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The Crystal Structure of Ximenynic Acid

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(*Received* 13 *March* 1954 *and in revised form* 28 *May* 1954)

An attempt to determine the crystal structure of ximenynic acid is described. The main findings are:

The crystals are triclinic ($P\bar{1}$). $Z = 2$.

There is a tendency for the molecule to form a straight carbon chain, as in other simpler fatty acids, but the presence of the triple and double bonds prevents this to a certain extent.

The double bond carries its attachments in the *trans* position. The spatial arrangement of the double-bond group presents an unexpected feature.

Ximenynic acid is a conjugated unsaturated monobasic fatty acid with the bulk formula $C_{18}H_{30}O_2$ isolated by Ligthelm & Schwartz (1950) from kernels of *Ximenia Caffra*. According to Ligthelm, Schwartz & von Holdt (1952), the structural formula of the acid is

$$COOH.(CH_2)_7.C\vdots C.CH{:}CH.(CH_3)_5.CH_3$$

and examination of the infra-red absorption of methyl ximenate by Ahlers & Ligthelm (1952) indicates the possibility of a *trans* configuration of the double bond.

An X-ray examination of crystals of the acid was undertaken to determine (*a*) whether the molecule of the acid is straight or whether it bends back on itself at the double bond, and (*b*), whether the bond is of the *cis* or *trans* type, the two questions being of course related. It has not been possible in the time available to make a complete determination of the structure, but its general nature is clear and a definite answer can be given to the stereochemical questions.

The crystals available were very thin white plates, oblong in shape and showing no definite faces except those of the plates themselves. X-ray examination showed one important axis—later called the *b* axis—to lie parallel to the long axis of the plates. A second axis, *a*, was found to lie in the plate. Oscillation photographs gave the axial lengths

$$a = 4{\cdot}634 \pm 0{\cdot}032 \text{ Å},\quad b = 5{\cdot}572 \pm 0{\cdot}004 \text{ Å},$$

with $\gamma = 84^\circ\, 51'$.

The determination of the *c* axis is less easy owing to the thinness of the plates. The area $ab \sin \gamma$ is 25·7 Å^2, which is greater than the cross-sections of the known fatty acids, which are of the order of 18 Å^2. On the other hand, it is not large enough for a chain doubled back on itself. The figures suggest that the *c* axis will be a long one, inclined at a considerable angle to the plane of the plates.

The (001) *spacing* can be determined at once from an oscillation photograph. It is 34·20±0·13 Å, and the unit cell has a volume 879 Å^3. The molecular weight of the cell is 278·2 and the density 1·04 g.cm.$^{-3}$. There are two molecules in the unit cell.

Oscillation photographs taken about an axis perpendicular to the plate, and therefore parallel to the c^* reciprocal axis, show row-lines, closely set with points. By taking such photographs with the rays travelling along the *a* and the *b* axes it is possible to estimate the directions of valid a^* and b^* axes and so to determine the direction of a possible *c* axis. The *c* axis first determined was that lying most nearly perpendicular to the *ab* face. It was 34·4 Å in length with a cross-section of 25·7 Å^2, and was therefore probably not the structural unit cell. Photographs showed the 016 spectrum referred to the cell to be very strong and to be accompanied by very well marked, nearly circular, thermal diffuse spots. This indicates that the plane (016) is probably parallel to the direction of the acid chains, and, as a result of considerations of this kind, a cell

