	.308	25.0	-25.0
$40\bar{5}$	.314	32.5	33.5
$40\bar{6}$	.335	59.0	-48.0
$40\bar{7}$	.369	10.0	11.0
$40\bar{8}$	.410	1.0	0.5
$40\bar{9}$	.463	7.5	-7.0
$40\overline{10}$	.518	7.5	-5.5
$40\overline{11}$	.576	6.0	-4.5
$40\overline{12}$	.638	36.5	-29.0
$40\overline{13}$	.698	11.0	10.5
$40\overline{14}$	.761	8.0	-6.0
$40\overline{15}$	.825	3.0	2.5
$40\overline{16}$	.893	<1.0	0.0
$40\overline{17}$	.960	3.0	-1.0
606	.979	0.5	0.5
605	.918	4.0	5.0
604	.858	2.5	2.0
603	.795	2.5	1.0
602	.740	2.0	-5.0
601	.688	3.5	6.0
$60\bar{1}$	.590	14.5	17.0
$60\bar{2}$	.549	1.0	1.5
$60\bar{3}$	.514	4.0	-4.0
$60\bar{4}$	.488	2.0	-2.5
$60\bar{5}$	.470	11.0	11.5
$60\bar{6}$	.436	29.5	-30.0
$60\bar{7}$	.465	6.0	-6.0
$60\bar{8}$	.479	5.0	5.0
$60\bar{9}$	.503	10.0	-10.0
$60\overline{10}$	.535	11.5	11.0
$60\overline{11}$	.573	10.0	-9.0
$60\overline{12}$	.618	22.5	-19.0
$60\overline{13}$	.668	3.5	-1.0
$60\overline{14}$	.719	1.5	-1.0
$60\overline{15}$	.773	1.0	0.5

		F	
hkl	sinθ	meas	calc
$60\overline{16}$	.831	2.5	2.0
$60\overline{17}$	.891	4.5	-1.5
$60\overline{18}$	.953	7.0	4.0
803	.990	2.5	-1.5
802	.950	<0.5	0.5
801	.900	1.0	1.0
$80\overline{1}$	.803	4.5	4.0
$80\overline{2}$	.758	2.0	5.5
$80\overline{3}$	.720	5.5	-8.5
$80\overline{4}$	.688	6.0	7.0
$80\overline{5}$	.660	3.5	-3.5
$80\overline{6}$	.636	3.5	-6.0
$80\overline{7}$	.623	13.5	-16.5
$80\overline{8}$	.618	5.0	4.5
$80\overline{9}$	.618	5.5	-6.0
$80\overline{10}$	.628	7.5	9.0
$80\overline{11}$	.645	9.0	-9.5
$80\overline{12}$	.670	3.0	-3.5
$80\overline{13}$	.700	11.5	-10.5
$80\overline{14}$	.738	3.5	2.5
$80\overline{15}$	.777	1.0	-0.0
$80\overline{16}$	.823	1.5	1.5
$80\overline{17}$	.873	4.0	-2.5
$80\overline{18}$	.922	12.5	7.0
$80\overline{19}$	.978	4.5	-2.0
$100\overline{2}$	.970	0.5	1.0
$100\overline{3}$	.928	1.0	-2.5
$100\overline{4}$	.889	2.5	4.0
$100\overline{5}$	.858	2.5	-4.0
$100\overline{6}$	.828	1.5	0.5
$100\overline{7}$	.806	9.5	-10.5
$100\overline{8}$	.788	3.0	-2.5
$100\overline{9}$	.776	4.5	3.0
$100\overline{10}$	.770	2.0	0.5
$100\overline{11}$	.771	1.5	-2.5
$100\overline{12}$	.778	1.0	0.5
$100\overline{13}$	.793	8.0	-7.5
$100\overline{14}$	.011	1.0	0.5
$100\overline{15}$	.835	2.5	2.5
$100\overline{16}$	.866	3.0	-4.5
$100\overline{17}$	.902	1.0	1.0
$100\overline{18}$	.940	8.0	4.0
$100\overline{19}$	.983	3.0	0.5
$120\overline{7}$	.990	2.5	-2.5
$120\overline{8}$	.978	2.5	-3.5
$120\overline{9}$	.958	4.0	4.0
$120\overline{10}$	.940	3.0	-2.5

		F	
hkl	sinθ	meas	calc
$120\overline{11}$	.930	1.5	1.5
$120\overline{12}$	.925	1.0	-0.5
$120\overline{13}$	.925	2.0	-1.5
$120\overline{14}$	.930	1.0	-1.0
$120\overline{15}$	.941	2.0	2.0
$120\overline{16}$	.958	2.5	-2.0
$120\overline{17}$	.978	2.5	2.0
011	.170	28.5	-26.6
012	.209	3.0	3.0
013	.262	2.5	-2.0
014	.321	6.5	6.0
015	.384	7.0	1.5
016	.450	16.5	21.0
017	.516	7.5	-7.5
018	.585	<2.5	2.0
019	.654	<2.5	1.5
0110	.721	3.0	-2.0
0111	.788	3.0	-3.0
0112	.861	6.5	7.0
0113	.928	3.0	-2.5
021	.315	27.0	26.0
022	.339	14.5	-11.5
023	.373	11.5	11.5
024	.417	9.0	-7.5
025	.468	28.0	28.0
026	.523	10.0	-13.0
027	.581	<2.5	-2.0
028	.642	<2.5	-0.5
029	.710	<3.0	2.5
0210	.770	3.0	-3.5
0211	.834	<2.5	1.5
0212	.900	5.0	-4.5
0213	.966	<1.5	-0.0
031	.467	3.5	4.0
032	.483	11.5	-12.5
033	.507	5.0	5.0
034	.541	10.0	11.0
035	.581	2.5	3.0
036	.626	3.0	4.0
037	.676	8.0	8.5
038	.729	4.5	-3.5
039	.785	5.0	5.5
0310	.843	<2.5	-4.0
0311	.903	<2.0	2.5
0312	.964	<1.5	0.5

		F	
hkl	sinθ	meas	calc
041	.619	<2.5	-1.0
042	.632	2.5	2.5
043	.351	6.0	-7.5
044	.677	13.5	18.0
045	.709	5.5	-6.6
046	.747	4.5	3.5
047	.789	5.0	-5.5
048	.835	3.5	-3.5
049	.885	3.5	2.0
0410	.936	<2.0	1.5
051	.773	<2.5	1.5
052	.782	<2.5	1.5
053	.798	3.0	4.0
054	.820	2.5	2.5
055	.846	<2.5	-2.0
056	.878	<2.5	1.5
057	.914	<2.0	-0.5
058	.953	2.0	3.0
061	.926	2.0	2.5
062	.934	2.5	-3.0
063	.947	<1.5	-0.5
064	.965	<1.5	0.5
065	.989	<1.0	-0.0
$11\bar{1}$	.189	8.5	5.0
$12\bar{1}$	.326	11.0	-12.5
$13\bar{1}$	.474	4.5	4.0
$14\bar{1}$	.625	2.5	3.5
$15\bar{1}$	.776	5.0	5.0
$16\bar{1}$	.930	<1.0	.0.0
$21\bar{2}$	.218	15.5	15.0
$22\bar{2}$	.344	7.0	7.0
$23\bar{2}$	.486	14.5	-14.5
$24\bar{2}$	.635	5.5	-6.0
$25\bar{2}$	.784	4.0	4.5
$26\bar{2}$	.935	2.5	-2.5
$31\bar{3}$	.277	<1.0	0.5
$32\bar{3}$	.384	14.0	14.0
$33\bar{3}$	.515	4.0	-2.5
$34\bar{3}$	.657	2.0	2.5
$35\bar{3}$	.807	3.5	-3.5
$36\bar{3}$	.950	3.5	3.5

		F	
hkl	sinθ	meas	calc
$41\bar{4}$	.343	8.0	-7.5
$42\bar{4}$	.434	9.0	8.0
$43\bar{4}$	.559	6.5	-7.0
$44\bar{4}$	.687	6.5	5.0
$45\bar{4}$	.827	3.5	4.5
464	.973	2.0	2.5
$51\bar{5}$	.413	10.0	9.0
$52\bar{5}$	.490	10.5	11.0
$53\bar{5}$	.600	4.0	6.5
$54\bar{5}$	.725	8.0	9.0
$55\bar{5}$	.860	<1.5	-1.0
$56\bar{5}$	.999	<0.5	-1.5
$61\bar{6}$	.484	9.5	-11.5
$62\bar{6}$	.553	<1.5	1.5
$63\bar{6}$	.650	2.0	4.5
$64\bar{6}$	.768	<1.5	1.5
656	.895	2.0	-2.0
$71\bar{7}$	.557	9.0	-8.5
$72\bar{7}$	.618	5.5	6.5
$73\bar{7}$	.708	2.5	-4.0
$74\bar{7}$	.815	<1.5	-1.0
$75\bar{7}$	.936	<1.0	-1.0
$81\bar{8}$	.632	6.5	5.5
$82\bar{8}$	.685	12.5	-12.5
$83\bar{8}$	.767	7.5	9.0
$84\bar{8}$	.867	<1.5	1.0
$85\bar{8}$	.934	<0.5	-0.5
$91\bar{9}$	.705	4.5	3.5
$92\bar{9}$	.755	7.0	-6.0
$93\bar{9}$	.830	3.0	-1.5
$94\bar{9}$	.924	<1.0	-0.5
$101\overline{10}$	.780	5.0	6.0
$102\overline{10}$	.824	<1.5	0.0
$103\overline{10}$	.892	<1.5	1.5
$104\overline{10}$	.982	<0.5	0.5
$111\overline{11}$	.855	<1.5	-1.0
$112\overline{11}$	.896	<1.0	-2.0
$113\overline{11}$	.960	<1.0	-1.5
$121\overline{12}$	.930	<1.0	-0.5
$122\overline{12}$	.969	<1.0	-0.5

Table 20

Reflections of $2\sin\theta$ value < 0.8 showing effect of hydrogen contribution.

