CCCCXXX.—*Crystallography of the Aliphatic Dicarboxylic Acids.*

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THE straight-chain saturated acids of this series, besides being all solid at the ordinary temperature, lend themselves better to crystallographic study than the corresponding monocarboxylic acids, in that their crystals are harder and less liable to distortion. An advantage, moreover, of dealing with acids of comparatively low molecular weight is that crystals can be procured which have a reasonable thickness in the direction of the *c* axis instead of being excessively thin and tabular.

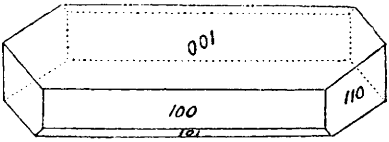
Angle measurements on crystals of the lower members of the series, up to pimelic acid (C_7) have been made by various workers. From C_4 onwards they all crystallise in the monoclinic–prismatic class. The results of an *X*-ray examination of succinic acid (C_4) have been published by Yardley (*Proc. Roy. Soc.*, 1924, *A*, **105**, 451). A number of data bearing on the spacings of the basal planes, obtained by *X*-ray powder photographs and carried up to C_{34}, are due to Normand, Ross, and Henderson (J., 1926, 2632; *Proc. Roy. Soc. Edin.*, 1928, **48**, 20). It is assumed by the latter workers, and is now amply confirmed, that the length of the unit cells of these crystals, along *c*, depends on the number of carbon atoms in the molecule, as established by Shearer and Müller for other long-chain compounds.

The acids available in the form of single crystals for the present examination were adipic (C_6), pimelic (C_7), suberic (C_8), azelaic (C_9), sebacic (C_{10}), brassylic (C_{13}), and hexadecanedicarboxylic (C_{18}). For obtaining crystals of adequate quality, ethyl acetate was found in most cases to be the best solvent. With all the acids, cooling of hot aqueous solutions leads to crystals which are well-shaped except for extreme thinness upon (001), whereby they are rendered useless; but pimelic acid crystallises best by isothermal evaporation from water, in which it is moderately easily soluble in the cold. For sebacic acid, cooling of warm solutions in concentrated nitric acid gave the best results. Good crystals of suberic acid were not obtained until the method was adopted of heating the substance with ether in sealed tubes to about 100° and allowing it to cool in the oven.

Externally, the crystals of all the acids conform to the same type, with variations in face-development due to impurities and to the kind of solvent employed. The principal forms are always (001), (100), and (110), with, occasionally, (10$\bar{1}$) and (010). On pimelic acid crystals, (011) was also observed. Throughout the series, (001), (100), and (110) are pronounced cleavage-planes. The crystals are tabular upon (001) and become progressively thinner as the molecular weight rises. The majority of them are elongated along the *b* axis, so that on the whole the characteristic habit is that shown in Fig. 1. The β-angle is unusually large, varying from 128° to 137°. Swallow-tail twins about (001), with the *b* axes aligned, are common, and crossed twins about (001), with the *b* axes at right angles, also occur.

In the lower members of the series (101) is almost as well developed as (100), and earlier observers have sometimes chosen the former as containing the *c* axis, thus reducing β to the neighbourhood of 90°. As one ascends the series, however, the crystals seldom or never display the nearly orthogonal (10$\bar{1}$) face, whilst the highly tilted (100) face is always in evidence, besides being a definite cleavage-plane. The large β-angle therefore appears to be a reality. Angles lying in the same region of magnitude have been observed by Müller (*Proc. Roy. Soc.*, 1927, *A*, **114**, 542) in bromostearic, stearolic, and behenolic acids.

FIG. 1.



The β-angle of adipic acid (Brugnatelli, *Z. Kryst.*, 1896, **26**, 298) is known from earlier measurements. Those of the other acids concerned were now determined goniometrically. Whereas reflexions from (001) were uniformly good, those from (100) were less satisfactory, owing to the narrowness of the face and its tendency to unevenness. It was therefore considered advisable to select the results of the best reflexions from several crystals and to state the mean to the nearest 10′. The angles so found agree, within the experimental limits, with those which may be independently calculated from the *X*-ray spacings of the (001) and (100) planes.

