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The Crystal Structure of *trans* D,L 9-10 Methylene Octadecanoic Acid

BY T. BROTHERTON, B. CRAVEN AND G. A. JEFFREY
University of Pittsburgh, Pittsburgh, Pa., U.S.A.

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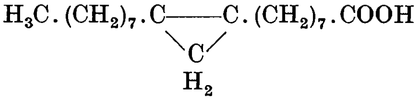
A two-dimensional Fourier analysis of the structure was carried out. It was complicated by a false solution in the early stages of the refinement and by difficulties in obtaining reliable intensity data.

Despite the presence of the cyclopropane ring in the center of the long chain, the crystal structure is similar to that of the monoclinic normal long-chain fatty acids of comparable chain length. This is in direct contrast to the C_{19} acid with a methyl group substituted at the 9 position. The stereochemistry of the molecule is more complex than that of the normal straight-chain acids since the methylene groups along the chain are not all coplanar.

Introduction

trans D,L 9-10 Methylene octadecanoic acid, $C_{19}H_{36}O_2$, (I), m.p. 36 °C., is one of four synthetic methylene octadecanoic acids prepared by Hofmann and his coworkers (Hofmann *et al.*, 1954; Hofmann, Orochena & Yoho, 1957) during the course of a chemical investigation into the structure of two natural 'cyclopropane fatty acids', lactobacillic and dihydrosterculic acids (Hofmann & Lucas, 1950; Hofmann, Lucas & Sax, 1952).



$$H_3C.(CH_2)_7.C\!-\!\!-\!\!-C.(CH_2)_7.COOH \quad (\text{ring } C\,H_2)$$

(I)

(The carbon atoms are numbered 1 to 18 along the chain from the carboxyl end, the methylene ring carbon is C_{19}.)

The crystal and powder data for these acids and their amides have been reported by Brotherton & Jeffrey (1957). Of the four synthetic acids, the *trans* D,L 9-10 and *trans* D,L 11-12, the *cis* D,L 9-10 and *cis* D,L 11-12, are respectively isomorphous in pairs, as judged by the close similarity in unit-cell dimensions and the intensity distribution of the side spacings in the powder diagrams.

The 9-10 acid was selected as the first of a series of detailed crystal-structure analyses of these compounds for the simple reason that, at the start of the investigation, it was the only compound of the series available in sufficient quantity and purity to give single crystals from which reasonable intensity Weissenberg photographs could be obtained.

Crystal data

Monoclinic,

$$a = 9{\cdot}75 \pm 0{\cdot}05,\quad b = 4{\cdot}98 \pm 0{\cdot}05,\quad c = 41{\cdot}1 \pm 0{\cdot}1 \text{ Å},\quad \beta = 89^\circ\, 28',$$

$$U = 1996 \text{ Å}^3,\quad D_m = 0{\cdot}96 \text{ g.cm.}^{-3},\quad Z = 4,\quad D_X = 0{\cdot}98 \text{ g.cm.}^{-3};$$

space group $P2_1/a$, from systematic extinctions.

Experimental

Crystals were obtained from solution in an acetone–water mixture as soft, thin colorless plates. Considerable difficulty was experienced in obtaining single crystals suitable for X-ray study.

Initially the unit-cell dimensions were measured from Weissenberg and precession photographs. With the exception of the long spacing, $c \sin \beta$, this was not very satisfactory owing to the absence of high orders and the spread of the spots on the photographs. Later it was possible to repeat the measurements with better accuracy, using the General Electric single-crystal orienter on an XRD-5 diffractometer unit. For comparison with the counter measurements given above, the photographic data were

$$a = 10{\cdot}1,\quad b = 4{\cdot}78,\quad c \sin \beta = 41{\cdot}4 \text{ Å}.$$

The intensities were recorded with Cu $K\alpha$ radiation on multi-film equi-inclination Weissenberg photographs, and were estimated visually. This also presented a problem owing to the large variation in spot size and shape from the best crystals we could obtain, which had dimensions of about $0{\cdot}6 \times 0{\cdot}6 \times 0{\cdot}2$ mm. Thus, on the zero-layer of the b axis, although the relative intensities within the groups of $00l$, $20l$, $40l$, and $60l$ were reasonably reliable, the correlation between groups was uncertain. The 206 reflection was so outstandingly intense that it could not be correlated satisfactorily with the other measurements. A 24-hr. exposure with Ni-filtered radiation recorded 106 reflections extending to $\sin \theta/\lambda = 0{\cdot}41$. The intensities were corrected for the usual angle factors; no attempt was made to correct for absorption.