Table 1. *Observed and calculated values of structure factors, F(0kl)*

0*kl*	F_o	F_c	0*kl*	F_o	F_c	0*kl*	F_o	F_c
001	−15·9	−14·9	$0,1,\overline{27}$	2·7	+2·1	$0,2,\overline{40}$	−4·8	−5·4
002	Nil	−1·5	$0,1,\overline{26}$	−1·6	+5·6	$0,2,\overline{39}$	3·4	+5·1
003	−12·1	−10·8	$0,1,\overline{25}$	1·7	−2·0	$0,2,\overline{38}$	2·4	−1·1
004	4·7	+1·2	$0,1,\overline{24}$	−3·3	−7·5	$0,2,\overline{36}$	5·6	+4·8
005	−7·5	−6·1	$0,1,\overline{23}$	3·1	+5·1	$0,2,\overline{22}$	−3·7	−4·9
006	−3·0	−3·2	$0,1,\overline{21}$	2·6	+3·0	0,2,21	3·6	+1·0
007	−7·6	−6·8	$0,1,\overline{18}$	2·5	+4·4	$0,2,\overline{20}$	−3·7	−1·4
008	−4·7	−3·9	$0,1,\overline{17}$	1·5	+8·8	$0,2,\overline{19}$	3·7	+9·9
009	Nil	−0·1	$0,1,\overline{16}$	5·0	−9·1	$0,2,\overline{18}$	−4·6	−7·7
0,0,10	−2·9	−3·1	$0,1,\overline{15}$	−1·7	−3·1	$0,2,\overline{17}$	3·2	+5·5
0,0,11	Nil	+5·0	$0,1,\overline{14}$	6·6	+9·9	$0,2,\overline{16}$	−4·2	−2·9
0,0,12	−5·5	−2·9	$0,1,\overline{13}$	−1·2	+1·1	$0,2,\overline{15}$	1·9	+10·6
0,0,13	Nil	−2·5	$0,1,\overline{12}$	3·2	+4·3	$0,2,\overline{14}$	−2·8	−6·5
0,0,14	−1·7	−2·5	$0,1,\overline{11}$	Nil	−5·2	$0,2,\overline{13}$	2·1	+2·2
0,0,15	Nil	+0·7	$0,1,\overline{10}$	3·0	+8·0	$0,2,\overline{12}$	1·7	−1·6
0,0,16	−2·1	+5·9	$0,1,\overline{9}$	1·1	+9·6	$0,2,\overline{10}$	−2·0	−8·6
0,0,17	−3·2	−8·3	$01\overline{8}$	−1·4	−1·5	$0,2,\overline{6}$	−3·3	−3·4
0,0,18	Nil	−1·5	$01\overline{7}$	Nil	−0·5	$02\overline{4}$	−3·4	−3·7
0,0,19	−3·6	−1·8	$01\overline{6}$	1·1	+0·1	$02\overline{3}$	3·1	+4·9
0,0,20	3·7	+5·1	$01\overline{5}$	2·9	+12·4	020	8·6	+23·2
0,0,21	−3·9	−0·4	$01\overline{4}$	−2·8	−0·6	022	7·1	+4·1
0,0,22	2·8	+2·0	$01\overline{3}$	Nil	−3·0			
0,0,23	−2·9	−7·8	$01\overline{2}$	3·6	+4·7	$0,3,\overline{40}$	10·4	+6·9
0,0,24	2·8	+10·5	$01\overline{1}$	2·3	+4·8	$0,3,\overline{39}$	−4·8	−8·3
0,0,25	−1·6	−0·4	010	−40·0	−68·4	$0,3,\overline{36}$	−6·0	−6·0
0,0,26	1·3	−2·8	011	4·1	+2·6	$0,3,\overline{23}$	−2·2	−2·1
0,0,27	−2·2	−4·8	012	−9·5	−5·2	$0,3,\overline{22}$	2·2	+8·6
0,0,33	−2·4	−2·0	013	Nil	0·0	$0,3,\overline{21}$	−2·2	−2·3
0,0,35	−1·7	+2·3	014	Nil	−1·2	$0,3,\overline{20}$	2·2	+6·9
0,0,36	2·0	+3·5	015	−2·4	−0·4	$0,3,\overline{19}$	−2·2	−9·1
0,0,37	−1·9	−0·7	016	6·4	+5·1			
0,0,38	−1·7	+0·3	017	2·3	+7·2	$0,4,\overline{40}$	−3·7	−5·1
0,0,39	−1·2	+0·5	018	3·0	+1·2	$0,4,\overline{39}$	3·0	+9·8
0,0,41	−3·9	−0·8	019	−4·2	−0·5	$0,4,\overline{38}$	2·1	−2·1
			0,1,10	2·7	+3·7	$0,4,\overline{36}$	−2·9	+4·8

$$a = 4{\cdot}634\ \text{Å},\ b = 5{\cdot}572\ \text{Å},\ c = 49{\cdot}03\ \text{Å},$$
$$\alpha = 135^\circ\, 29',\ \beta = 89^\circ\, 39',\ \gamma = 84^\circ\, 51'$$

was chosen. This cell has the same *a* and *b* axes as the first, and the same (001) spacing, but a longer and more oblique *c* axis. Its relation to the cell first determined is given by the matrix $100/010/0\bar{6}1$, by means of which indices referred to the first set of axes can be transformed to those appropriate to the second. For example, the strong spectrum 016 referred to the old cell now becomes 010. The new cell has a cross-section of 18 Å², and a length parallel to the *c* axis of 49·03 Å, consistent with the assumption that the cell contains two molecules set end to end.

The cell is triclinic, and of the two possible space groups $P\bar{1}$ was tentatively chosen, since it is reasonable to suppose the two molecules to be related by a centre of symmetry between the carboxyl groups. The existence of a centre of symmetry is also indicated by Wilson's (1950) method of statistical intensity distribution.

A series of Weissenberg photographs was taken about the *a* axis, to determine the intensities of the spectra 0*kl* necessary for an electron-density projection on the *bc* plane. The intensities were determined visually, by comparison with a set of spots of graded intensity; and after correction for the Lorentz factor, for differential absorption, and also as far as possible for the non-isotropic nature of the temperature factor, the resulting *F* factors were put on an approximately absolute scale by a method similar to that of Wilson. The resulting values of *F*(0*kl*) are shown in the column headed F_o in Table 1. Many of the spectra were too weak to observe, but some of the spectra of high order, for example $0,3,\overline{40}$, are still quite strong. Conditions are not therefore very favourable for a good projection.