	F	F	
hkl	meas	calc	calc incl H
200	94.0	99.5	103.0
400	15.0	18.0	19.0
001	33.5	-47.5	-34.5
002	11.0	17.0	12.5
003	4.0	4.5	4.5
004	9.5	-9.5	-9.5
005	8.0	7.0	7.0
020	2.0	1.5	1.5
203	9.0	8.5	9.0
202	2.5	-2.0	-2.0
201	18.5	-17.5	-17.5
$20\bar{1}$	11.5	4.0	11.5
$20\bar{2}$	3.0	-0.0	-4.0
$20\bar{3}$	13.5	15.5	14.0
$20\bar{4}$	23.5	-28.5	-24.5
$20\bar{5}$	25.5	26.0	22.5
$20\bar{6}$	19.5	-19.0	-19.5
$20\bar{7}$	<0.5	0.0	0.5
$40\bar{1}$	26.0	29.0	28.0
$40\bar{2}$	9.0	-8.0	-8.0
$40\bar{3}$	10.0	11.5	11.5
$40\bar{4}$	25.0	-25.0	-24.0
$40\bar{5}$	32.5	33.5	32.0
$40\bar{6}$	59.0	-48.0	-54.5
$40\bar{7}$	10.0	11.0	8.5

	F	F	
hkl	meas	calc	calc incl H
011	28.5	-26.5	-30.0
012	2.0	2.0	3.5
013	2.5	-2.0	-3.0
014	6.5	6.0	6.5
015	7.0	1.5	3.0
021	27.0	26.0	26.5
022	14.5	-11.5	-11.5
023	11.5	11.5	10.5
$11\bar{1}$	8.5	5.0	8.0
$12\bar{1}$	11.0	-12.5	-8.5
$21\bar{2}$	15.5	15.0	14.5
$22\bar{2}$	7.0	7.0	5.0
$31\bar{3}$	1.0	0.5	0.0
$32\bar{3}$	14.0	14.0	15.0
$41\bar{4}$	8.0	-7.5	-8.0
Discrepancy-		13.8%	8.4%

β-Glutaric Acid.

Crystal Data. - β-glutaric acid $C_5H_8O_4$. M. 132.1

m.pt.-97.5°C. D calc = 1.388 D found = 1.400

monoclinic prismatic.

$a = 10.05 \pm 0.03$ Å; $b = 4.87 \pm 0.01$ Å; $c = 17.4 \pm 0.05$ Å;

$\beta = 132.6 \pm 0.4°$

Absent spectra, hkl when h+k+l odd, h0l when h or l odd.

Space group C_{2h}^6 (I2/a), equivalent to A2/a with change of c axis. Four molecules per unit cell.

Molecular symmetry, two fold axis. Volume of the unit cell - 627 $Å^3$.

Absorption coefficient for X rays, (λ = 1.54 Å), μ = 13.0 cms^{-1}.

Total number of electrons per unit cell - F(000) - 280.

The space group Aa is also possible, but this is ruled out by the complete analysis.

Crystal Habit.

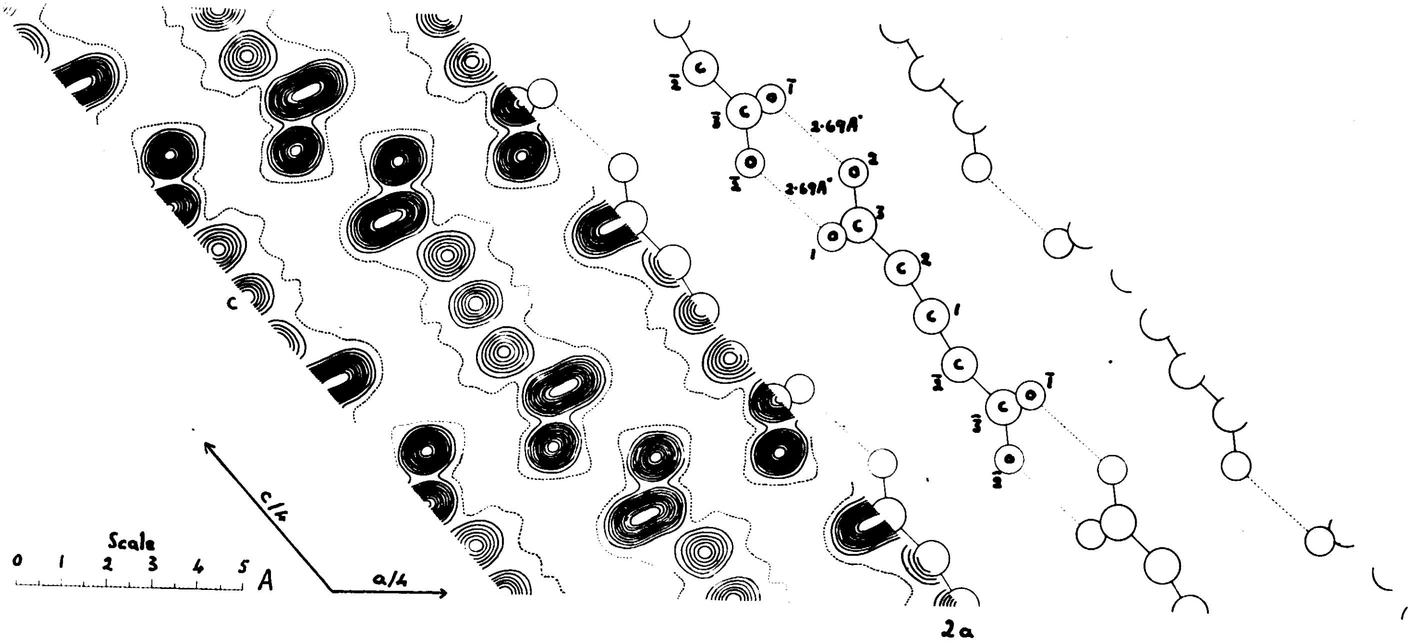
Glutaric acid is very soluble in almost all solvents save benzene, in which it is practically insoluble. The only satisfactory method of obtaining crystals suitable for X ray work proved to be that of making a very concentrated solution in ethyl alcohol, and allowing the alcohol to evaporate off till the syrup solidified. This method gave large, soft, sometimes well formed crystals which could easily be cut to suitable dimensions. Crystals so obtained showed generally well developed (001) and (100) faces, and there was a tendency for elongation along the b axis. There is pronounced cleavage on (111). Further goniometric and optical crystal data are given by Dupré la Tour (12), who has also investigated the crystal structure. He determined the lattice constants and space group, but did not carry the work any farther.

Analysis of the Structure.

The asymmetric unit in the crystal structure consists of one half molecule, with a two fold rotation axis passing through the central carbon atom in the molecule. The dimensions of the a and b axes are very similar to those of adipic and sebacic acids in the even-carbon dicarboxylic acid series and the length of the c axis indicates that the molecules must lie stretched along it in two groups of two, related to one another by the glide plane. Unlike the even acids, the molecule possesses no centre of symmetry. However experience with these even acids indicates that the governing factor in the crystal structure should probably be the possibility of the carboxyl oxygen atoms forming hydrogen bridges of about 2.68 A° between the ends of adjacent molecules.

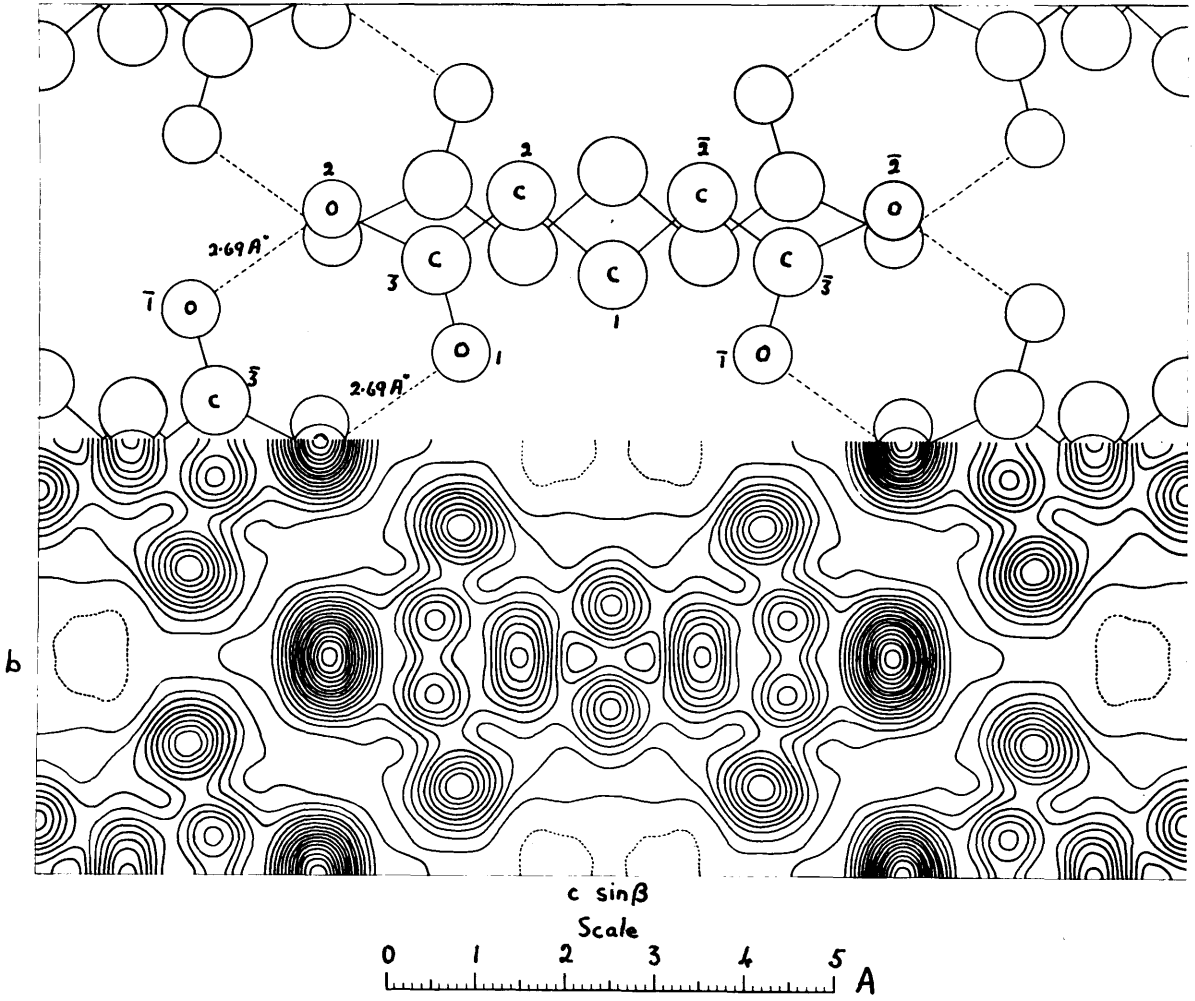
Taking into account also the fact that the lattice

Figure 16



Projection of structure on (010) plane.

