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The Crystal Structure of α-Pimelic Acid

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The structure of the high-temperature phase of pimelic acid has been determined by X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/c$. Unit cell dimensions are $a = 5{\cdot}68 \pm 0{\cdot}05$, $b = 9{\cdot}71 \pm 0{\cdot}02$, $c = 22{\cdot}45 \pm 0{\cdot}10$ Å; $\beta = 136{\cdot}8 \pm 0{\cdot}5°$. Zachariasen's method was used to determine signs for some structure factors. A trial structure was found from a bounded Fourier projection calculated using these signs, and from information contained in an $(0kl)$ Patterson projection. Refinement of the structure was by three-dimensional least-squares methods. One carboxyl group and the average plane of the carbon atoms are turned out of the b, c plane in about the same direction (55° and 11° respectively) while the other carboxyl group is turned 8° out of the b, c plane in the opposite direction. As with other dicarboxylic acids, the molecules of α-pimelic acid are hydrogen bonded at each end, forming a series of 'infinite' chains. The molecular symmetry of the low-temperature form is lost in the high-temperature modification.

Introduction

The dicarboxylic acids have long been of interest because of the well known alternation of such physical properties as melting point, solubility, and heat of combustion. Generally speaking, the acids with an odd number of carbon atoms have more energy per carbon atom than the acids with an even number of carbons. Attempts have been made to explain this alternation in properties in terms of the structural features of the crystals (MacGillavry, Hoogschagen & Sixma, 1948; Morrison & Robertson, 1949*a*, *b*, *c*, *d*; Goedkoop & MacGillavry, 1957).

Also of interest is the fact that oxalic acid, succinic acid, and all of the odd acids investigated undergo phase transitions below the melting point (Dupre la Tour, 1932). The only high-temperature phase structure determination reported for these acids was by Rieck (1944) for succinic acid. In the present paper the structure of the high-temperature (α) form of pimelic acid, $COOH(CH_2)_5COOH$, is reported. Judging from the space group and unit-cell determinations given by Dupre la Tour (1932), the structure of α-pimelic acid may be typical of the α phases of the higher odd acids. The structure of the β modification of pimelic acid has already been determined (MacGillavry *et al.*, 1948).

Experimental

The transition temperature for pimelic acid is about 75° C. Crystals of the α form were grown from a melt inside a capillary. The crystals could be maintained at room temperature for two weeks and longer, so that no special heating was used during photography.

Laue symmetry was determined from precession and Weissenberg photographs to be C_{2h}. The b axial length was found from a rotation photograph; a, c, and β were found from a zero-level Weissenberg photograph. The unit-cell dimensions,

$$a = 5{\cdot}68 \pm 0{\cdot}05, \quad b = 9{\cdot}71 \pm 0{\cdot}02, \quad c = 22{\cdot}45 \pm 0{\cdot}10 \text{ Å}, \quad \beta = 136{\cdot}8 \pm 0{\cdot}5°,$$

are within the limits of error of Dupre la Tour's (1932) results.

The systematic absences observed were for $(h0l)$ when l was odd and $(0k0)$ when k was odd. The probable space group is thus C_{2h}^5–$P2_1/c$.

By assuming a density close to that of the low-temperature form, the number of molecules per unit cell is established as four. There is thus no space-group requirement for molecular symmetry.

Six levels (0 through 5) of Weissenberg photographs were taken with b as the rotation axis. Cu $K\alpha$ radiation was used. $(0kl)$ data were taken on the precession camera using Mo $K\alpha$ radiation. Intensities were measured by the visual-estimation method, using the multiple-film technique for the Weissenberg data and a series of timed exposures for the precession data. An attempt to correlate the levels of Weissenberg data, using reflections appearing also on the precession photograph, did not give very satisfactory results. For the sake of greater internal consistency, Weissenberg data were used whenever possible at the outset of the problem. (However, the finally reported observed $(0kl)$ structure factors for reflections appearing on both Weissenberg and precession photographs are averages.) Wilson's (1942) method was used to put the observed $|F_{\text{rel.}}|^2$ values on an approximately absolute scale.