At the conclusion of the analysis, the single-crystal orienter was available and was used to establish a better correlation between the groups of *h*0*l* intensities. The stationary-counter/moving-crystal technique was used (Furnas, 1957). These measurements showed that some reflections were spread over a range of 5° of crystal rotation. As had previously been inferred from the photographic observations (Brotherton & Jeffrey, 1957), even the best apparent single crystals were disarranged stacks of very thin plates like loose pages of a book.

The structure determination

The *b*-axis projection was likely to be the only one giving a resolved view of the molecule. A plot of the weighted reciprocal lattice for the *h*0*l* reflections showed a marked sub-cell distribution (Fig. 1). Using the sub-cell theory of Vand (1951), an orthorhombic sub-cell was derived, 2·60 Å in the long-chain direction and 4·18 Å at right angles.

The structure amplitudes $|F_{HL}|$ for the sub-cell were derived from those of the main cell $|F_{hl}|$ in the following way:

(i) when HL fell on hl,

$$|F_{HL}| = |F_{hl}|+|F_{h,l}\pm 1|+\tfrac{1}{2}|F_{h,l\pm 2}| \;,$$

(ii) when HL fell between hl and $h, l+1$,

$$|F_{HL}| = |F_{hl}|+|F_{h,l+1}|+\tfrac{1}{2}|F_{h,l-1}|+\tfrac{1}{2}|F_{h,l+2}| \;.$$

Approximate values for x_j, z_j, the atomic coordinates in the sub-cell, were obtained by an analytical solution from the amplitudes of $H0$ and $0L$. This gave the signs of the structure factors and the sub-cell Fourier projection shown in Fig. 2. The parameters from this were $x_j = \pm 0{\cdot}077$, $z = \pm 0{\cdot}290$, with the symmetry center as origin.

The structure factors of the main cell are related to those of the sub-cell by the expression given by Vand (1951):