Figure 17



Projection of structure along [a] axis.

is centred, and considering the strongest reflections, it proved a matter of no great difficulty to postulate a trial structure which gave fair agreement between observed and calculated structure factors. The coordinates of this were then refined by successive Fourier syntheses, giving projections of the structure on the (010) plane. The final projection obtained is shown in Figure 16, from which accurate values of the x and z coordinates for three of the atoms are obtained.

The y coordinates were also obtained by trial, and another Fourier projection made along the a axis using the 0kl structure factors. This is shown in Figure 17. The z coordinates can be obtained for all the atoms, and the y coordinates for C_1 , C_3 and O_1 accurately. Atoms C_2 and O_2 can not be determined with such precision.

A projection along the [101] axis was also tried, using the $hk\bar{h}$ structure factors, but no satisfactory resolution was obtained. Nevertheless, the atomic coordinates arrived at are of a fair degree of accuracy.

Orientation, Coordinates and Dimensions.

The straight line joining the mid points of the two central carbon-carbon bonds in the molecule was chosen as the principal axis (L) of the molecule.

Table 21.

Orientation of the molecule in the crystal.

$\chi_L = 57.9°$	$\cos\chi_L = 0.533$	$\chi_M = 90.0°$	$\cos\chi_M = 0.000$
$\psi_L = 90.0°$	$\cos\psi_L = 0.000$	$\psi_M = 0.0°$	$\cos\psi_M = 1.000$
$\omega_L = 32.1°$	$\cos\omega_L = 0.847$	$\omega_M = 90.0°$	$\cos\omega_M = 0.000$

$\chi_N = 142.9°$	$\cos\chi_N = -0.847$
$\psi_N = 90.0°$	$\cos\psi_N = 0.000$
$\omega_N = 57.9°$	$\cos\omega_N = 0.533$

Table 22.

Coordinates of atoms w.r.t. crystallographic axes.

Atom	x A°	y A°	z A°	x'A°	z'A°	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
C_1	0.000	0.593	0.000	0.000	0.000	0.0°	43.8°	0.0°
C_2	0.299	-0.288	1.138	0.666	1.053	10.7°	-21.2°	29.7°
C_3	0.168	0.419	2.682	1.647	1.980	6.0°	31.0°	55.5°
O_1	-0.657	1.474	2.296	2.207	1.694	-23.5°	109.0°	47.5°
O_2	1.068	-0.149	4.253	1.810	3.139	38.2°	-11.0°	88.0°

Table 23.

Coordinates of atoms w.r.t. molecular axes. (A).

Origin at (0·000 , 0·152 , 0·000) w.r.t. origin of crystal. axes

Atom	L	M	N
C_1	0.000	0.441	0.000
C_2	1.242	-0.441	0.000
C_3	2.547	0.267	0.333
O_1	2.607	1.322	0.960
O_2	3.603	-0.302	-0.147

The second molecular axis (M) was chosen as the line at right angles to (L) in the plane of the three central carbon atoms (i.e. it coincides with the crystallographic b axis). (N) is the axis at right angles to (L) and (M).

The orientation of the molecule, expressed by the angles these molecular axes make with the crystallographic axes a, b, and c' are listed in Table 21. The coordinates of the atoms in the asymmetric unit with respect to the crystallographic axes are collected in Table 22. The coordinates of all the other atoms in the unit cell can be obtained from these by the usual symmetry relations.

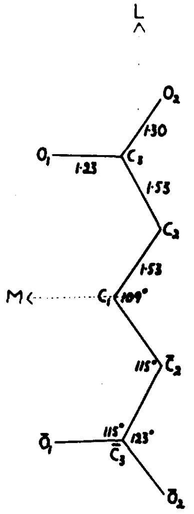
The molecular dimensions and bond lengths calculated from these coordinates are shown in Figure 18 and listed in Table 24.

The coordinates of the atoms with respect to the molecular axes are gathered in Table 23.

The carboxyl groups are planar (atoms C_1, C_3, O_1, O_2), but are tilted out of the plane of the three methylene groups by about 32°, a value very much greater than the corresponding tilt in even carbon acids.

Figure 18.

Intramolecular distances.



Glutaric Acid

Table 24.

Bond	Length	Bond Angles
$C_1 - C_2$	= 1.53±0.02 A°	$\bar{C}_2 - C_1 - C_2$:- 109°
$C_2 - C_3$	= 1.53 "	$C_1 - C_2 - C_3$:- 115°
$C_3 - O_1$	= 1.23 "	$C_2 - C_3 - O_1$:- 123°
$C_3 - O_2$	= 1.30 "	$C_2 - C_3 - O_2$:- 115°

Intermolecular Distances.

The hydrogen bonding between adjacent carboxyl groups along the c axis is again the closest approach between different molecules. The distances are listed in Table 25 and shown in Figure 19.

Figure 19.

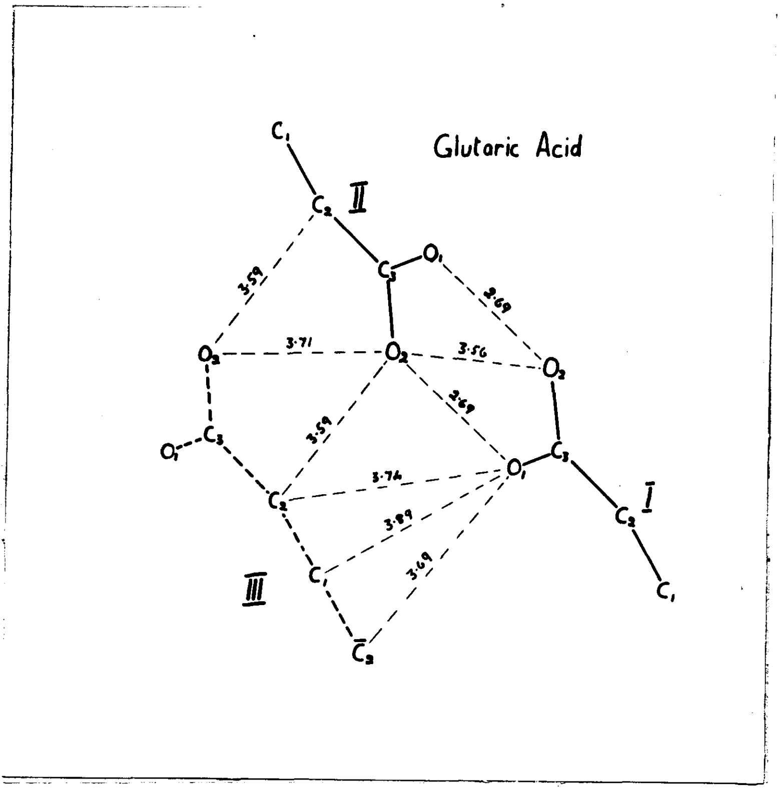


Table 25.

Bond	Distance	Bond	Distance
$O_1^{I} - O_2^{II}$ =	2.69±0.05A°	$O_1^{I} - C_2^{III}$ =	3.74±0.05A°
$O_2^{I} - O_1^{II}$ =	2.69 "	$O_2^{II} - C_2^{III'}$ =	3.77 "
$O_2^{II} - C_2^{III}$ =	3.59 "	$O_2^{II} - O_2^{III}$ =	3.71 "
$O_1^{I} - \bar{C}_2^{III}$ =	3.69 "	$O_1^{I} - C_1^{III}$ =	3.89 "

Experimental.

X ray Measurements.

Suitable crystals were cut from larger fragments. Copper Kα radiation was used throughout, rotation, oscillation and moving film photographs being taken of the principal zones.

For the h0l zone, the principal crystal used had cross-section normal to the b axis of 0.14 × 0.25 mm. Absorption corrections were not made, as the crystal dimensions made them unnecessary. To increase the range of intensities covered, a larger crystal 0.28 × 0.50 mm was employed. The intensities from this, without coorection, were in good agreement with those from smaller specimens. Combining these, 80 out of a possible 86 reflections were recorded.

For the 0kl zone, a specimen 0.45 × 0.28 mm cross-section was employed, and for the $hk\bar{h}$ zone one 0.68 × 0.58 mm.

These crystals were completely immersed in the X ray beam, and the spectra recorded on series of moving films. The total range of intensity covered was of the order of 10,000 to 1. The intensities for the different zones were correlated, and the structure amplitudes calculated from them in the usual manner. They are listed as F meas. in Table 26. Absolute measurements were not made, and the F values obtained on an absolute scale by comparison with the final F's calculated.

Fourier Analysis.

The structure was first determined by trial, then refined by successive two dimensional syntheses, giving projections of the structure normal to the a and b axes. For the projection along b, the electron density was computed at 450 points on the asymmetric unit, the a and c axes each being divided into 60 parts, - intervals of 0.167 A° on a and 0.290 A° on c. The final summations were carried out to three figure accuracy, and the contour maps of the electron density drawn in the same manner as for the other acids. The asymmetric unit for the h01 zone, one eighth of the unit cell, is given in Figure 21, the final atomic centres chosen being marked by small crosses.

The a axis projection was computed similarly, in this case b being divided into 30 parts of 0.167 A° and a sinβ into 60 parts of 0.214 A°. The finally calculated structure factors are listed in Table 26.