The crystals were subjected to *X*-ray analysis by means of rotation photographs of single crystals about their three axes, upon glass quarter-plates. When required for closer investigation of particular reflexions, oscillation photographs were also taken. The β-angles and cell-dimensions (in Å.U.) of the several crystals are summarised in Table I.

TABLE I.

Acid.	*a*.	*b*.	*c*.	*β*.	Mols. in cell.
C_6, Adipic	10·27	5·16	10·02	137° 5′	2
C_7, Pimelic	9·93	4·82	22·12	130° 40′	4
C_8, Suberic	10·12	5·06	12·58	135° 0′	2
C_9, Azelaic	9·72	4·83	27·14	129° 30′	4
C_{10}, Sebacic	10·05	4·96	15·02	133° 50′	2
C_{13}, Brassylic	9·63	4·82	37·95	128° 20′	4
C_{18}, Hexadecanedicarboxylic	9·76	4·92	25·10	131° 10′	2

The first point of interest which is brought out by these figures is that the unit cells of all the acids have about the same breadth and depth. From this alone it necessarily follows that the carbon-atom chain of the structural molecule must be strung out along the *c* axis.

As regards the *c* dimensions of the several unit cells, it is seen that the crystals fall into two groups, according to the odd or even number of carbon atoms in the molecule. The *c* axes of the even-carbon series are nearly proportional to the number of carbon atoms, whilst in the odd-carbon series they are proportional to twice that number. In the latter series the heights of the cells are doubled and must be taken up by two molecules end to end; correspondingly the cells contain the substance of four instead of two molecules.

This difference in crystal structure between even-carbon and odd-carbon acids cannot be unconnected with the well-known alternation in their melting points. Ultimately the melting point must depend on the ease with which molecules are torn out of the crystal lattice, and it is plausible to suppose that the double cells of the odd-carbon acids (having relatively lower m. p.'s) are less stable in this respect than the more compact cells of the even-carbon acids. A full explanation, however, must be deferred until not only the exact structures of the crystals but also the degree of molecular association in the molten substances are better known.

An alternation in most of the data in Table I is apparent as the homologous series is ascended, and is especially striking with the β-angles, which are always considerably smaller for odd-carbon than for even-carbon acids. The gentle alternation in the *a* and *b* cell-dimensions shows a tendency to die out as the molecular weight rises.

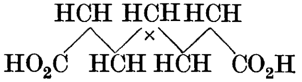
With each crystal, reflexions from planes to the number of 30—50 were identified upon the photographs. Owing to the close similarity of all the *a* and *b* axial lengths, the rotation photographs about these respective axes were much alike among themselves, whilst the *c* axis photographs varied characteristically with the crystal. Reflexions from (110) and (200) were very strong throughout, and (211) fairly strong. In the even-carbon series, (210), which did not appear at all in the odd-carbon series, was also fairly strong. On the other hand, (011) appeared intensely in the latter but only faintly or not at all in the former series; this confirms the structures in Fig. 2, where (011) planes in the odd-carbon series are seen to have a greater reticular density than (011) planes in the even-carbon series.

Orders of (001) attained at most only moderate intensity and were represented by both odd and even orders, beginning with (001), in the even-carbon acids, but by even orders only, beginning with (002), in the odd-carbon acids. By a simple application of the structure factor of intensity, this disappearance of the odd orders indicates a division of the unit cell across *c* into halves of nearly equivalent reflecting power, and is what would be expected from the structure (Fig. 2) of odd-carbon acids. A minor subdivision of the *c* heights is caused by successive layers of the carbon atoms themselves in the plane of (001). The effect of this, again by operation of the structure factor, is well brought out in the *c* axis photographs, where remote hyperbolas (layer-lines) show a certain intensity after an interval of weak or unrepresented hyperbolas. Thus, in adipic acid the 3rd and 4th hyperbolas are relatively strong, in suberic the 4th and 5th, in sebacic the 6th, and in the C_{18} acid the 8th and 9th. In pimelic acid the 8th hyperbola emerges strongly, in azelaic the 10th, and in brassylic the 14th.