Trial structure

As a start in the determination of the trial structure, a sharpened $(0kl)$ Patterson projection was computed. This projection indicated that the carbon chain was stretched out more or less along c and that the carbon atoms could be roughly in a plane making an angle of less than 35° with the b, c plane. In addition, the Patterson was consistent with the central carbon atom of a molecular chain near $z = \frac{1}{4}$. Further interpretation was difficult since peaks resulting from the repeating set of carbon–carbon interactions obscured the contributions of the carboxyl groups.

Reflections with odd k were on the whole appreciably weaker than reflections with even k. Trial models were not successful in fitting these weaker, odd k, reflections. Unfortunately, an $(0kl)$ Fourier using only terms with even k would result in a molecular projection with a mirror line at $z = \frac{1}{4}$. It was clear that the two halves of the molecule could not be mirror images even in projection. In order to account for the reflections with odd k it would be necessary to find the differences between the two halves of the molecule.

Some further information about the molecule was obtained by plotting structure factor maps of several strong $(h0l)$ reflections. These revealed that the molecule must lie near $x = 0$ or $x = \frac{1}{2}$.

A set of unitary structure factors was then calculated and Zachariasen's method was used to relate and determine signs. 65 signs were assigned in this way and 24 others were related to each other. An absolute assignment for these 24 was made from the sign of (068) which had remained positive for a number of trial structures. 77 of the 89 signs chosen later proved to be correct.

Since only two signs were found for $(0kl)$ reflections with k odd, it was not profitable to calculate an $(0kl)$ Fourier projection. It was, however, decided to prepare a bounded projection down b between $y = +\frac{1}{4}$ and $y = -\frac{1}{4}$. In all 37 $(h0l)$ terms, 11 $(h1l)$ terms with l odd and 1 $(h3l)$ term with l odd were used. With such few terms—particularly with k odd—it is not surprising that accurate atomic positions did not result. However, the projection showed the molecule quite clearly and, in particular, showed how the planes of the carboxyl groups were twisted with respect to an average carbon chain plane. Five of the seven carbon atoms were in fact resolved and in a fairly straight line, one of the carboxyl groups was nearly resolved, and the other gave the appearance of being viewed edge on. This bounded projection made possible a trial structure which provided a measure of fit for the $(0kl)$ reflections with k odd.

Refinement of parameters

An $(0kl)$ Fourier was calculated using z parameters from the bounded projection and y parameters estimated from the x and z values obtained from this projection and from expected bond lengths. Two carbon atoms and two oxygen atoms were unresolved. Since there appeared to be no satisfactory two-dimensional method for refining these parameters further, an attempt was made at refinement using Sayre's three-dimensional least-squares program on the I.B.M. 704 (weighting scheme (min. $100/F^2$, 1)). Of approximately 1000 reflections used, about 300 were non-observed. These non-observed reflections were included by assigning them one-half the value of their upper bound. The first calculation of structure factors for all the reflections resulted in a horrifying R factor of 0·51. Three cycles of refinement brought the R factor to 0·42. Omitting the non-observed reflections reduced R to 0·35.

Starting with the parameters obtained from the application of the least-squares program, a new $(0kl)$ Fourier refinement was made. Fig. 1 shows the result.

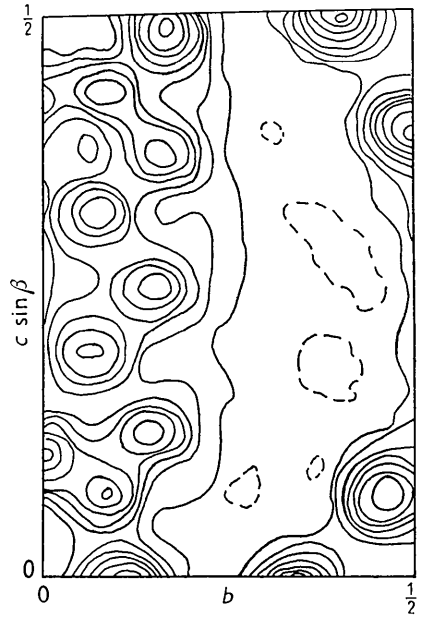

Fig. 1. $0kl$ Fourier. The contours are at intervals of 1 e.Å^{-2} starting at zero (dashed line).