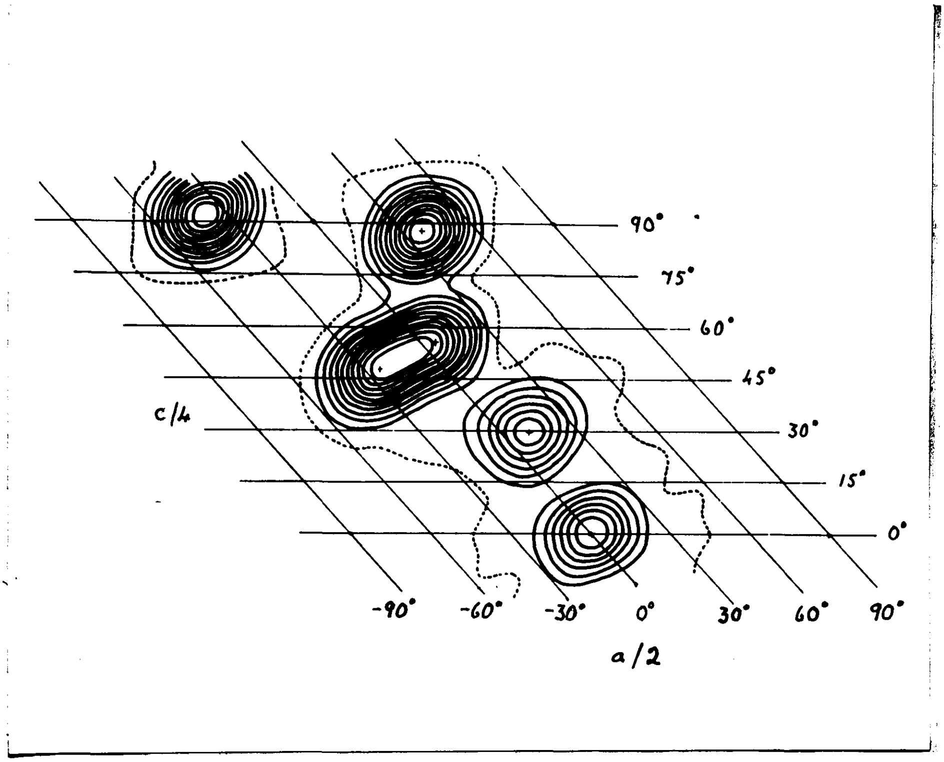
For these final calculations a new composite atomic scattering curve was derived which gave best agreement between F meas and F calc, loading oxygen as before.

New glutaric acid atomic scattering curve.

$\sin\theta$ (λ=1.54Å)	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

Figure 21.

Asymmetric unit, h0l zone, showing positions assigned to atoms.



The discrepancies finally obtained for the various zones were :-

h0l	18.5%
0kl	14.5%
All reflections	18.6%

Table 26.

Observed and calculated structure factors.

		F	
hkl	sinθ	meas	calc
200	.208	96.5	115.5
400	.416	9.5	10.0
600	.624	2.0	-4.5
800	.832	5.0	2.5
002	.119	28.0	-37.5
004	.238	20.0	-19.5
006	.357	15.5	-13.5
008	.476	41.5	39.0
0010	.595	22.0	-20.5
0012	.714	18.0	15.5
0014	.833	7.5	5.5
0016	.952	3.5	4.0
020	.312	30.5	32.5
040	.624	3.0	3.5
060	.936	3.5	-0.5
2014	.995	<.5	0.0
2012	.875	9.0	6.5
2010	.758	3.5	1.0
208	.640	20.0	19.5
206	.524	11.0	-11.0
204	.413	24.0	-24.0
202	.304	15.0	15.5
$20\bar{2}$	.155	6.5	-9.5
$20\bar{4}$	.185	30.0	-38.0
$20\bar{6}$	.270	42.0	42.0
$20\bar{8}$	.374	10.0	9.0
$20\overline{10}$	.486	23.5	-22.5
$20\overline{12}$	.599	15.0	11.5
$20\overline{14}$	.717	29.0	28.5
$20\overline{16}$	.833	7.5	-4.0
$20\overline{18}$	.957	3.5	-2.5
4010	.935	4.5	8.0
408	.822	4.5	-2.5
406	.711	6.0	3.0
404	.603	19.5	-21.0
402	.504	24.0	29.0
$40\bar{2}$	.346	25.0	30.0
$40\bar{4}$	.309	29.0	-29.0
$40\bar{6}$	.317	71.5	70.5
$40\bar{8}$	.368	45.5	-38.0
$40\overline{10}$	.444	10.0	-8.5
$40\overline{12}$	.537	14.5	8.0
$40\overline{14}$	.639	49.0	44.5
$40\overline{16}$	.744	21.5	-16.5
$40\overline{18}$	.861	1.5	.5
$40\overline{20}$	.974	1.5	.5

		F	
hkl	sinθ	meas	calc
606	.909	4.0	3.0
604	.807	2.5	-3.5
602	.712	5.0	8.0
$60\bar{2}$	.548	21.0	21.5
$60\bar{4}$	.493	< 1.5	8.5
$60\bar{6}$	.462	24.5	24.5
$60\bar{8}$	.463	28.0	-25.5
$60\overline{10}$	.493	12.0	-7.5
$60\overline{12}$	.551	25.0	20.5
$60\overline{14}$	.623	26.5	28.0
$60\overline{16}$	.707	11.5	-8.5
$60\overline{18}$	.808	<1.0	0.0
$60\overline{20}$	.910	10.5	6.0
802	.918	4.5	-6.5
$80\bar{2}$	.755	7.5	9.0
$80\bar{4}$	.690	11.0	22.0
$80\bar{6}$	.643	8.0	-10.5
$80\bar{8}$	.615	6.5	4.0
$80\overline{10}$	.612	14.0	-14.5
$80\overline{12}$	.633	22.0	23.0
$80\overline{14}$	.672	2.0	-1.0
$80\overline{16}$	.729	13.0	10.5
$80\overline{18}$	.804	2.5	-1.5
$80\overline{20}$	.888	15.0	9.5
$80\overline{22}$	.981	13.0	-5.0
$100\bar{2}$	.959	3.0	4.0
$100\bar{4}$	.891	1.5	8.0
$100\bar{6}$	.835	5.5	-9.0
$100\bar{8}$	.793	7.0	9.5
$100\overline{10}$	.769	5.5	-4.0
$100\overline{12}$	.763	3.0	3.5
$100\overline{14}$	.775	2.0	-2.0
$100\overline{16}$	.805	12.5	12.5
$100\overline{18}$	.854	1.5	3.5
$100\overline{20}$	.915	5.0	2.5
$100\overline{22}$	.988	<1.0	-3.0
$120\bar{8}$	.982	1.0	2.0
$120\overline{10}$	.945	<1.0	2.5
$120\overline{12}$	.922	6.0	-7.5
$120\overline{14}$	.914	6.0	5.0
$120\overline{16}$	.922	5.0	5.0
$120\overline{18}$	.946	3.5	4.5
$120\overline{20}$	.985	<1.0	5.0

		F	
hkl	sinθ	meas	calc
011	.168	50.0	47.5
013	.239	5.0	-6.0
015	.336	3.5	3.0
017	.445	10.5	-6.5
019	.558	4.5	-1.0
0111	.671	5.0	6.0
0113	.789	15.0	15.0
0115	.904	4.5	-3.0
022	.335	30.5	-22.0
024	.394	34.5	33.0
026	.475	27.0	-25.0
028	.569	<3.5	-1.0
0210	.672	7.5	-7.5
0212	.779	17.5	18.5
0214	.890	3.0	-4.5
031	.473	11.0	9.5
033	.502	17.5	-17.0
035	.555	13.0	-11.5
037	.626	<4.0	1.5
039	.711	<4.0	3.5
0311	.804	6.0	-9.0
0313	.903	<3.0	-1.5
042	.636	7.5	-13.0
044	.668	<4.0	4.5
046	.718	13.5	-12.5
048	.785	<3.5	5.0
0410	.863	<3.0	-4.5
0412	.948	<2.5	-1.0
051	.781	11.5	-13.5
053	.799	8.0	8.5
055	.834	<3.5	4.0
057	.883	7.5	-8.0
059	.945	<2.5	-0.0

		F	
hkl	sinθ	meas	calc
062	.943	<2.5	-1.5
064	.965	<2.0	2.0
$12\bar{1}$	.323	12.0	-5.0
$22\bar{2}$	.348	22.0	-24.5
$32\bar{3}$	.389	19.5	-12.0
$42\bar{4}$	.439	27.5	-27.5
$52\bar{5}$	.496	8.0	-7.5
$62\bar{6}$	.560	2.5	-1.0
$72\bar{7}$	.623	16.5	-18.0
$82\bar{8}$	.691	9.5	14.5
$92\bar{9}$	.759	8.0	7.5
$102\overline{10}$	.831	10.0	15.0
$112\overline{11}$	.902	<1.5	-1.0
$122\overline{12}$	.974	<1.0	-2.5
$14\bar{1}$	.628	5.0	-5.0
$24\bar{2}$	.641	5.5	6.5
$34\bar{3}$	.664	10.0	12.5
$44\bar{4}$	.695	2.5	-7.0
$54\bar{5}$	.733	9.0	11.0
$64\bar{6}$	.776	5.0	1.0
$74\bar{7}$	.824	2.0	3.0
$84\bar{8}$	.876	2.5	-2.0
$94\bar{9}$	.931	4.5	3.5
$104\overline{10}$	.990	<1.0	1.0
$16\bar{1}$	.940	9.0	-6.5
$26\bar{2}$	.950	2.0	2.5
$36\bar{3}$	.966	<1.0	-2.5
$46\bar{4}$	.987	<1.0	0.5

<u>Note</u> The origin of the crystal coordinates given on page 59 was taken at the intersection of the glide plane and the two fold axis of the molecule, and the h0l and 0kl structure factors were calculated on this basis. For the $hk\bar{h}$ zone, for simplicity in calculation, a new origin was taken at $00\frac{1}{4}$ w.r.t. the first. Neither of these are true centres of symmetry, but apparent ones in projection.

Analysis of the Method.

Before commencing any detailed discussion on the significance of the results obtained in this work, it might be of value first to define clearly the limitations of the methods of analysis used.

The Fourier method has been very fully described in the literature (13), and is so well known that no detailed description of it is necessary. The results obtained are in the form of contour maps of the density distribution of the orbital electrons of the atoms in the crystal lattice, this taking the form of a triple Fourier series. More often, projections of the electron density obtained from double Fourier series are employed, these entailing very much less work, and, providing the atoms are resolved, not a very great sacrifice of accuracy.

Critical treatments have been made of the errors likely to arise in two-dimensional syntheses (14), and the conclusions drawn are that convergence of the Fourier series employed is more important than extreme accuracy of intensity measurements. The probable error in bond measurements when the series is reasonably convergent and carefully estimated intensities are employed is of the order of 0.01 to 0.03 A.