The signs of the *F* factors used for the projection were obtained mainly by a method given by the author (Tesche, 1953). If the long molecule lies entirely within the unit cell, the electron density over the walls of the cell is low, and nearly uniform. Considering the projection on the *bc* plane, this has the consequence that the values of summations of the types

$$\tfrac{1}{2}F(000)+\sum_{1}^{l} F(00l),\quad F(0k0)+\sum_{1}^{l}\{F(0kl)+F(0k\bar{l})\},$$

and
$$F(00l)+\sum_{1}^{k}\{F(0kl)+F(0k\bar{l})\}$$

should be small. If the signs of some of the stronger spectra can be otherwise determined, it may therefore be possible to find the signs of a number of others. The signs of spectra of the type 00*l* were first determined by making a linear projection of the density parallel to *c*. This density should be low for regions near $z/c = 0$, between the two molecules, and then fairly

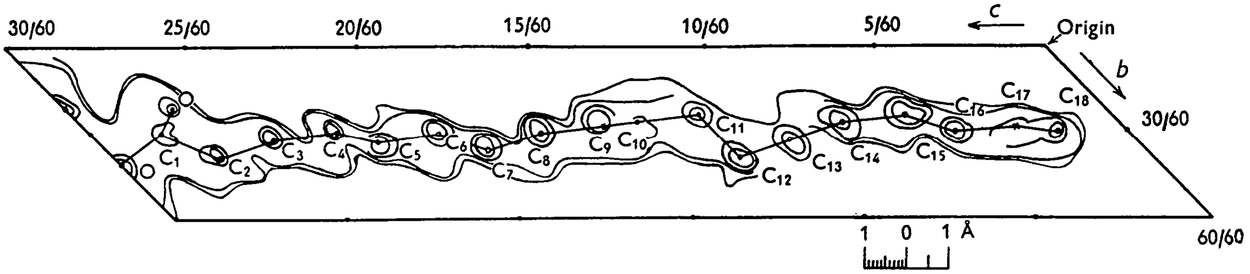

Fig. 1. Electron-density projection along *a* axis on to the (100) plane.

uniform over most of the chain, rising to higher values near $z/c = \frac{1}{2}$, as the carboxyl groups are approached. Only if the stronger $00l$ spectra have certain signs is such a distribution of density possible, and, assuming these signs, it is possible to use the summations given above to determine the signs of enough of the spectra $F(0kl)$ to give a projection. The signs used in making the projections are shown in Table 1, in the column headed F_o.

The projection obtained from these figures is shown in Fig. 1. It is by no means perfect, but nevertheless yields a certain amount of information. Peaks occur for the 18 carbon atoms in the structure, although these are not of equal height and there is some false detail. Estimates were made of the position of the atoms from this projection, and from these a set of structure factors was calculated. These factors, with the appropriate signs, are shown in the column headed F_c in Table 1. A few of the signs are different from those used in making the projection, but no further refinement was attempted.

In interpreting the projection it is necessary sometimes to use chemical evidence to decide between possibilities. The carboxyl group shows up clearly. Atoms C_1 to C_7 form an ordinary aliphatic chain, and the apparent displacement of C_4 from its position in the zigzag is probably due to false detail. The group of atoms C_8 to C_{11} contains the triple bond, between C_9 and C_{10}, and for the stereochemical reasons we should expect these atoms to lie in a straight line. Unfortunately C_{10} is not very clearly resolved.

The distance C_8–C_{11} should be 4·28 Å and the measured distance is about 3·75 Å, which indicates that the line C_8C_{11} deviates from the direction of the *c* axis of the cell. There is some evidence, which cannot be given in detail, that C_{11} is higher than C_8 in the projection as shown.

The atoms C_{11} and C_{12} are joined by the double bond, and the distance between them is normal, 1·35 Å. The bonds from C_{11} to C_{10} and from C_{12} to C_{13} are nearly parallel, as would be expected, but, rather surprisingly, C_{12} is bent out of the main direction of the chain.

The remaining atoms C_{12} to C_{18} must be considered as a possibly somewhat distorted, zigzag carbon chain.

The whole projection requires greater refinement, and too much reliance must not be based on it in its present form, but it is clear that the chain is not bent back on itself and that the configuration at the double bond is the *trans* one.

It is a pleasant duty to thank Prof. R. W. James for the great and unfailing interest he has taken in the work, and for his aid in many ways. The author would also like to thank Dr S. P. Ligthelm for his interest, and for the trouble he took in preparing the crystals. The author is indebted to the South African Council for Scientific and Industrial Research for the grant of a Senior Research Bursary which made the present work possible.

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