The Crystal Structure of Adipic Acid

By Sakutaro HIROKAWA

(Received April 10, 1950)

Introductoin

The X-ray investigation of normal chain dicarboxylic acids is very important in various respects. W.A. Caspari[1] reported preliminarily the results of his investigation on some dicarboxylic acids. These are listed in Table 1, in which are added the data on succinic acid given by H.J. Verweel and C.H. MacGillavry.[2]

Table 1

Acids		a, Å.	b, Å.	c, Å.	β	Molecules in the unit cell
Succinic	(C_4)	5.10	8.88	7.61	133°37′	2
Adipic	(C_6)	10.27	5.16	10.02	137° 5′	2
Pimelic	(C_7)	9.93	4.82	22 12	130°40′	4
Suberic	(C_8)	10.12	5.06	12.58	135°	2
Azelaic	(C_9)	9.72	4.83	27.14	129°30′	4
Cebacic	(C_{10})	10.05	4.96	15.02	133°50′	2
Brassylic	(C_{13})	9.63	4.82	37.95	128°20′	4
Hexadecanedicarboxylic	(C_{16})	9.76	4.92	25.10	131°10′	2

As for the series of even acids, the lengths of crystallographic axes a and b of succinic acid are considerably different from those of adipic and higher acids. The question thus arises how and why the crystal structure of succinic acid differs from that of adipic or other members of the series. On the other hand, as adipic acid is an important material for the synthesis of Nylon, it is also of interest to investigate this substance from the view point of highpolymer chemistry.

In 1941 T. Ohashi[3] and the present author started the crystal analysis of polymethylenediamine adipates, the so-called Nylonsalts, together with that of adipic acid, but unfortunately the work was interrupted by the War. After the War, the present author took this problem up again and finished some time ago the work on the crystal structure of adipic acid. Although he found recently that the structure determination of this crystal had been completed by C.H. MacGillavry[4] and also by J.M. Robertson,[5] it will not be insignificant to publish the results of the independent determination of the present author.

Crystallographic Data

According to the description by P. Groth,[6] the crystal of adipic acid is monoclinic holohedral, and the values of axial ratio and axial angle are $a:b:c=1.9673:1:1.79$ (?), $\beta=137°\ 5'$. This crystal is optically negative, and the axial plane is $b(010)$.

Cleavages parallel to (110) and to (011) are perfect and so the fibre cleavage is observed along (001). Single crystals used in the present experiment were prepared from ethylacetate solution by slow evaporation. They were well-formed tablets parallel to (001) and prisms elongated in the direction of the c-axis. The external forms are shown in Fig. 1. Specimens were cut out of these crystals into suitable shape and size.

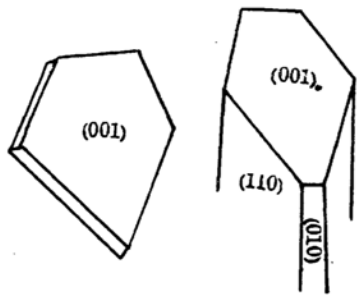

Fig. 1.—The external forms of crystals, smaller planes are not drawn.

From the Laue photographs taken parallel to (010) and perpendicular to (001) respectively, it was shown that the Laue symmetry was C_{2h}. The gnomonic projections of these photographs gave the following values; $a:b:c=1.95:1:1.93$, $\beta=137°$.

From the Oscillation and Weissenberg photographs taken of a, b and c-axes respectively, it was found that the unit cell of adipic acid was monoclinic and was of the following dimensions:

$$a = 10.14 \pm 0.05\text{kX},\ b = 5.16 \pm 0.03\text{kX},$$
$$c = 10.03 \pm 0.05\text{kX},\ \beta = 137°.$$

The axial ratio calculated from these values

(1) W.A. Caspari, *Jour. Chem. Soc.*, **1926**, 3235.

(2) H.J. Verweel and C.H. MacGillavry, *Z. Krist.*, **102**, 60 (1939).

(3) T. Ohashi, *Annual Report of the Fibre Research, Osaka, Japan*, Vol. 4. (1942).

(4) C.H. MacGillavry, *Rec. trav. chim.*, **60**, 605 (1941).

(5) J.D. Morrison and J.M. Robertson, *Jour. Chem. Soc.*, **1949**, 987.

(6) P. Groth, "Chemishe Krystallographie," Vol. III, 465.

is $a:b:c=1.964:1:1.945$. This is in good agreement with that obtained fromthe Laue photographs. Thus the values given by P. Groth may be concluded to be incorrect. On indexing all spectra of these photographs the following systematic absences were found; $(0k0)$ for $k=2n+1$, and $(h0l)$ for $h=2n+1$. All other types of spectra were found. Therefore, the space group of this crystal was concluded to be $P2_1/a-c^5_{2h}$.