The ultimate criterion which has been used for judging the accuracy of a structure obtained from Fourier projections is the discrepancy between observed and calculated structure factors, expressed by the formula :-

$$\% \text{ Discrepancy} = \frac{\sum ||F_{meas}| - |F_{calc}||}{\sum |F_{calc}|} \times 100$$

In well resolved projections, this function is fairly sensitive to changes in atomic coordinates, but with less well resolved cases, where a certain amount of lattitude is possible in assigning the centres of the atoms, it also unfortunately seems to become less sensitive.

The value of the discrepancy also depends on the atomic scattering factors employed in the calculation of the structure amplitudes, and on the thermal factors. Throughout the present work, curves combining these have been derived from the experimental data and used. They show slight differences from one another for the different substances, but all appear to have a somewhat higher temperature factor than that observed in aromatic compounds containing carbon and oxygen such as benzoquinone (15), i.e. they fall off more rapidly with increase in $2\sin\theta$ value.

The use of a composite curve for carbon and oxygen, loading the oxygen atoms by a constant factor, simplifies the calculation of structure factors, but it can be seen from the discrepancies obtained in the four acids, that as the amount of oxygen with respect to carbon becomes greater, the approximation becomes less satisfactory, and the discrepancy rises.

Acid		Overall discrepancy
Sebacic	$C_{10}O_4$	15.7%
Adipic	C_6O_4	17.4%
Glutaric	C_5O_4	18.6%
Succinic	C_4O_4	22.5%

There is the possibility that the atomic scattering curve is not symmetrical, but varies for different planes in the structure, and in addition as has been demonstrated in the case of sebacic acid, when the proportion of hydrogen atoms in the structure becomes appreciable, the contribution of these to the coherent scattering becomes large, and can not be neglected.

In the present studies, mathematical corrections of the results by the methods advocated by Booth (16) have not been carried out. The intensities have been carefully measured, to an accuracy estimated to be within 10% and in each zone almost all the reflections possible with Cu K radiation have been recorded, making the series fairly complete. Hence an accuracy of about 1-2% in bond distances is quoted. It is considered that any improvement on the figures obtained will only be gained by full three-dimensional syntheses.

The use of the discrepancy as a measure of the accuracy of a structure when applied to the two-dimensional case has been criticised (16), and may not be strictly accurate. The figures for it which have been obtained are sufficiently low to make it unlikely that any very great error is present, nevertheless, the bond length variations which are dealt with in the following discussion, and which are not so very much greater than the quoted experimental error, must be treated with caution, and any theories based on them regarded as tentative, until they have been confirmed by three-dimensional work.

Discussion.

General Structural Outlines.

The first step in discussing the structures which have been worked out in the present analyses must be to show their relationship to the series as a whole. The general formula of these acids is $COOH(CH_2)_nCOOH$ and the parent member of the series can be considered to be the anhydrous form of oxalic acid, none of the other acids possessing water of crystallisation.

The first three members of the series, oxalic, malonic, and succinic acids, have widely differing unit cells and crystal structures. From glutaric acid upwards, however, the acids form a well defined and closely related crystallographic series, composed of two subgroups, the acids with an even and those with an odd number of carbon atoms in the molecule. The dimensions of the a and b axes, and the angle β for both groups are similar, the only variant being the c axis with increasing chain length. The even acids have two molecules in the unit cell, while the odd acids, having no molecular centre of symmetry, require four.

The crystallography of the lower members of the series is further complicated by the fact that they exhibit dimorphism, and at temperatures below their melting points change into a second crystal modification. There is some evidence that the higher members of the series may also do this (17), but it has not been verified, and may be considered doubtful.

The most recent cell measurements of the series are given in Table 27, the values being for the modifications stable at ordinary temperatures. Where dimorphism occurs, the form stable at room temperature is given the prefix β-.

Table 27.

Acid	a	b	c	β	Space Group	No of mols /unit cell	
β-Oxalic	5.30	6.09	5.51	115°30'	$P2_1/c$	2	(H)
β-Malonic	5.14	5.33	8.36	104°	P_1	2	(G)
β-Succinic	5.10	8.88	7.61	133°37'	$P2_1/a$	2	(M)
β-Glutaric	10.05	4.87	17.40	132°35'	I2/a	4	(M)
Adipic	10.07	5.16	10.03	137°5'	$P2_1/a$	2	(M)
Pimelic	9.93	4.82	22.12	130°40'	$P2_1/a$	4	(C)
Suberic	10.12	5.06	12.58	135°0'	$P2_1/a$	2	(C)
β-Azelaic	9.72	4.83	27.14	129°30'	$P2_1/m$	4	(C)
Sebacic	10.10	5.00	15.10	133°50'	$P2_1/a$	2	(M)

(H) - Hendricks (18)

(G) - Gerstäcker, Möller and Reis (19)

(C) - Caspari (20)   (M) - checked in present work.

The variation in structure of the first three acids is probably due to the fact that there is strong interaction between the carboxyl groups of the same molecule in oxalic acid. On interference with this by the interposition of first one, then two methylene groups, there will presumably be large changes in intramolecular forces, and consequently in crystal packing. By the time glutaric is reached, this direct interaction effect through space will be very much reduced, and the further addition of methylene groups will cause only the regular lengthening of the c axis actually observed.

This similarity shown in the cell dimensions is farther borne out by the detailed structure examination. The h0l and 0kl zones for an even and odd acid are shown in diagram 22.

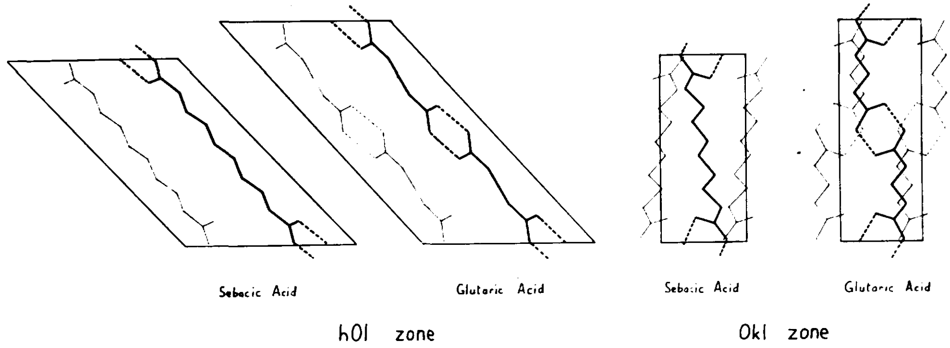


Diagram 22.

The unit of packing in the even acids is one molecule, in the odd acids it is two molecules end to end, but otherwise the arrangement of atoms and hydrogen bonds etc, is very similar.

In all these acids, the hydroxyl groups 2 of the carboxyl groups interleave to produce a structure of rigid layers of oxygen atoms, which are separated from each other by methylene chains.