This time all the atoms were resolved, although neighboring atoms were so close in projection that centers were not easy to determine. Structure factors calculated from these Fourier parameters resulted in $R(0kl) = 0·23$. A second bounded projection down b was also calculated. The carbon and an oxygen of one carboxyl group overlapped and the carbon of the other carboxyl group was not quite resolved. Using x parameters from this projection—estimating for the unresolved atoms with the help of the y and z parameters and expected bond lengths and angles—resulted in $R(h0l) = 0·30$.

A second least-squares refinement was then undertaken, omitting non-observed reflections. The overall R for observed reflections was 0·32 at the outset and after four cycles of refinement dropped to 0·27. Refinement of the temperature factors was stopped after the third round because the constants appeared to be increasing to values unreasonably larger than previous estimates had indicated.

The temperature factors used in the refinement were isotropic. Even a casual inspection of the data after the refinement ended, however, showed that there was

Table 1. *Final parameters from second least-squares refinement*

	x	y	z	B* (Å^2)
C_1	0·466	0·074	0·0742	3·70
C_2	0·439	0·147	0·1284	4·54
C_3	0·534	0·062	0·2002	3·64
C_4	0·531	0·151	0·2571	4·28
C_5	0·564	0·064	0·3209	3·68
C_6	0·570	0·157	0·3764	4·02
C_7	0·547	0·085	0·4299	3·82
O_1	0·243	0·102	−0·0060	4·12
O_2	0·700	−0·009	0·1071	4·55
O_3	0·514	−0·037	0·4309	4·62
O_4	0·586	0·168	0·4844	4·54

* Temperature factor constant in the thermal damping term in the atomic scattering factor. A further asymmetric factor, $\exp[-(0{\cdot}007h^2-0{\cdot}005hl)]$ was added later.

a marked dependence on l. An anisotropic temperature factor for each atom was called for, but, since means to make such a calculation were lacking, it was decided to make a partial correction and apply it to all the atoms in the same way. The anisotropic temperature factor may be written as

$$\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{23}kl+b_{13}hl)\right].$$

An inspection of the $(0kl)$ data revealed no pronounced trends calling for further temperature-factor correction, so it was assumed that b_{22}, b_{33}, and b_{23} were fairly well accounted for by the isotropic temperature factors already used. The constant which was first sought was b_{13}. This was found from plots of $\log F_c/F_o$ against l for constant h. Parallel lines were obtained for the different values of k. The intercepts of these

Table 2. *Observed and calculated structure factors for the* $(0kl)$ *reflections*