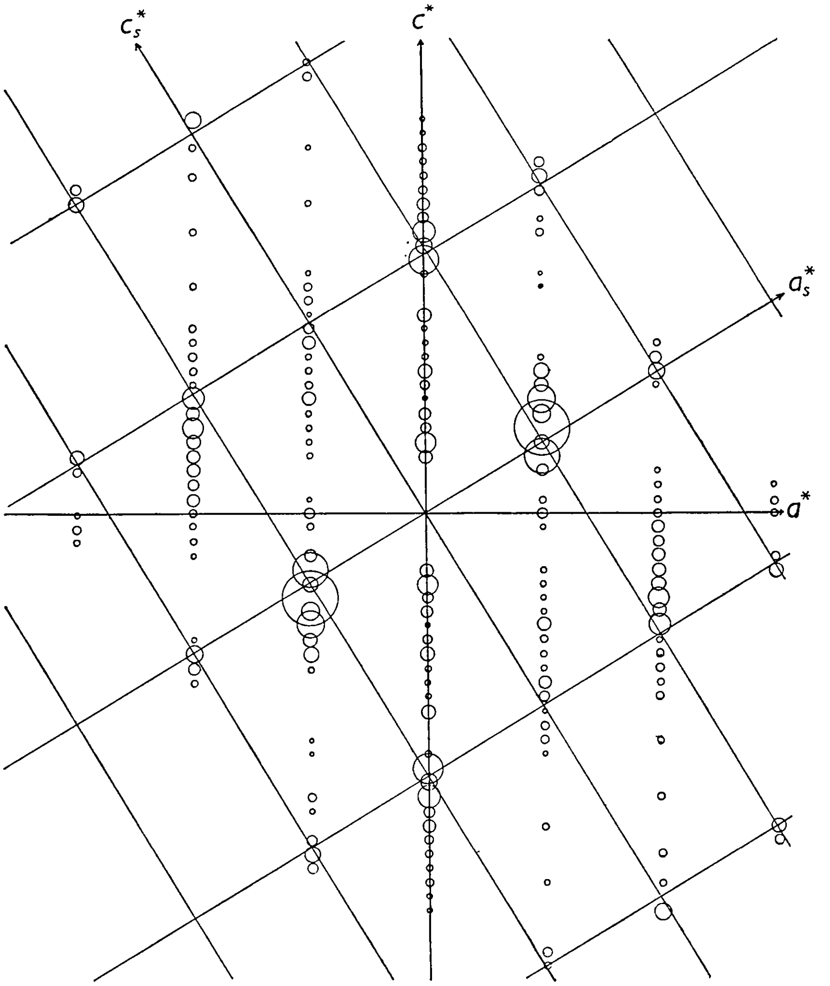


Fig. 1. The weighted reciprocal lattice for *h*0*l* reflections, showing the sub-cell lattice.

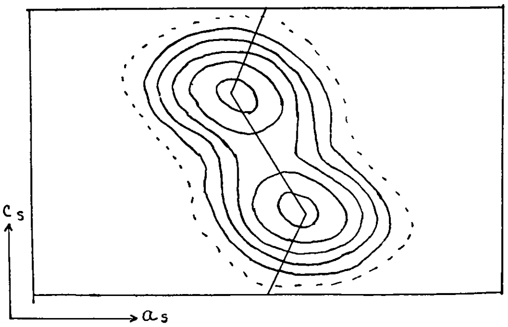


Fig. 2. The sub-cell Fourier projection.

$$F_h = F_h^0 + LF_H \exp 2\pi i(x_m h + y_m k + z_m l)\ ,$$

where F_h^0 is the contribution of the non-sub-cell atoms, and F_H is structure factor for the sub-cell,

$$L = \Pi_j \frac{\sin \pi N^j H_j}{\sin \pi H_j}\ ,$$

where N^j is the number of sub-cells in the sub-cell region in the jth direction, the H_j are the three sub-cell indices.

This relationship was used to obtain the signs of the structure factors for the 00l reflections; it reduced to

$$F_{00l} = \frac{2 \sin \pi 8 H_z}{\sin \pi H_z} \cos 2\pi(HX+LZ) \cos 2\pi l z_m\ .$$

z_m was given by $u+\frac{1}{2}\Sigma'(N^J-1)S_j$, in which u is the distance from the origin of the main cell to the nearest corner of the sub-cell region and was assigned a value of 2·4 Å from consideration of the probable dimensions of the carboxylic groups; S_j is the length of the edge of the sub-cell, 2·60 Å. Hence $z_m = 0{\cdot}278$ (fractional of G) when $N^j = 8$.

A one-dimensional Fourier projection on to the c axis was computed and refined with the aid of a model until there were no sign changes in the 21 (00l) orders which were included. The two strongest $h0l$ reflections (204 and 206) were then included to compute a Fourier projection. The main-cell reciprocal-lattice points for 204 and 206 are on either side and equidistant from the sub-cell point 100 (Fig. 1), and the signs of the terms could be determined from the Laue functions which were large and opposite in sign. Since in the b-axis projection there are symmetry centers at $z = 0$ and $x = 0$, 0·25, 0·50, 0·75, the choice of sign for one of the planes was arbitrary; (204) was taken as negative, and (206) was therefore positive. On the basis of this simple Fourier projection, the signs of more $h0l$ terms were computed and included in the synthesis by means of four cycles on X-RAC and S-FAC at the Crystal Structure Analysis Laboratory of Prof. Raymond Pepinsky of Pennsylvania State University. Owing to the limitation of the capacity of X-RAC, Fourier terms of orders above 20 could not be included in the synthesis. Since 0,0,20 has a spacing of 2·07 Å, the atoms along the chain were not completely resolved at this stage.