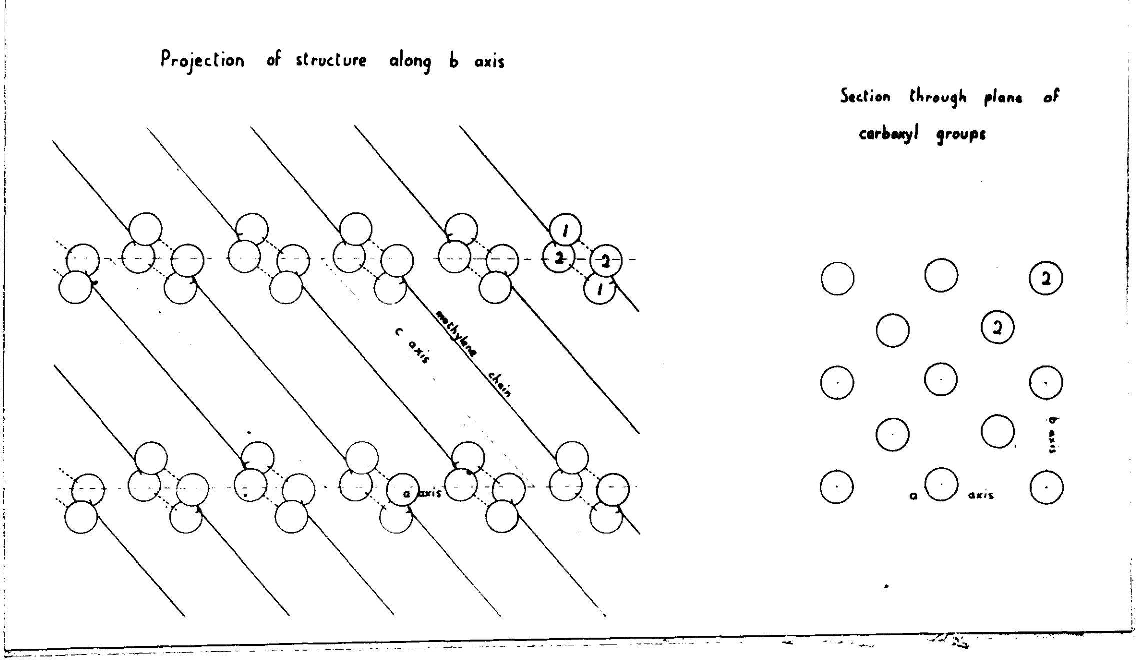


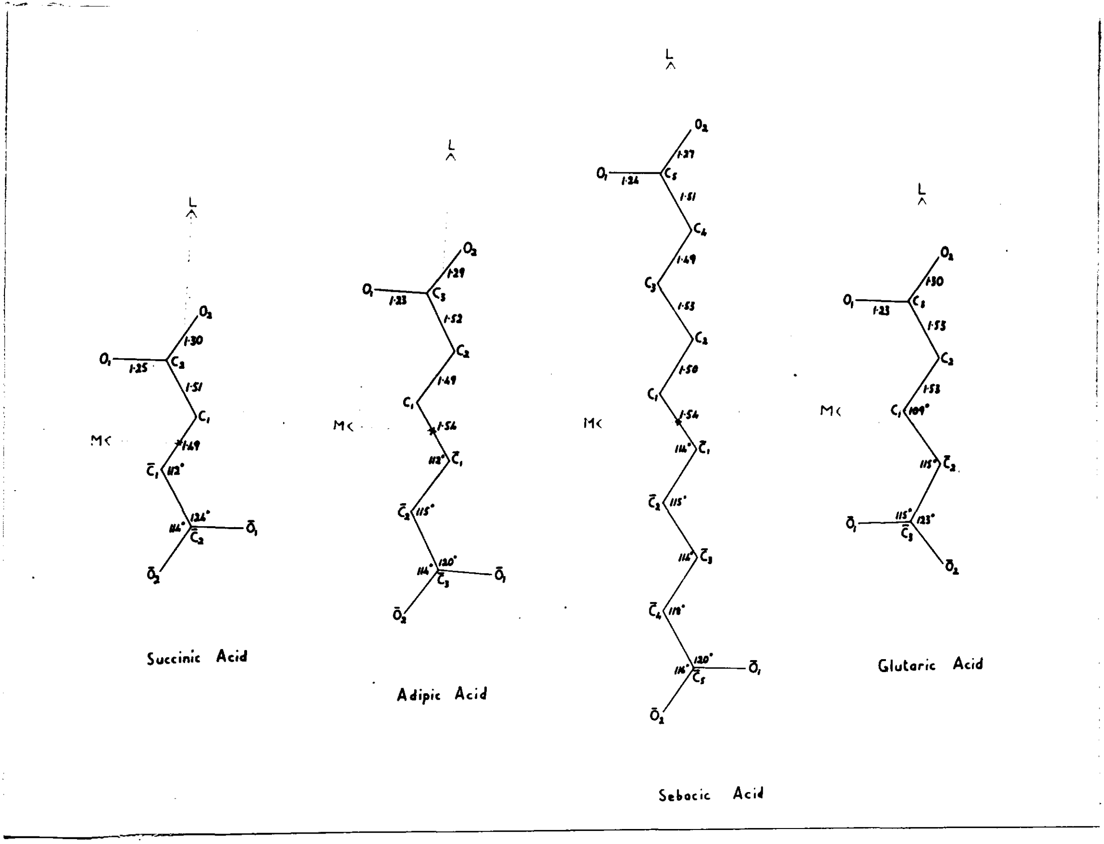
Figure 23.

In succinic acid this arrangement is altered slightly, but still persists in a modified form.

Detailed Intramolecular Structure.

Examination of the detailed intramolecular structure of these acids reveals a number of most interesting and unusual features. For comparison these structures are collected in Figure 24.

Figure 24.



Succinic Acid

Adipic Acid

Sebacic Acid

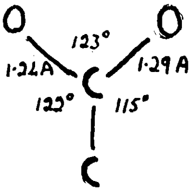
Glutaric Acid

As might be expected, the structures of adipic and sebacic acids, which are so similar crystallographically, resemble one another very closely. Succinic acid also, however, shows the same structural features.

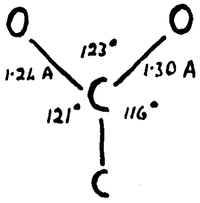
On the other hand, glutaric acid, though similar in crystal type to adipic and sebacic acids, is markedly different in internal structure.

In all the acids, the carboxyl group shows remarkable constancy in form. It appears to be unsymmetrical, with the two mean carbon - oxygen distances 1.24 A and 1.29 Å.

$COOH(CH_2)_nCOOH$



Oxalic acid dihydrate



These values compare very closely with those found for oxalic acid dihydrate (21). Another indication that the carboxyl hydrogen is more closely associated with one oxygen atom than with the other is afforded by the length of the hydrogen bonding between the carboxyl groups of adjacent molecules - 2.68 Å, which is much greater than twice the O-H bond distance of 0.96 Å observed in water (22).

In all the even acids, the carbon atoms of the methylene chain are perfectly coplanar, and the carboxyl groups are twisted out of this plane by a small angle, of the order of 3° - 5°. In contrast to this, in glutaric acid the carboxyl groups are twisted out of the plane of the three methylene carbons by about 32°. It is in the bond lengths of the methylene chain, however, that the most peculiar variations occur.

It has become increasingly evident, from recent accurate measurements that the covalent carbon - carbon single bond distance is by no means a fixed quantity. The first measurements which were made of aliphatic C-C single bond distances by various methods, e.g. X ray and electron diffraction, and spectroscopic work, showed great constancy in their value, it being 1.54 ± 0.01 A°. This value was found for such varied molecules as diamond, ethane, cyclopropane, cyclohexane, and others (23).

On examination of substances in which the single bond is between carbon atoms joined by multiple bonds to other groups, i.e.

$$=\overset{|}{C}-\overset{|}{C}=$$

contractions in its value were observed. A number of values for such single bonds are given in Table 28.

Table 28.

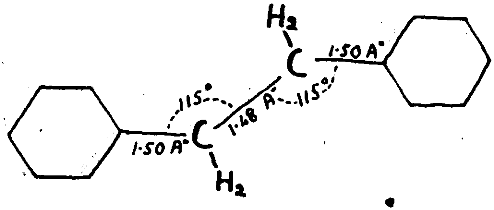
Substance	Single bond length	
Oxalic acid dihydrate	1.46 A°	(21)
Butadiene	1.46 A°	(24)
Glyoxal	1.47 A°	(25)
Diacetylene	1.36 A°	(26)

That such contractions should occur is predicted by ordinary resonance theory, which states that single bonds in such positions would be expected to have something of the character of double bonds, and hence the bond length would be shortened nearer to the value of the pure double bond. These facts are generally accepted, and have been provided with a sound theoretical basis by the application of quantum mechanics to molecular structure. Pauling and co-workers (27), have derived the empiric relationship :-

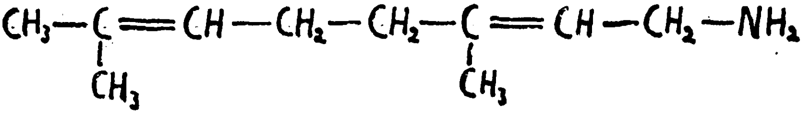
$$p = \frac{100(r_s - r)}{2r + r_s - 3r_D}$$

where if r is the observed length of the bond, and r_s and r_D are the lengths of the pure single and double bonds respectively, p is the percentage double bond character of the single bond. This enables a quantitative correlation to be obtained between the observed length of the bond, and the relative contributions of the singly and doubly bonded structures to the actual resonance hybrid.

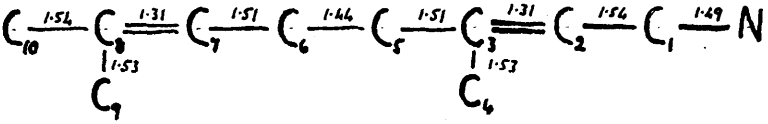
In the structure of dibenzyl, which has been measured very accurately by Jeffrey (28), a new type of contraction of carbon - carbon single bond has been observed. The central bonds in the molecule were, in the original paper, given the values :-



Elaborate mathematical corrections carried out on these figures have raised the values slightly (29), but still leave them significantly less than the expected 1.54 A. An earlier three-dimensional study by Jeffrey, on the structure of geranylamine hydrochloride (30), also reported a contracted value for a carbon-carbon single bond in a similar position.

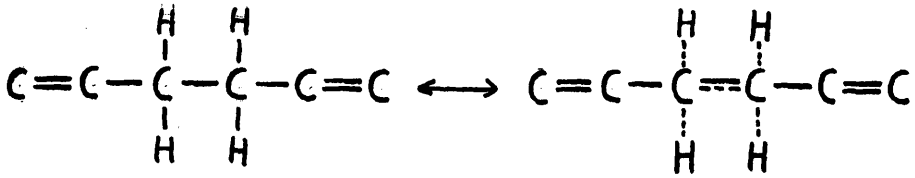


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-NH_2$$



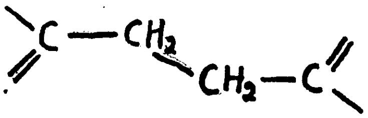
The bond between carbon atoms 5 and 6 is shortened by about three times the experimental error.

Jeffrey points out that these results are in keeping with observations that had been made on certain carbalkoxyl derivatives of hexadiene. Bateman in 1942 (31), had suggested that the greater resistance of $\Delta 1:5$ diene systems, as compared with $\Delta 1:4$ dienes, to isomerisation on heating with alkali, might be due to some slight degree of conjugation in the former which would enhance their stability. It might be possible to write the structure :-



the methylenic C-H electrons becoming partially localised in the central C-C bond and the second form being stabilised by the extra resonance of the extended conjugation of double - single - double bonds.

The marked resemblance of these results found by Jeffrey to the structure of succinic acid now proposed is evident. In all these cases, there is the same basic structure :-



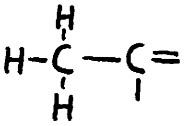
of the Δ 1:5 hexadiene type, and in each case, the central C-C bond shows contraction from the pure single bond value. Obviously the ordinary simple theory of resonance in conjugated systems does not account for these variations in bond length.

Very little attention has been paid to systems in which there are unsaturated centres separated by a number of saturated atoms. The unsaturated centres were believed to behave as perfectly discrete units, with no possible electronic interaction between them through the intervening saturated groups. Nevertheless, numerous theories of organic reactivity have called for the development of such interactions. Flurscheim, in 1902 and later (32), developed Werner's theory of alternating affinities, which stated that if a carbon chain were attached to a group X such that a strong bond was required from the first carbon, then the greater part of the bond forming properties of this atom would be used up, and only a weak bond could be formed to the next atom. This next carbon would be able to form a strong bond to the following carbon, and so would be developed a chain of alternately weak and strong bonds.

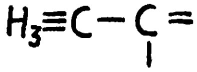
Other theories, notably that of Lapworth (33), suggested that there would be the formation of alternate positive and negative polarities along the carbon chain. These ideas were expanded in the electronic theory of bonds (34), and later developed in the theory of resonance (35), but were only applied to systems containing single and multiple bonds.

Effects which were much less well understood were the transmission of the influence of certain groups along an apparently saturated chain. Attempts were made to classify and interpret these effects in terms of two methods of electronic polarisation, - the Inductive effect, which involved the displacement of bond electrons towards either of the atoms forming the bond (36), and the Tautomeric effect, in which there was a tendency for the bond electrons to be actually transferred to another bond, giving covalency change (37)

These attempts were not completely satisfactory, and during the last decade, the concept of hyperconjugation has been introduced (38), to account for the observed data. Some of the ideas with regard to specific details appear to be still controversial, but briefly, the theory states that systems such as I. can be written in the form II, where the three bonds to the hydrogen atoms are regarded as one triple bond.