k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_c
0	2	37	+59*	3	2	5	− 6	5	14	< 4	− 1	8	11	5	− 8
0	4	4	− 3	3	3	3	− 1	5	15	4	− 5	8	12	< 5	− 2
0	6	14	−12	3	4	8	− 8	5	16	< 4	− 5	8	13	< 5	− 3
0	8	17	+13	3	5	4	+ 0	5	17	< 5	+ 0	8	14	< 5	− 2
0	10	21	+19	3	6	6	− 4	6	0	7	+ 7	8	15	< 5	+ 2
0	12	9	+10	4	7	6	+ 8	6	1	4	+ 4	9	1	9	+12
0	14	7	+ 7	3	8	11	+11	6	2	4	− 1	9	2	5	− 2
0	16	13	+14	3	9	19	+22	6	3	15	+14	9	3	6	+ 4
0	18	< 4	− 1	3	10	< 3	+ 3	6	4	5	− 9	9	4	< 5	− 3
0	20	< 4	− 3	3	11	< 3	+ 1	6	5	3	+ 5	9	5	< 5	+ 2
1	2	9	+ 7	3	12	5	+ 6	6	6	4	− 4	9	6	5	− 2
1	3	7	− 8	3	13	5	− 5	6	7	13	−13	9	7	6	+ 7
1	4	5	+ 5	3	14	5	+ 4	6	8	29	+24	9	8	6	− 3
1	5	< 2	− 2	3	15	4	− 5	6	9	< 5	+ 5	9	9	< 5	+ 4
1	6	11	+ 9	3	16	5	− 4	6	10	< 5	− 2	9	10	< 5	+ 2
1	7	17	+17	3	17	< 4	− 0	6	11	< 5	− 4	9	11	< 5	+ 3
1	8	11	+11	3	18	< 4	+ 3	6	12	5	− 7	9	12	< 5	+ 1
1	9	28	+30	4	0	30	−33	6	13	< 5	− 3	9	13	< 5	+ 1
1	10	8	+11	4	1	6	− 4	6	14	< 5	− 7	10	0	6	−10
1	11	4	+ 6	4	2	14	− 9	6	15	< 5	− 2	10	1	8	+ 9
1	12	5	+ 7	4	3	20	+14	6	16	< 5	− 1	10	2	7	+ 5
1	13	5	− 6	4	4	27	−25	7	1	< 5	+ 1	10	3	7	+ 9
1	14	4	+ 6	4	5	6	+ 6	7	2	< 5	− 1	10	4	< 5	+ 1
1	15	< 4	+ 1	4	6	14	−17	7	3	6	− 8	10	5	< 5	+ 4
1	16	< 4	− 1	4	7	12	−14	7	4	5	− 6	10	6	< 5	+ 1
1	17	< 4	− 4	4	8	15	−19	7	5	7	−10	10	7	< 5	+ 2
1	18	< 4	+ 4	4	9	24	+25	7	6	4	− 6	10	8	< 5	+ 1
1	19	< 4	− 1	4	10	< 3	+ 2	7	7	< 5	+ 2	10	9	< 5	+ 4
2	0	67	+75	4	11	7	+ 7	7	8	4	+ 3	10	10	< 5	+ 2
2	1	88	−77	4	12	4	− 3	7	9	5	− 4	10	11	< 5	+ 1
2	2	14	+14	4	13	4	+ 3	7	10	6	+ 6	10	12	< 5	+ 2
2	3	12	−14	4	14	5	− 5	7	11	< 5	+ 1	11	1	< 5	+ 2
2	4	23	−25	4	15	< 3	+ 0	7	12	< 5	+ 5	11	2	< 5	− 0
2	5	3	− 3	4	16	6	− 6	7	13	< 5	− 3	11	3	< 5	+ 1
2	6	25	−24	4	17	4	+ 0	7	14	< 5	+ 1	11	4	< 5	+ 0
2	7	5	+ 5	4	18	4	+ 1	7	15	< 5	− 2	11	5	< 5	− 1
2	8	25	−29	5	1	16	−16	7	16	< 5	− 3	11	6	< 5	− 0
2	9	3	− 5	5	2	7	−10	8	0	9	− 8	11	7	< 5	− 0
2	10	11	+11	5	3	21	−24	8	1	< 5	− 3	11	8	< 5	− 2
2	11	< 3	− 1	5	4	13	−14	8	2	< 5	+ 1	11	9	< 5	+ 1
2	12	5	+ 5	5	5	16	−22	8	3	10	+ 9	12	0	4	+ 6
2	13	4	+ 1	5	6	14	−16	8	4	6	− 4	12	1	5	+ 6
2	14	< 4	+ 3	5	7	6	− 9	8	5	8	+ 6	12	2	< 5	+ 2
2	15	4	+ 3	5	8	6	+ 5	8	6	< 5	− 2	12	3	< 5	+ 1
2	16	< 4	+ 3	5	9	5	− 5	8	7	< 5	+ 2	12	4	< 5	− 1
2	17	6	− 8	5	10	4	− 3	8	8	11	+12	12	5	< 5	− 0
2	18	< 4	+ 1	5	11	< 4	− 3	8	9	12	−13	12	6	< 5	− 1
2	19	< 4	− 1	5	12	< 4	+ 2	8	10	< 5	− 1	13	1	< 3	+ 0
3	1	24	+20	5	13	< 4	− 6								

* A hydrogen contribution of −10 was estimated for (002) but was not added.