The additional terms to the full extent of the data were added by hand computation. After correcting for sign changes the terminal Fourier synthesis in the successive refinement was that shown in Fig. 3. This was computed on an IBM 650 in the University of Pittsburgh Computing Center.

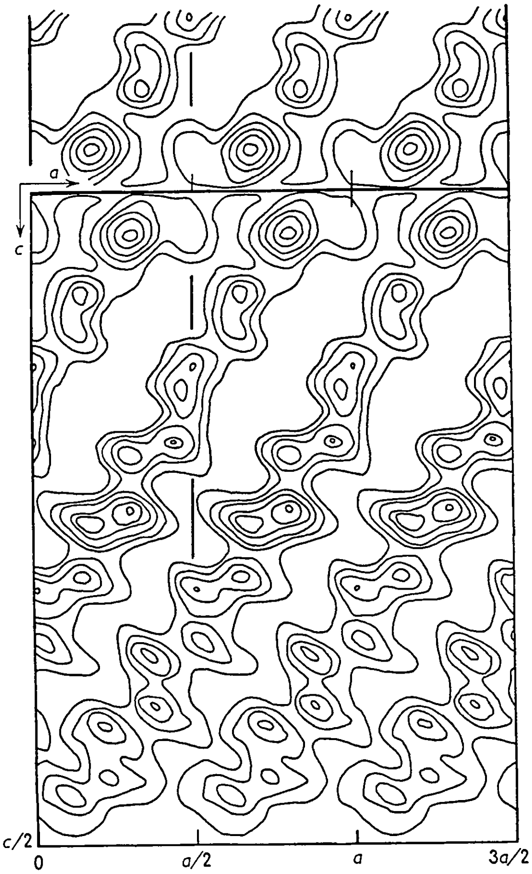


Fig. 3. The terminal Fourier projection from first attempt at structure refinement (false solution).

The poor resolution in the upper part as compared with the lower part of the molecule was rather striking and the structure factor agreement was poor, $R = 0{\cdot}45$. The refinement had apparently converged on to a false solution.

Returning to the 00l reflections, three successive Fourier line projection syntheses followed by difference syntheses were computed, starting with the signs derived from previous refinement. The last Fourier line synthesis is shown in Fig. 4. The R-factor was reduced to 0·19 for the 00l reflections alone. Examination of these z coordinates showed that in projection the C–C bond lengths were almost all alternately 1·54 and 0·5 Å. This fixed the orientation of the chain with alternate bonds nearly parallel to the c axis. The equal separation between $z(\text{C}_1)$, $z(\text{C}_2)$ and $z(\text{C}_3)$ in-

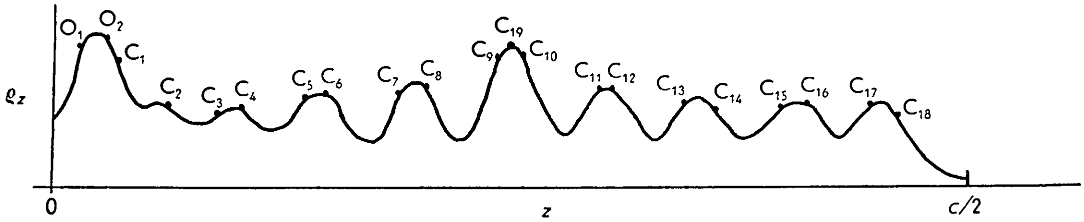


Fig. 4. One-dimensional Fourier synthesis on [c].

dicated that these atoms were nearly colinear in the b-axis projection and that the carboxyl end of the molecule was twisted relative to the plane of the rest of the long chain.