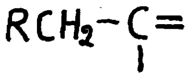
I.



$H_3{\equiv}C-C=$

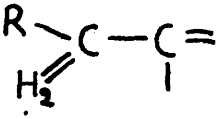
II.

More generally structures of the type III. can also be regarded in the same manner as IV.



$RCH_2-C=$

III.



IV.

Systems of these types II. and IV. can then be considered to undergo resonance in the same manner as an ordinary conjugated system e.g. butadiene. This is referred to as first order hyperconjugation, and is believed to contribute appreciably to the resonance energy of the compound.

In addition to this, structures of the type of ethane, and more generally $R-CH_2-CH_2-R$ are also assumed to be capable of a much weaker type of hyperconjugation, referred to as of the second order. This type of hyperconjugation will presumably function in all but the simplest molecules, and hence can not be evaluated separately in normal cases. The net result of such hyperconjugation effects, according to a quantum mechanical treatment of molecular orbitals (39), would be a gain in energy, and consequently a more stable structure than would otherwise be predicted.

Applying this concept to the structure of succinic acid, resonance due to the first order hyperconjugation will produce some shortening of the carbon - carbon bonds next to the carboxyl groups. The second order hyperconjugation on the other hand, will operate on all the C—C bonds in the molecule. The very much greater scope for resonance of the ordinary kind that would occur if there were a conjugated system of double bonds running from end to end of the molecule might favour the electron acceptor properties of the central C—C bond, at the expense of the other two, and the whole structure would be stabilised in this form by the energy gained from the additional resonance made possible. This would account for the contracted values found.

What is very much more surprising is, that if the experimental data are correct, a hyperconjugation effect of this kind can be propagated along an extended chain of as many as eight carbon atoms between the two carboxyl groups, as would appear to be the case in sebacic acid.

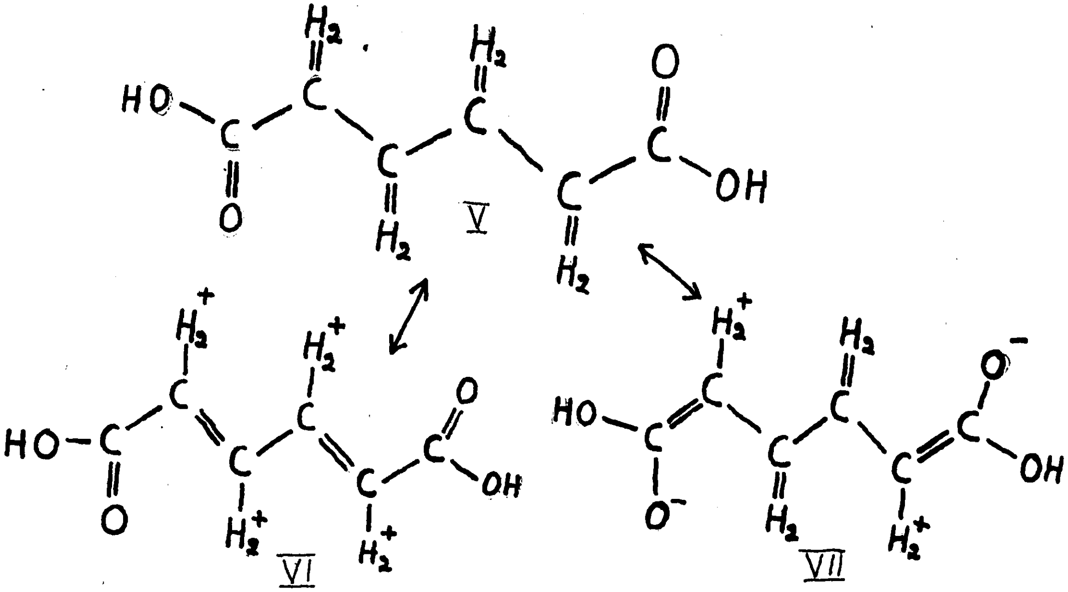
If the observed contractions in the three acids succinic, adipic, and sebacic, are expressed in terms of double bond character according to the Pauling formula, each alternate bond would seem to have as much as 10% double bond character.

$$\mathrm{HOOC}\overset{5\%}{-}\mathrm{C}\overset{10\%}{-}\mathrm{C}\overset{5\%}{-}\mathrm{COOH}$$

$$\mathrm{HOOC}\overset{3\%}{-}\mathrm{C}\overset{10\%}{-}\mathrm{C}\overset{0\%}{-}\mathrm{C}\overset{10\%}{-}\mathrm{C}\overset{3\%}{-}\mathrm{COOH}$$

$$\mathrm{HOOC}\overset{5\%}{-}\mathrm{C}\overset{10\%}{-}\mathrm{C}\overset{0\%}{-}\mathrm{C}\overset{7\%}{-}\mathrm{C}\overset{0\%}{-}\mathrm{C}\overset{7\%}{-}\mathrm{C}\overset{0\%}{-}\mathrm{C}\overset{10\%}{-}\mathrm{C}\overset{5\%}{-}\mathrm{COOH}$$

These figures are borne out by the C-C-C bond angles, all of which are greater than 109.5°. This would mean that in adipic acid, say, the structure could be represented by resonance between the normal form V. and the two extreme forms VI. and VII. as well as the normal resonance in the carboxyl group.



Another possible explanation for a contraction in bond length such as is observed in succinic acid has been put forward recently by Walsh (40). He suggests that if two of the hydrogen atoms of ethane are substituted to give a compound of the type of CH_2X-CH_2X, when X is a group of greater electronegativity than hydrogen, then the mechanical strength of the central C-C bond will be increased. In a sense this idea is complementary to the theory of hyperconjugation, and can be used to put it on a semi-quantitative basis, but its extension to longer aliphatic chains is rather more elaborate. In the present theory the electronegativity of the end groups will determine the particular bonds in the molecule which will be strengthened by the hyperconjugation, and to what extent.

The explanation given of the structure of the even acids, which at first sight seems extremely hypothetical, is not however entirely unsupported by physical and chemical evidence.

1. None of the odd acids should show this conjugation effect, because of their lack of symmetry. The carbon - carbon bond lengths found in glutaric acid would appear to be normal, and the middle C-C-C bond angle is 109°.
2. The carbon chain in the even acids is planar throughout its length, and the carboxyl groups also very nearly lie in this plane. This could be accounted for by assuming a certain amount of double bond character in the chain. In glutaric acid the carboxyl groups are appreciably out of the plane of the three methylene carbon atoms.
3. The abnormally wide spacing, 4.1 - 4.5 A°, which is observed between adjacent methylene chains in sebacic acid. If there were a tendency for there to be a cloud of incipient positive charge surrounding each chain, there would be repulsion between adjacent chains.
4. The heats of combustion of the n-aliphatic dibasic acids have been determined accurately (41), and have the values given in Table 29. From succinic acid (C_4) upwards, on going from an even to the next higher odd acid, $\Delta CH_2 = 158.3$ k.cals, while the increment going

from an odd to the next higher even is 155.1 k.cals. These values were measured for the combustion of crystalline material, and all or part of the alternating effect might be due to the stronger crystal forces in the even acids than in the odd. (see page 91.). Unfortunately, no reliable heats of fusion or vaporisation for these compounds were available, so no calculation could be made of the resonance energies.

Table 29.

No of carbon atoms	Qp (k.cals)	Δ CH_2
2 (oxalic)	60.1	
		146.4
3	206.5	
		150.6
4	357.1	
		157.8
5	514.9	
		154.0
6	668.9	
		158.8
7	827.7	
		155.5
8	983.2	
		158.5
9	1141.7	
		155.6
10	1297.3	
		158.3
11	1455.6	
		155.1
12	1610.7	
		157.9
13	1768.6	

It has been observed, however, by certain organic workers (42), that in general, whereas the even members of the oxalic acid series are produced very easily by the direct oxidation of suitable substances, the yield of the odd members in similar reactions is very poor, large quantities of the next lower even member being formed, except under carefully regulated conditions. Furthermore, there is a tendency in homologous series for only the even members to occur in nature, the odd being usually purely synthetic products (43).

Taken altogether, these facts would seem to indicate the presence of resonance effects in the even acids which do not occur in the odd.

Detailed Intermolecular Structure.

The full significance of the foregoing discussion does not, however, become apparent, until account is taken of some of the other physical properties of the series. As has already been noted, members of homologous series show alternations in physical properties, these alternations being very pronounced in the case of the n-aliphatic dibasic acids. Such properties are the melting points, the solubility in various solvents, the molecular refractivity, etc. Two of these are shown in Figure 25.

Fig. 25.

Alternation in properties.

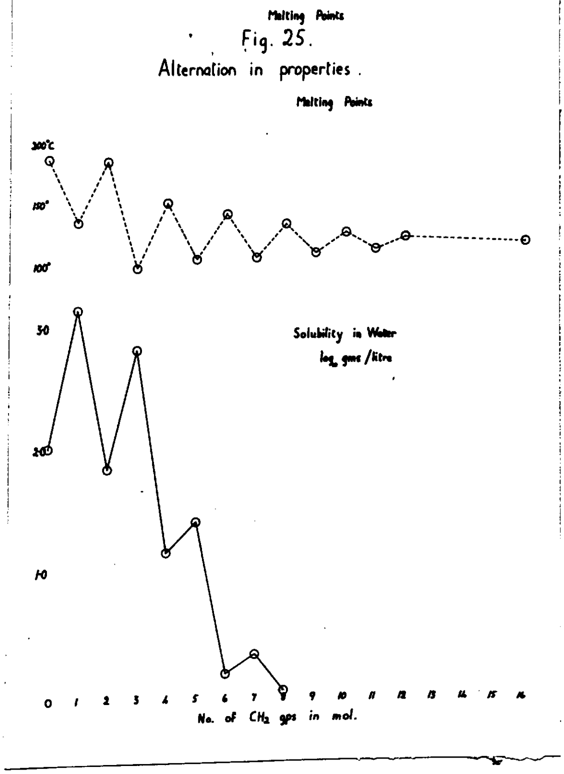


Fig. 25.
Alternation in properties.
Melting Points

A number of theories attempted to explain these alternations by assuming that it was connected in some way with the tilt of the chains (44), or with the fact that the crystal structure was different in the even acids to that on the odd (45). Another suggested that the directions in which the terminal groups pointed might affect the properties (46). It can be seen from diagram 22, page 74 , that the results of the present work do not confirm this, the arrangement being very similar in both even and odd.