On scrutinising all the planes represented by *X*-ray reflexions, it was found that in no case is there a general halving in the (hkl) series; hence the space-lattice is the simple lattice Γ_m. On the other hand, such planes as (100), (101), (300), etc., did not appear, but (200), (205), (402), etc., were frequent; that is, $(h0l)$ is halved when h is odd. Lastly, since (020) appears but never (010), we may conclude that the space-group is C_{2h}^5.

If the molecule is asymmetrical, four differently oriented molecules must constitute a unit cell. Such is the case with odd-carbon acids; their molecules therefore must be without symmetry. In the case of even-carbon acids there are only two in the cell, and the molecule must have a centre of symmetry of its own which it contributes to the symmetry of the cell. From the structural formulæ, it is easily seen how the one series of acids can have central symmetry and the other none, thus :

Odd :—



Even :—

Any straight line drawn through the centre of symmetry at × cuts equivalent atoms or groupings at opposite boundaries of the molecule when the carbon-atom number is even, but not when it is odd. Similar considerations apply, for example, to hydrocarbons; and, indeed, it is found by Müller (*loc. cit.*) that octadecane, $C_{18}H_{38}$, has two molecules to the cell, but $C_{29}H_{60}$ has four. All monocarboxylic acid molecules may be expected to be asymmetrical and to form four-molecule cells.

Some further points of similarity and contrast between the several acids may be gathered from Table II.

TABLE II.

Acid.	*d.*	*ab* sin *β*.	*D.*	Gap.
C_6, Adipic	1·340	36·18	—	3·70
C_7, Pimelic	1·313	36·26	—	3·47
C_8, Suberic	1·270	36·24	2·56	3·73
C_9, Azelaic	1·252	36·22	2·50	3·47
C_{10}, Sebacic	1·240	35·96	2·48	3·65
C_{13}, Brassylic	1·173	36·41	2·50	3·81
C_{18}, Hexadecanedicarboxylic	1·138	36·20	2·64	3·62
Mean		36·21	2·53	3·63

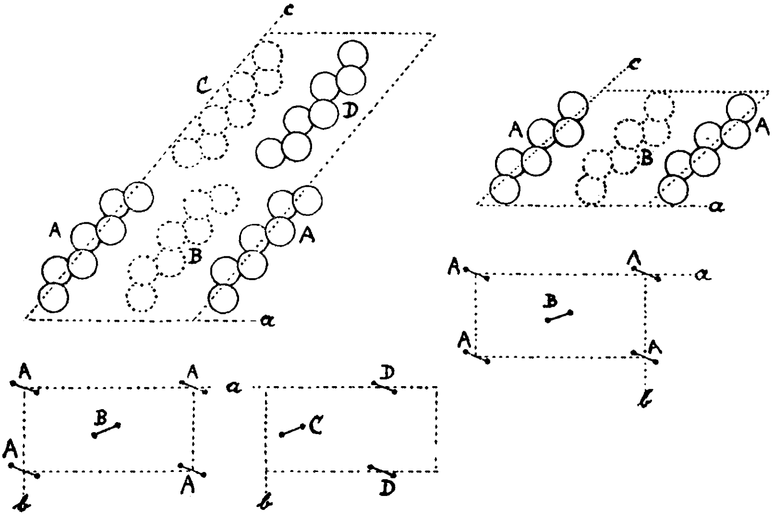
The densities are calculated by the relation $d = 1{\cdot}66MN/abc \sin \beta$, where M is the molecular weight and N the number of molecules in the unit cell. Values so found contain the errors of four separate experimental quantities, and are not precise enough to decide whether there is an alternation along the series; if there is, however, it can be but slight.