The density measured by the flotation method using carbontetrachloride and ethanol was $\rho=1.357$ at 18°C. Accordingly the number of molecules in the unit cell was calculated to be $Z=2$.

Determination of Structure

There are four general positions x, y, z; $1/2+x, 1/2-y, z$; $\bar{x}, \bar{y}, \bar{z}$; $1/2-x, 1/2+y, \bar{z}$, for the space group $P2_1/a$. These are shown in Fig. 2. However, in the present case, as the unit cell contains only two molecules, a molecule must either have a plane or a centre of symmetry. As the plane of symmetry can be elim-

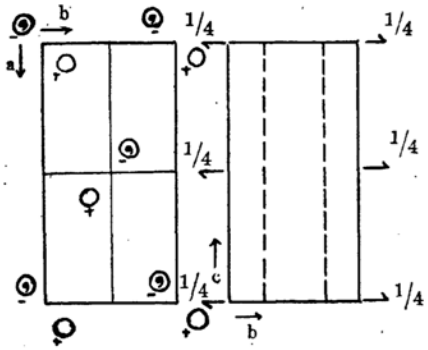

Fig. 2.—Symmetry of $P2_1/a$.

inated from the observed relative intensities of $(0k0)$ reflections, the molecule must have a centre of symmetry, which may be assumed to lie at the origin of the unit cell. Thus, neglecting all the hydrogen atoms as usual, five sets of parameters x, y, z are needed to be determined to fix the positions of carbon and oxygen atoms in the molecule; namely, three sets for C atoms and two for O's. Now it is preliminarily assumed, from the inspection of the size of the unit cell for the series of dicarboxylic acids given above, that (1) the molecule, neglecting hydrogen atoms is planar; (2) the carbon atoms in the molecule form a zigzag chain; (3) the axis of the carbon chain orientates itself parallel or nearly parallel to the c-axis; (4) the bond distances are roughly C—C=1.54 Å., and C—O=1.28 Å.; and finally(5) the bond angles are also roughly $\angle CCC=110°$, $\angle OCC=120°$. and $\angle CCO=120°$. A rough model of the molecule thus assumed is shown in Fig. 3.

The line connecting a mid-point of the two oxygen atoms at one end with that of the two

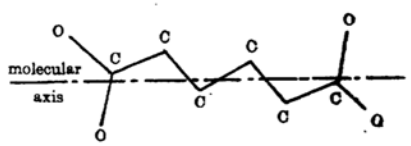

Fig. 3.

oxygen atoms at the other end is chosen for the molecular axis. Evidently this axis passes through the centre of symmetry. Since this axis and the plane of the carbon chain together fix a rectangular coordinate axes in the molecule, we can conveniently use the Eulerian angles to describe the orientation of the molecule in the unit cell.

Using these assumptions, the method of trial and error could lead to a possible approximate solution of parameter values for the atoms. The methods of the Patterson and the Fourier series were then applied to obtain more precise values of parameters.

These are shown in Figs. 4, 5 and 6. The final result of the determination is as follows;

	C_1	C_2	C_3	O_1	O_2
x	0.021	0.056	−0.021	−0.078	0.106
y	−0.090	−0.160	0.038	0.110	−0.240
z	0.329	0.210	0.054	0.290	0.479

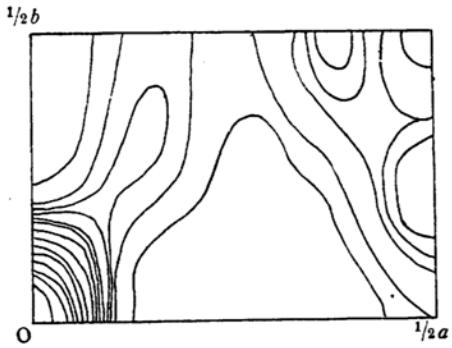

Fig. 4.—$P(x, y)$.

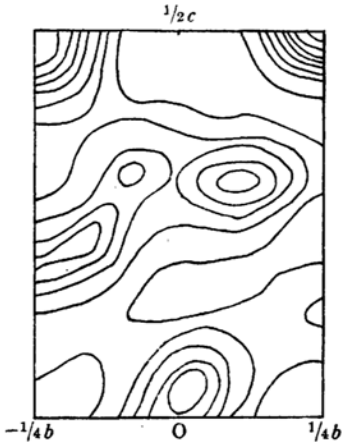

Fig. 5.—$\rho(y, z)$.