Table 3. *Observed and calculated structure factors for the (h0l) reflections*

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
1	0*	110	−170	2	10	5	− 3	3	$\overline{12}$	3	− 1	5	$\overline{4}$	4	+ 5
1	2	10	−16	2	$\overline{2}$	30	−37	3	$\overline{14}$	19	−17	5	$\overline{6}$	4	+ 7
1	4	12	+ 9	2	$\overline{4}$	20	−22	3	$\overline{16}$	21	−17	5	$\overline{8}$	< 5	+ 5
1	6	9	+ 9	2	$\overline{6}$	43	−49	3	$\overline{18}$	57	+49	5	$\overline{10}$	5	− 4
1	8	5	− 0	2	$\overline{8}$	64	−73	3	$\overline{20}$	22	+19	5	$\overline{12}$	9	−11
1	10	5	+ 1	2	$\overline{10}$	44	−38	3	$\overline{22}$	8	+ 6	5	$\overline{14}$	< 5	− 2
1	12	4	+ 1	2	$\overline{12}$	5	+ 6	4	0	6	+ 9	5	$\overline{16}$	< 5	− 1
1	$\overline{2}$	7	−14	2	$\overline{14}$	13	+11	4	2	5	+ 8	5	$\overline{18}$	23	+23
1	$\overline{4}$	12	+13	2	$\overline{16}$	12	+ 9	4	$\overline{2}$	8	−12	5	$\overline{20}$	9	− 9
1	$\overline{6}$	40	+48	2	$\overline{18}$	45	−38	4	$\overline{4}$	5	− 6	5	$\overline{22}$	< 5	− 1
1	$\overline{8}$	33	+29	2	$\overline{20}$	16	−15	4	$\overline{6}$	< 4	− 2	5	$\overline{24}$	< 5	− 1
1	$\overline{10}$	15	−12	2	$\overline{22}$	4	− 4	4	$\overline{8}$	4	− 3	5	$\overline{26}$	15	−11
1	$\overline{12}$	23	−21	3	0	14	−19	4	$\overline{10}$	5	+ 1	6	$\overline{10}$	3	+ 1
1	$\overline{14}$	13	−12	3	2	13	−15	4	$\overline{12}$	12	+12	6	$\overline{12}$	4	+ 7
1	$\overline{16}$	16	−16	3	4	6	− 7	4	$\overline{14}$	18	+16	6	$\overline{14}$	< 5	− 1
1	$\overline{18}$	12	+12	3	6	4	+ 5	4	$\overline{16}$	21	+21	6	$\overline{16}$	7	− 8
1	$\overline{20}$	2	+ 5	3	$\overline{2}$	21	+27	4	$\overline{18}$	37	−31	6	$\overline{18}$	16	−21
2	0	32	+43	3	$\overline{4}$	10	+10	4	$\overline{20}$	< 4	− 2	6	$\overline{20}$	5	+ 7
2	2	< 4	+ 6	3	$\overline{6}$	9	+10	4	$\overline{22}$	< 4	− 1	6	$\overline{22}$	< 5	+ 1
2	4	< 4	+ 1	3	$\overline{8}$	28	+33	4	$\overline{24}$	5	+ 4	6	$\overline{24}$	< 5	− 2
2	6	7	− 8	3	$\overline{10}$	30	+30	4	$\overline{26}$	13	+ 9	6	$\overline{26}$	7	+ 5
2	8	6	− 6												

* Extinction.

plots at $l = 0$ also indicated that b_{11} was important. To find b_{11} these intercepts were plotted against h^2. The result was a factor $\exp[-(0{\cdot}007h^2-0{\cdot}005hl)]$. No further attempt was made to expand on the temperature-factor correction, but a scale-factor adjustment was made for each level in k. With these corrections R dropped to 0·20. The atomic coordinates are listed in Table 1. No hydrogen contributions were included in the calculated structure factors (Tables 2 and 3).