The quantity $ab \sin \beta \times 10^{-16}$ cm.² expresses the area of a section of the unit cell taken, not along (001), but at right angles to the c axis, and is seen to be fairly constant. Moreover, all the long-chain aliphatic compounds hitherto examined, including bromostearic acid, show similar values for $ab \sin \beta$, ranging from 35·8 to $37{\cdot}8 \times 10^{-16}$ cm.². This remarkable uniformity leaves it hardly doubtful that all the crystals concerned are built up in the same way, *viz.*, of parallel bundles of carbon-atom chains along the c axis, with ample space between them to accommodate hydrogen, oxygen, and other atoms.

The lengths of the c axes in Table I would not permit a row of carbon atoms of diameter 1·54 Å.U. to lie with their centres in a straight line; these atoms must therefore lie in zigzag formation along the chain. The unit cells of adipic and pimelic acids, on this hypothesis, are shown diagrammatically in Fig. 2, with the (010) face or monoclinic plane of symmetry in the plane of the paper. The ground-plans of the corresponding (001) or basal sides of the cell are given underneath. The molecules are shown as flat zigzag chains of carbon atoms, the angle of zigzag being not far from the tetrahedral angle. There is as yet no evidence as to the arrangement of the methylenic hydrogen atoms or of the groups of hydrogen and oxygen atoms which cluster at each extremity, and they are not shown in the figure; in the case of even-carbon acids, however, we know that all these atoms must be disposed in harmony with the centro-symmetry of the molecule.

Those molecules which lie half-way across the cell are drawn in dotted lines. Molecules B, in the case of even-carbon acids, are so disposed as to lie symmetrically both across a glide-plane and about a screw-axis towards molecules A. In the odd-carbon cell, molecules B are reflexions of A, molecules C are derived by rotation from A, and molecules D are reflexions of C. The upper half of the cell is provisionally shown slightly displaced against the lower half in the *a* direction, on the analogy of the structure of $C_{29}H_{60}$ as worked out by Müller (*Proc. Roy. Soc.*, 1928 *A*, **120**, 437), but space-group considerations alone afford no information as to this. The planes of the zigzag chains will not lie exactly parallel to (010) or (100), because the central molecule B would then be almost identical with A, in which case we should expect halvings of the (*hkl*) planes in the *X*-ray spectra. In Fig. 2 the projections of the molecules upon the base are shown inclined at an undetermined angle, which angle, or its symmetrical counterpart, must be the same for all molecules.

FIG. 2.



Pimelic acid. *Adipic acid.*

The available data enable us to calculate the distance (*D*) between successive carbon atoms on any one side of the chain—the wave-length, as it were, of the zigzag. By subtracting $2c$ of each even-carbon acid from $2c$ of adipic acid, and c of odd-carbon acids from c of pimelic acid, and dividing by the difference in the number of carbon atoms in the molecules, we obtain the required distances, which are stated in col. 3 of Table II. Although the results are only roughly constant, they point to a uniform mean distance, between centres of carbon atoms, of 2·53 Å.U. Here again there is striking agreement with other crystal structures. For diamond, the corresponding distance is 2·52 Å.U., whilst for the hydrocarbon $C_{29}H_{60}$ it has been evaluated (Müller, *loc. cit.*, 1928) as 2·537 Å.U.

Lastly, it is clear that in each crystal there must be a gap between successive molecules, measured in the line of the c axis, since the quotient c/n decreases as the molecules grow longer. This gap, as between centres of terminal carbon atoms, is found by calculating $c - 2{\cdot}53(n - 1)/2$ or $c/2 - 2{\cdot}53(n - 1)/2$, and the results are given in the fourth column. If the diameter of the carbon atom be assumed to be 1·54 Å.U., the mean gap of 3·63 Å.U. between centres corresponds to a clear gap of 2·09 Å.U., to the filling of which the oxygen and hydrogen atoms of two carboxyl groups must contribute. The extent of the gap is somewhat larger than that found for $C_{29}H_{60}$, *viz.*, 3·09 Å.U. between centres, as might be expected when the molecule has carboxyl groups at each end.

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