The orientation of the chain had to be such as to give an outstandingly large (206) structure amplitude. The positions of the atoms C_{10} to C_{18} were taken from the previous refinement and were slightly adjusted to make them compatible with the new z-coordinates, since these atoms had been well resolved and their positions had remained practically unchanged throughout all the previous syntheses. The appropriate positions for the atoms in the other half of the molecule then followed from the criteria given above. After six cycles of Fourier syntheses and difference syntheses computed on the IBM 650, the final projection shown in Fig. 5 was obtained. As compared with the terminating syntheses of the previous refinement, there were 36 sign changes of which 19 were for amplitudes greater than 10.

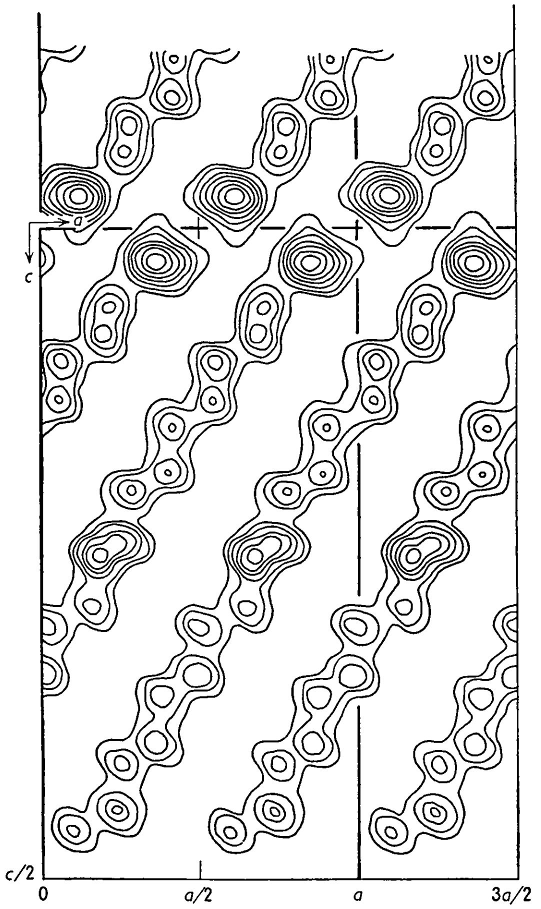


Fig. 5. The final Fourier projection from second refinement (true solution).

The agreement between observed and calculated structure amplitudes was now qualitatively good out to high orders of l, but the overall R factor was still relatively unsatisfactory at 0·35. The inclusion of an anisotropic temperature factor of the form $(A+B\cos\varphi)$, where φ is the angle between the reciprocal-lattice vector and that of (206), A = 7·0 Å^2 for O_1 and O_2, 6·0 Å^2 for C_1 to C_{10} and C_{19}, 8·0 Å^2 for C_{11} to C_{18}, and B = 5·0 Å^2 for all atoms, together with the contributions from 36 hydrogen atoms, further reduced R to 0·29.

At this time it became possible to check the correlation of the $h0l$ intensities by counter measurements, using the single-crystal orienter. Although these measurements could not be made accurately owing to the imperfections of the crystals, they showed that the allowance for the size of the spots in the eye estimation of the photographs had been somewhat misjudged and required adjustment in the following ratios, $(00l)$:$(20l)$:$(40l)$:$(60l)$ as 1·0:1·3:1·1:1·1. There was a corresponding improvement in the structure-amplitude agreement. This was further improved by omitting the anisotropic term in the temperature factors, reducing R to 0·24.

A Fourier synthesis computed with the rescaled amplitudes showed no significant changes in the atomic positions or the electron-density distribution.