A reliability factor of 0·20 is not as low as one would like, but for a number of reasons to be mentioned later it appears that the structure is correct, albeit not highly accurate. One reason for the high value for R probably lies in the original data. Photographs were made with the capillary axis between 15° and 20° away from normal to the X-ray beam. This may have resulted in absorption errors which were not a simple function of θ. In addition, the good single crystal occupied only a short length of the capillary. The X-ray beam also picked up slightly misoriented crystalline regions on either side of the desired portion, resulting in some split spots which made intensities more difficult than usual to read.

Table 4. *Bond lengths and angles*

Atoms	Distance	Atoms	Angle
C_1–O_1	1·26 Å	O_1–C_1–O_2	121·0°
C_1–O_2	1·24	O_1–C_1–C_2	117·8
C_2–C_1	1·50	O_2–C_1–C_2	121·2
C_3–C_2	1·52	C_3–C_2–C_1	115·7
C_4–C_3	1·56	C_4–C_3–C_2	111·2
C_5–C_4	1·55	C_5–C_4–C_3	112·9
C_6–C_5	1·52	C_6–C_5–C_4	110·1
C_7–C_6	1·48	C_7–C_6–C_5	114·7
C_7–O_3	1·20	O_4–C_7–O_3	119·8
C_7–O_4	1·34	O_3–C_7–C_6	126·6
		O_4–C_7–C_6	113·9

Table 5. *Short non-bonded approaches**

Atoms	Distance	Atoms	Distance
O_1–O_3''	3·69 Å	C_7–O_2''	4·06 Å
O_4–O_2''	3·44	C_6–O_2''	3·72
O_1–O_4'''	3·07	C_1–O_4'''	3·58
O_1–O_1'''	3·56	O_2–C_4''''	3·58
C_1–O_3''	3·78	O_2–C_5''''	3·64
C_2–O_3''	3·43	C_4–C_7''''	4·02
O_2–C_3''''	3·59	C_3–C_7''''	4·06

* Atom X_i' is related to atom X_i by a center of symmetry.

Atom X_i'' is related to atom X_i by a 2_1 screw axis operation, the axis being parallel to b and at $z = \frac{1}{4}$, $x = \frac{1}{2}$.

Atom X_i''' is related to atom X_i by a c glide perpendicular to b and at $b = \frac{1}{4}$.

Atom X_i'''' is related to atom X_i by a translation of one unit cell vector, a.

Table 6. *Hydrogen bond distances and angles*

Atoms	Distances	Atoms	Angle
O_1–O_2'	2·68 Å	O_3'–O_4–C_7	112·6°
O_4–O_3'	2·67	C_7'–O_3'–O_4	125·3
		C_1–O_1–O_2'	121·4
		O_1–O_2'–C_1'	117·3

Another reason for the high R factor probably lies in the need for individual anisotropic temperature factors. Certainly the way in which the temperature factors were handled had only expediency to recommend it. Finally, the inclusion of the hydrogen atoms would be expected to reduce R by 0·01 to 0·02.

In spite of the large R factor, the reasonableness, on the whole, of the bond lengths and bond angles (Table 4), van der Waals approaches (Table 5), hydrogen bond lengths and angles (Table 6), and carboxyl-group planarity argues for the essential correctness of the structure found.