Table 2

hkl	sin θ/λ	$F_{calc.}$	$F_{obs.}$	hkl	sin θ/λ	$F_{calc.}$	$F_{obs.}$
001	0.071	−20	22	001	0.071	−20	22
$20\bar{1}$	0.107	3	3	011	0.121	10	12
$20\bar{2}$	0.107	−13	9	002	0.135	− 8	7
200	0.146	61	49	012	0.182	2	2
002	0.146	− 7	6	020	0.193	− 7	5
$20\bar{3}$	0.149	29	15	021	0.211	22.5	21
$40\bar{3}$	0.199	22	22	003	0.224	5	7
201	0.208	6	3	013	0.237	− 6	2
$40\bar{2}$	0.211	− 7	6	022	0.244	− 8	7.5
$20\bar{4}$	0.211	−18	17	004	0.297	17	17
$40\bar{4}$	0.218	−42	47	023	0.299	19	23
003	0.221	5	6	031	0.306	5	3
$40\bar{1}$	0.244	18	16	014	0.312	14.5	15
$40\bar{5}$	0.247	9	8	032	0.323	1	<2
202	0.256	−10	9	033	0.357	1	<2
$20\bar{5}$	0.283	− 5	4	024	0.360	− 7.5	4
400	0.296	− 2	4	005	0.374	13.5	16
004	0.297	17	17	015	0.375	− 1	<2
$60\bar{4}$	0.299	−16	16	040	0.388	− 3	—
$40\bar{6}$	0.302	5	5	034	0.406	0	<2
$60\bar{5}$	0.305	− 2	3	025	0.410	1.5	—
$60\bar{6}$	0.325	6	6	042	0.419	14	12
203	0.344	2	2	016	0.444	− 1	<2
401	0.351	12	9	043	0.446	− 7.5	6
$20\bar{6}$	0.354	7	5	006	0.446	5	6
$60\bar{7}$	0.354	−11	8	026	0.460	− 2.5	3
$40\bar{7}$	0.364	− 2	2	035	0.474	7	7
005	0.377	−14	13	052	0.514	3.5	2
$60\bar{1}$	0.390	9	9	017	0.526	− 3	2
$60\bar{8}$	0.399	− 4	4	027	0.540	3	3
804	0.406	6	6	008	0.593	4	3
$80\bar{5}$	0.406	−10	10	018	0.601	− 4	3
$80\bar{7}$	0.410	− 6	5	028	0.602	0	—
204	0.413	13	10	110	0.062	55	45
402	0.416	− 5	3	200	0.147	61	49
$40\bar{8}$	0.429	−16	15	210	0.175	−37	40
$80\bar{8}$	0.432	5	3	020	0.194	− 6	5.5
006	0.452	6	5	120	0.208	−15	12.5
$60\bar{9}$	0.457	0	—	310	0.244	17.5	17
$80\bar{3}$	0.457	− 9	5	220	0.244	6	4
$80\bar{9}$	0.458	− 7	6	400	0.295	− 2	4
403	0.478	5	6	320	0.295	−22	19
205	0.487	− 5	3	130	0.300	− 9	7
$20\bar{8}$	0.494	−13	10	410	0.312	19	17
$100\bar{7}$	0.500	4	2	230	0.325	− 0.5	<2
$100\bar{8}$	0.510	0	—	420	0.351	12	10
$100\bar{6}$	0.510	− 3	<2	330	0.364	1	<2
$104\bar{9}$	0.517	− 4	3	510	0.376	1	3
007	0.517	− 2	2	040	0.388	− 3	2
$100\bar{5}$	0.530	− 6	6	140	0.394	− 2.5	2
$80\bar{1}$	0.532	2	2	430	0.413	− 6	6
404	0.545	0	—	240	0.413	− 4.5	4
602	0.552	1	<2	520	0.414	−10	9
$20\bar{9}$	0.566	4	2	600	0.439	− 6	2
$100\bar{11}$	0.572	− 3	3	340	0.439	− 1	<2
$60\bar{11}$	0.572	− 4	2	610	0.449	− 0.5	3
008	0.588	− 3	4	530	0.466	4	<2
$80\bar{12}$	0.604	− 4	5	620	0.480	4.5	2.5
$100\bar{12}$	0.604	0	2	440	0.485	− 3	2
$120\bar{8}$	0.608	− 5	3	150	0.489	− 4	2
$120\bar{10}$	0.608	0	2	250	0.505	− 2	<2
207	0.621	− 2	<2	710	0.519	0	—
$120\bar{11}$	0.621	2	2	540	0.525	− 1	<2
$120\bar{7}$	0.624	5	3	630	0.526	− 6	5
$40\bar{11}$	0.627	− 2	<2	350	0.528	− 2.5	<2
$20\bar{10}$	0.634	0	3	720	0.544	− 2	3
$120\bar{6}$	0.634	− 3	2				