The atomic coordinates for the carbon and oxygen atoms are shown in Table 1. The observed and cal-

Table 1. *The coordinates of the atoms*

Atom	X	Z
C_1	0·333	0·031
C_2	0·230	0·058
C_3	0·215	0·083
C_4	0·070	0·101
C_5	0·065	0·133
C_6	0·436	0·152
C_7	0·431	0·187
C_8	0·290	0·202
C_9	0·292	0·243
C_{10}	0·183	0·260
C_{11}	0·168	0·291
C_{12}	0·030	0·307
C_{13}	0·013	0·345
C_{14}	0·400	0·360
C_{15}	0·383	0·395
C_{16}	0·267	0·413
C_{17}	0·250	0·449
C_{18}	0·114	0·465
C_{19}	0·194	0·247
O_1	0·356	0·014
O_2	0·450	0·028

Table 2. *Observed and calculated structure factors*

h	l	F_c	F_o
0	1	61	—
0	2	−1	—
0	3	53	—
0	4	34	32
0	5	35	51
0	6	−21	21
0	7	32	32
0	8	13	11
0	9	18	24
0	10	−27	33
0	11	23	9
0	12	−5	7
0	13	2	—
0	14	−38	34
0	15	5	—
0	16	−18	16
0	17	−4	—
0	18	−82	74
0	19	−40	27
0	20	48	54
0	21	−15	20
0	22	−18	26
0	23	−19	20
0	24	−8	22
0	25	−11	17
0	26	−11	28
0	27	−11	12
0	28	−1	13
2	0	−39	42
2	1	7	19
2	2	−13	15
2	3	41	48
2	4	−127	151
2	5	−59	61
2	6	268	258
2	7	65	95
2	8	84	96
2	9	42	42
2	10	56	52
2	11	25	23
2	12	9	13
2	13	15	—
2	14	19	12
2	15	5	—
2	16	−8	17
2	17	8	16
2	18	6	—
2	19	4	—
2	20	−13	24
2	21	11	14
2	22	3	—
2	23	27	28
2	24	−59	56
2	25	−31	37
2	$\bar{1}$	15	14
2	$\bar{2}$	7	8
2	$\bar{3}$	−20	8
2	$\bar{4}$	−46	43
2	$\bar{5}$	3	9
2	$\bar{6}$	−5	17
2	$\bar{7}$	−30	24
2	$\bar{8}$	−46	51
2	$\bar{9}$	−11	30
2	$\overline{10}$	−24	17
2	$\overline{11}$	−37	28
2	$\overline{12}$	−62	46
2	$\overline{13}$	−41	38
2	$\overline{14}$	−25	12
2	$\overline{15}$	−51	29
2	$\overline{16}$	−47	35
2	$\overline{17}$	−18	16
2	$\overline{18}$	−9	—
2	$\overline{19}$	−13	—
2	$\overline{20}$	−14	11
2	$\overline{21}$	−8	—
2	$\overline{22}$	5	14
2	$\overline{23}$	1	12
2	$\overline{24}$	−3	—
2	$\overline{25}$	1	—
2	$\overline{26}$	12	17
4	0	13	19
4	1	14	19
4	2	−15	19
4	3	−24	12
4	4	3	10
4	5	−3	8
4	6	−13	12
4	7	−13	12
4	8	−14	8
4	9	17	14
4	10	−63	56
4	11	−50	41
4	12	19	13
4	$\bar{1}$	−19	23
4	$\bar{2}$	−17	28
4	$\bar{3}$	6	23
4	$\bar{4}$	−15	21
4	$\bar{5}$	−28	36
4	$\bar{6}$	−44	55
4	$\bar{7}$	−23	44
4	$\bar{8}$	−75	90
4	$\bar{9}$	3	18
4	$\overline{10}$	26	21
4	$\overline{11}$	10	16
4	$\overline{12}$	10	11
4	$\overline{13}$	−11	14
4	$\overline{14}$	3	—
4	$\overline{15}$	−1	9
4	$\overline{16}$	9	—
4	$\overline{17}$	−4	14
4	$\overline{18}$	0	—
4	$\overline{19}$	0	—
4	$\overline{20}$	16	16
4	$\overline{21}$	−3	—
4	$\overline{22}$	5	14
4	$\overline{23}$	2	—
4	$\overline{24}$	17	14
4	$\overline{25}$	7	—
4	$\overline{26}$	12	14
4	$\overline{27}$	2	—
4	$\overline{28}$	−37	61
6	0	−13	12
6	1	−7	16
6	2	−8	13
6	$\bar{1}$	8	10
6	$\bar{2}$	−19	10
6	$\bar{3}$	41	19
6	$\bar{4}$	60	40
6	$\bar{5}$	−6	—
6	$\bar{6}$	0	—
6	$\bar{7}$	−14	—
6	$\bar{8}$	8	—
6	$\bar{9}$	−2	—
6	$\overline{10}$	−4	—
6	$\overline{11}$	−9	—
6	$\overline{12}$	2	—
6	$\overline{13}$	−2	—
6	$\overline{14}$	2	—
6	$\overline{15}$	−6	—
6	$\overline{16}$	1	—
6	$\overline{17}$	4	—
6	$\overline{18}$	3	—
6	$\overline{19}$	2	—
6	$\overline{20}$	0	—
6	$\overline{21}$	1	—
6	$\overline{22}$	−23	38
6	$\overline{23}$	19	20