It is of interest to look at the R factors in a more detailed way. For the $(0kl)$ reflections $R = 0{\cdot}18$. By levels of k:

$$R(h0l) = 0{\cdot}21;\ R(h1l) = 0{\cdot}23;\ R(h2l) = 0{\cdot}17;$$
$$R(h3l) = 0{\cdot}24;\ R(h4l) = 0{\cdot}17;\ R(h5l) = 0{\cdot}25.$$

It is clear that the levels of odd k have higher R factors than levels of even k. The average magnitudes of the reflections on each level are:

$$\bar{F}(h0l) = 15{\cdot}4;\ \bar{F}(h1l) = 8{\cdot}2;\ \bar{F}(h2l) = 12{\cdot}2;$$
$$\bar{F}(h3l) = 7{\cdot}2;\ \bar{F}(h4l) = 9{\cdot}5;\ \bar{F}(h5l) = 6{\cdot}4.$$

The average residuals between observed and calculated structure factors are:

$$\bar{r}(h0l) = 3{\cdot}2;\ \bar{r}(h1l) = 1{\cdot}9;\ \bar{r}(h2l) = 2{\cdot}1;$$
$$\bar{r}(h3l) = 1{\cdot}7;\ \bar{r}(h4l) = 1{\cdot}6;\ \bar{r}(h5l) = 1{\cdot}6.$$

Now, by assuming that the average residual will have a part proportional to F_o and a part independent of F_o, i.e., $= K\bar{F}_0+d$, the above data were used to find $K(0{\cdot}13)$ and $d(0{\cdot}7)$. It is found that this form does in fact fit the data rather well (although $\bar{r}(h0l)$ is higher than expected) and that the average residuals observed are consistent. This is equivalent to saying that the discrepancies for levels of odd k are no worse than those for even k since the higher R factors for odd levels are consistent with their smaller observed structure factors.

One cycle of refinement was run beyond the one for which parameters and structure factors are reported. The results were used as an indication of the errors to be expected in the parameters. The average change in x was 0·005 Å, the maximum 0·013 Å; in y, 0·002 Å and 0·004 Å; in z, 0·007 Å and 0·016 Å. The terms in the least-squares equations were not obtained so an arbitrary estimate of probable error was taken equal to 0·02 Å; which is larger than the maximum observed shift. This results in a probable error in bond length of 0·03 Å and in the angles of about 2°.

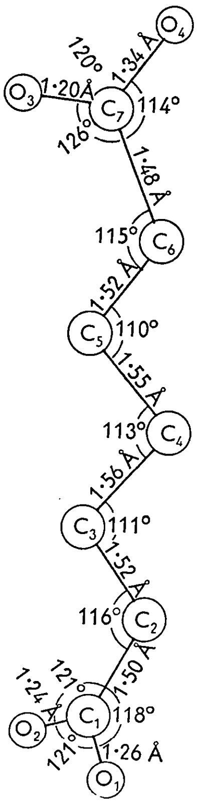

Fig. 2. Schematic drawing of the α-pimelic acid molecules.

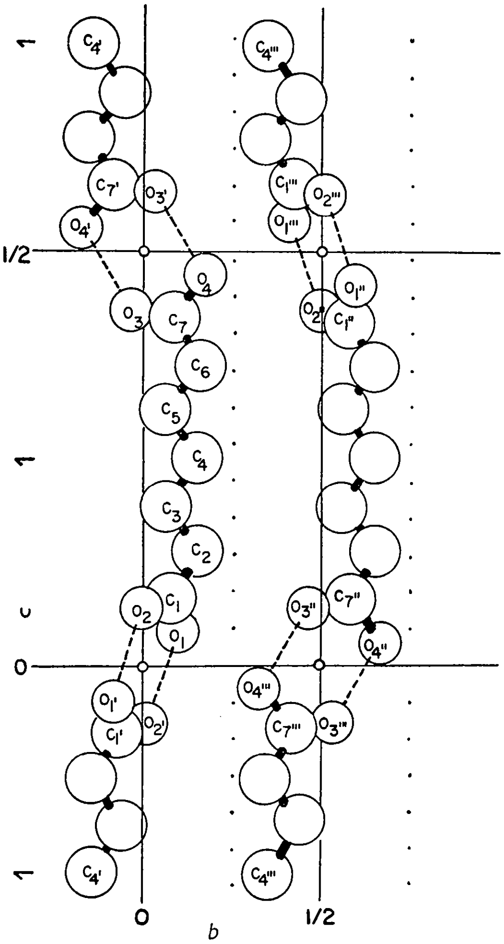

Fig. 3. View of the hydrogen-bonded chains down a^*. The coordinate grid shown is at $x = \frac{1}{2}$.