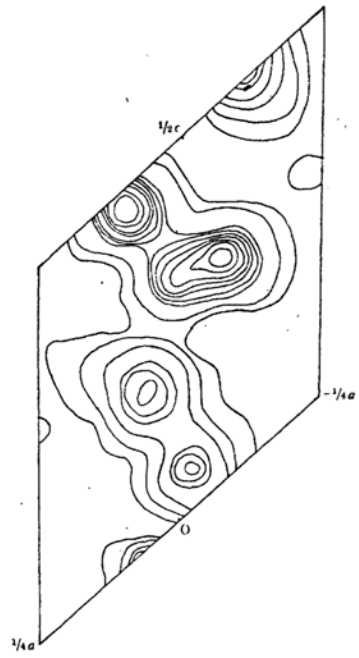

Fig. 6.—$\rho(x, z)$.

Discussion of the Structure

Using the obtained parameter values, the following interatomic distances and bond angles were calculated as follows:

$C_3'-C_3=1.54$ Å.,
$\angle C_3' C_3 C_2=110°$,
$C_3-C_2=1.52$ Å.,
$\angle C_3 C_2 C_1=115°$,
$C_2-C_1=1.48$ Å.,
$\angle C_2 C_1 O_1=126°$,
$C_1-O_1=1.28$ Å.,
$\angle C_2 C_1 O_2=110°$,
$C_1-O_2=1.31$ Å.,
$\angle O_1 C_1 O_2=124°$.

The length of hydrogen bond is $O_1.....O_2'=2.63$ Å., and the shortest Van der Waals distance is 3.20 Å. (between C_2 and O_2''). These are shown in Fig. 7.

As for the difference of lattice parameters of succinic acid crystal from others, it is only due to that of the packing of the molecular chains, each of which being similarly hydrogen-bonded.

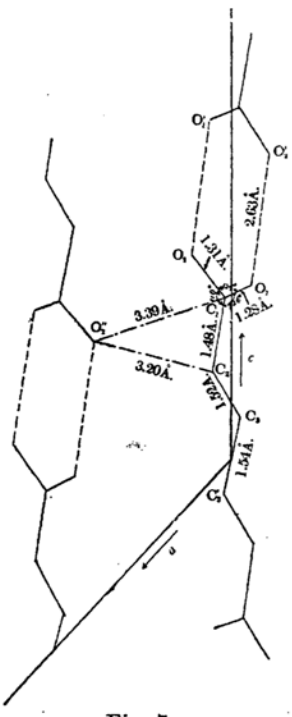

Fig. 7.

The structure determined so far agrees approximately with that given by MacGillavry [4] and by Robertson. [5] However, there can be seen some difference with respect to C-O distances. These are listed in the following table.

	MacGillavry	Robertson	Hirokawa
C_1-O_2	1.38 Å.	1.29 Å.	1.31 Å.
C_1-O_1	1.28	1.23	1.28

Thus, on one hand, the distance of C_1-O_2 obtained by the present author agrees more closely with that of Robertson, while, on the other hand, the distance of C_1-O_1 agrees better with that of MacGillavry.

It seems rather difficult to decide which of these come closest to the actual state of the structure of carboxylic radical in the crystal.

Summary

Oscillation and Weissenberg photographs using CuK_α($\lambda=1.539$ Å.) radiation show that the crystals of adipic acid are built upon a monoclinic unit cell having $a=10.14$ kX, $b=5.16$ kX, $c=10.03$ kX, and $\beta=137°$.

The space group is $C^5_{2h}-P2_1/a$. This unit cell contains two molecules of $HOOC-(CH_2)_4-COOH$, the centres of the mass of the molecules being at 0, 0, 0 and 1/2, 1/2, 0 respectively. Positions of atoms in the unit cell are given by the following parameters; the carboxyl carbon (C_1), $x=0.021$, $y=-0.090$, $z=0.329$; α-methylenic carbon (C_2), $x=0.056$, $y=-0.160$, $z=0.210$; β-methylenic carbon (C_3), $x=-0.021$, $y=0.038$, $z=0.054$; oxygen I (O_1), $x=-0.078$, $y=0.110$, $z=0.290$; oxygen II (O_2), $x=0.106$, $y=-0.240$, $z=0.479$. The molecule is approximately planar and the plane of carboxyl radical is slightly twisted about the molecular axis.

The plane of zigzag carbon chain makes an angle about 40° to (010) and the molecules are linked with strong hydrogen bond along c-axis, and may be said to form a kind of chain lattice.

The author is indebted to Dr. Y. Go who suggested him to investigate this subject and to Prof. I. Nitta for his adequate suggestion and encouragement throughout this work. He also wishes to thank Mr. I. Taguchi for discussion of details.

Faculty of Science, Osaka University, Osaka