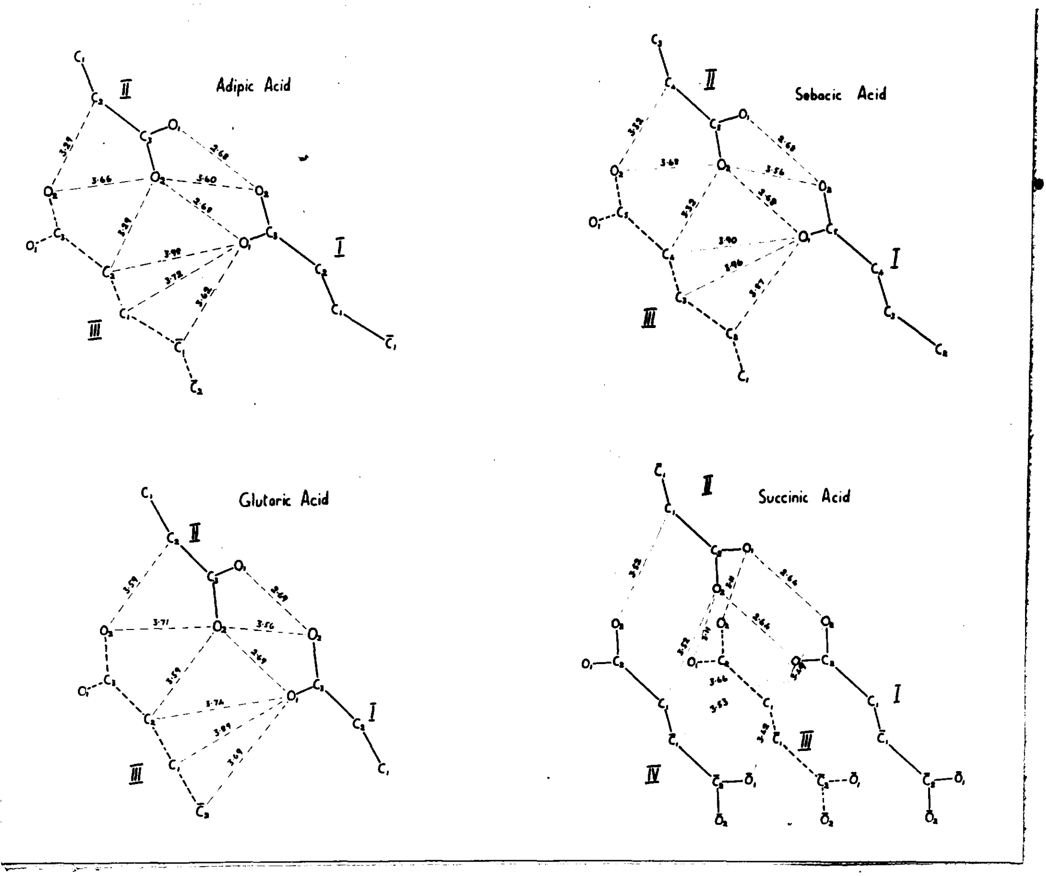
This alternating effect would seem to persist in some of the properties of the liquid state (47), but to a very much less degree. It is evident that almost all these properties will depend on the crystal forces. The melting point, for example, will vary as the ease of rupture of the intermolecular binding, also, the solubility will be a measure of the ratios of the various attractions :-

solvent ; solvent solvent : solute solute : solute

The most usual form of strong intermolecular binding in organic crystals is the hydrogen bridge (48), and as the presence of this can be inferred from the intermolecular distances, all these less than 4.0 A° were calculated. For convenience the various results are collected in Figure 26.

Figure 26.

Intermolecular distances.



Adipic Acid

Sebacic Acid

Glutaric Acid

Succinic Acid

The most important and strongest binding of this type is possessed by both the even and odd acids - the O-H-O bridges between the oxygen atoms of adjacent carboxyl groups. Certainly in the even acids the structure of this hydrogen binding is more regular than in glutaric, but the difference does not seem large enough to account for the variations. The presence of these hydrogen bridges has also been inferred in all four acids from infrared and polarised infrared measurements (49).

In the other intermolecular distances, however, there are certain divergences. The structures of glutaric, adipic, and sebacic, being of the same type, will be considered first. In the structures of both adipic and sebacic acids, the next shortest bond is between O_2^{II} of the carboxyl group of molecule II and the carbon atom adjacent to the carboxyl group of molecule III. That this is a bond, and not a Van der Waal's distance, seems to be borne out by its similarity in both cases, 3.29 and 3.32 A°, and by the fact that all the other comparable C-O distances are greater by about 0.3 - 0.4 A°. This bond does not exist in glutaric acid. All the other distances in these three acids are of 3.6 A° or greater. The distance between the methylene chains in adjacent molecules appears to be rather high, being of the order of 4.1 - 4.4 A°. This agrees with the observations made by Bunn on polyethylene (50).

The carbon - oxygen distance of about 3.30 A° would appear to be an example of a C-H-O hydrogen bridge, of the kind considered to exist in chloroform, HCN, and similar compounds (51), thus suggesting that a hydrogen on the carbon atoms next to the carboxyl groups has a tendency to ionisation with a positive charge. The most important point is that no such bridge seems to occur in glutaric acid. This fact appears to afford a reason for the difference in crystal properties between the even and odd acids.

There is one theory on the reason for the alternation of properties of homologous series which is of special relevance here. Biach in 1905 made the suggestion that if there were in the 'even' compounds a system of alternately weak and strong bonds in the molecules, which did not occur in the odd, then this might account for the observed differences. This theory was commented on in a theoretical paper by Gorin, Walter and Eyring in 1939, who speculated that owing to the symmetry of the even carbon hydrocarbons, some type of resonance might be possible which could not occur in the odd (53).

According to the theory of hyperconjugation which has been used to account for the observed contractions in the intramolecular dimensions, all the hydrogen atoms in the methylene chain should have some slight tendency to assume a positive charge. The first and second order hyperconjugation effects would combine, however, in the case of the hydrogen atoms attached to the carbons next to the carboxyl groups, and thus these would be the most positive positions. A hydrogen atom with acidic tendencies is known to be the most effective for hydrogen bridge formation (54), and hence could produce the observed bond with the nearest carboxyl oxygen. There being no second order hyperconjugation in the odd acids, the first order effect by itself would presumably be insufficient to loosen the hydrogen atom to form the bond, or at most would form a much weaker bond.

At first sight, the intermolecular distances of succinic acid appear to disprove this theory, as it is an even acid, and such a bond should be formed. Such is not the case, but the change in crystal structure makes possible two new bonds between oxygen atoms in molecules II and III of 3.1 Å, a value greater than the normal O-H-O hydrogen bridge distance of 2.68 Å and yet less than the Van der Waal's distance between oxygens of 3.6 Å (55). The attraction caused by these bonds would probably more than offset the loss of the C-H-O bonds, nevertheless, the non-existence of these latter severely upset the theory proposed.

If it is accepted, at any rate, that in the case of adipic and sebacic acids, the hydrogen on the carbon atom next to the carboxyl group is slightly charged, and forms a bond to the nearest oxygen of a carboxyl other than its own, then, in the case of glutaric, adipic, and sebacic acids, the nearest other carboxyl group is on another molecule. In succinic acid, the nearest other carboxyl group is at the other end of the same molecule, so that in this way the apparent non-formation of the bond could be accounted for. Both the C-H-O bonds could be intramolecular, and would thus contribute to the rigidity of the molecule, and hence to its high melting point.

Applying this idea to malonic acid, the only member of the odd series with a relatively high melting point, there is no second order hyperconjugation owing to the lack of symmetry, but on the other hand, in this case the first order hyperconjugations due to both carboxyl groups reinforce one another to activate the hydrogen atoms of the methylene group. The chemical reactivity of these hydrogens is a well known fact. Hence there could be the formation of the same type of bond and the raised melting point.

There is one other fact that should be mentioned here, and that is that the hydrogen atoms in the chain can be detected by the X ray method. (page 47). If all these atoms had a full positive charge, this of course would be impossible. As it is, the experimental data is not accurate enough to indicate whether the hydrogen atoms are neutral or do possess a very slight positive charge.

To sum up the theory proposed to explain the alternation in the normal dicarboxylic acids then, there are three factors governing the melting points;

- the Van der Waal's attraction which becomes gradually stronger with increase in size of the molecules until it reaches a limiting value,
- the very strong electrostatic attraction between carboxyl oxygen atoms,
- a weaker type of carbon - hydrogen - oxygen bonding which is present or absent depending on the intramolecular structure.

In the first member, oxalic acid, the electrostatic attraction is the dominating factor, and the lattice is almost ionic in character. In malonic and succinic acids, this attraction is diminished owing to the presence of the methylene groups, but in the latter, and also possibly to a lesser degree in the former, is compensated for by the appearance of the C-H-O weaker type of bond, and the melting points are still high. With glutaric acid, and with the following odd acids, the electrostatic effect becomes progressively less, the Van der Waal's attraction becomes the more important factor, and the melting points rise gradually to the limiting value for normal aliphatic hydrocarbon chains of about 123°C. With adipic and the higher even acids, the gradual lessening of the electrostatic forces is not so pronounced, owing to the formation of the weaker type of bond, and it is not until about duodecane-dicarboxylic acid that the Van der Waal's forces predominate, and the melting points of the even series also converge to the same limiting value.

Finally, there is the possibility of extending this theory to the other homologous series. Generally in these, there are no highly polar groups to give the high melting points of the first members, and the only factors applying are the Van der Waal's forces and presumably the hyperconjugation effect, depending on the symmetry, and which, by activating hydrogen atoms, might produce some weak hydrogen bonding between terminal groups. In this connection it is of interest to note that in the structure of hexamethylene diamine, which has recently been worked out (56), there is an alternation in bond lengths of exactly the type which would be predicted to occur in an even member of the series. Unfortunately, no other data is available, and in particular, the structures of no other odd members of any of the series have been determined.

Some knowledge of these is essential before the theory can be regarded as anything other than tentative, still, it would seem that there is a more fundamental connection between properties and molecular structure than would have appeared probable.

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