Discussion of the structure

The intramolecular bond lengths and bond angles which are listed in Table 4 are also shown in Fig. 2, which is a schematic drawing of the molecule. Fig. 3 shows the hydrogen-bonded chain arrangement of the molecules viewed down the reciprocal a direction.

By the least-squares method equations were found for the planes best fitting C_1, C_2, O_1, O_2 (plane I); C_6, C_7, O_3, O_4 (plane II); and the central five carbon atoms (plane III). It was found that C_1, C_2, O_1, and O_2 are all less than 0·005 Å from plane I. O_3, O_4, and C_6 are 0·006 Å from plane II and C_7 is 0·017 Å off. To speak of the central five carbon atoms as lying in a plane is only a rough approximation. However, the average distance of these five carbon atoms from plane III is 0·05 Å and the largest is 0·07 Å. C_1 is only 0·03 Å from this same plane but C_7 is 0·31 Å away. The carboxyl groups and their α carbon atoms then do show the expected planarity, C_7 being the worst offender. From Table 4 it may be noted that C_7–O_4 is 1·34 Å, somewhat longer than expected, and C_7–C_6 is 1·48 Å, somewhat shorter than expected. Since C_7 is involved in all of these possibly suspect distances, its location is probably the one most open to suspicion.

In spite of what has just been said about the C_7–O_4 bond length and the accuracy of the determination as a whole, it may be pointed out that the geometry of the carboxyl groups is consistent with a possible distribution of double-bond character. The observed bond lengths are 1·34 Å and 1·20 Å in one carboxyl group; 1·26 Å and 1·24 Å in the other. Using Vaughan & Donohue's (1952) suggested values of 1·42 for C–O and 1·20 for C=O in Pauling's equation would give 1·34 Å and 1·22 Å for 15 and 85% double-bond character; 1·27 Å and 1·24 Å for 40 and 60% double-bond character.

The hydrogen bond lengths and angles are altogether normal. The planes of the carboxyl groups which are hydrogen bonded to each other are parallel and 0·33 Å apart for those near $z = 0$, $y = 0$, and 0·25 Å apart for those near $z = \frac{1}{2}$, $y = 0$.

The differences between the α and β modifications may be described in terms of the angles between the planes. For the low-temperature phase (MacGillavry *et al.*, 1948), the carbon atom plane is approximately the *b*, *c* plane. The molecule has a twofold axis of symmetry parallel to *b* which passes through the central carbon atom. The two carboxyl groups are each turned 30° out of the *b*, *c* plane in opposite directions; their planes thus make an angle of about 60° with each other. The rotation is not confined to the bond between the end two carbon atoms but is partially transmitted to the bond between the second and third carbons from each end.

α-Pimelic acid, unlike the β form, does not have a rotation axis; the two ends of the molecule are not related by symmetry. The angle between the two carboxyl group planes is still about 60°. However, the average plane of the central five carbon atoms is now 44° from carboxyl plane I and 18° from carboxyl plane II. The carbon chain and the carboxyl group near $z = 0$ are turned out of the *b*, *c* plane in about the same direction (11° and 55° respectively), while the carboxyl group near $z = \frac{1}{2}$ is turned 8° out of the *b*, *c* plane in the opposite direction.

The transition from the β to the α forms, judging from room-temperature cell sizes of 819 Å^3 and 848 Å^3 respectively, results in an increase in volume. However, closest intermolecular approaches between non-bonded oxygens (3·07 Å and 3·44 Å) and the closest non-bonded intermolecular CH_2 to O approach of 3·43 Å are similar to those in room-temperature modifications in other dicarboxylic acids. The last mentioned approach appears to be shorter than in some of the dicarboxylic acids (Morrison & Robertson, 1949*a*, *d*) but is probably longer than the 3·3 Å approach which Morrison & Robertson note in adipic and sebacic acids and to which they attach responsibility for the energy lowering in the even acids.

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