culated structure factors are given in Table 2. Although the agreement is still somewhat short of modern standards it shows that the correct structure has been derived. Further attempts at refinement led to little improvement. The limiting factor appeared to be the measurement of the intensities due to the defective nature of the crystals.

Discussion of the structure

The arrangement of the molecules is shown in Fig. 6. It follows the usual head-to-head and tail-to-tail pattern associated with long-chain fatty acid crystal structures with an angle of tilt of approximately 60° between the axis of the molecules and the (001) plane (see von Sydow, 1956).

The *trans* substituted cyclopropane ring fits in surprisingly compactly with the regular arrangement of the methylene groups along the chain. The angle of tilt of the chain axis of 57° is determined by the steric requirements of the hydrogen bonding between the carboxylic acid groups and the van der Waals interactions along the length of the chains. This is in direct contrast to the crystal structure of 9,DL methyl octadecanoic acid studied by Abrahamsson (1956), in which the bulkiness of the substituted methyl group is a determining factor forcing a much greater angle of tilt on the molecular packing.

Assuming a normal C–C distance of 1·54 Å along the chain and tetrahedral angles, the following inferences can be made about the geometry of the molecules from the interatomic distances in projection.

(1) The molecules lie with the long axis of the chain nearly in the (010) plane, since the distances between alternate carbon atoms in projection from C_3 to C_{18} all lie between 2·50 and 2·60 Å.

(2) The molecules can be divided into five sections in which the atoms, excluding hydrogens, are

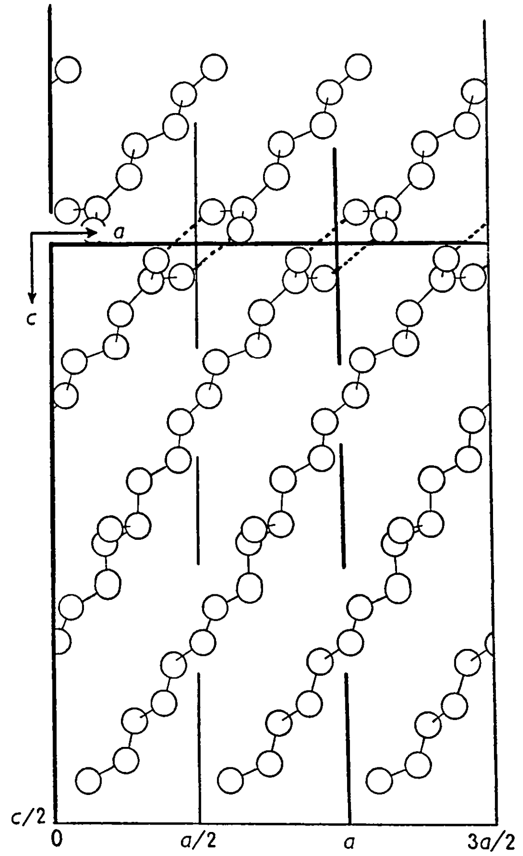


Fig. 6. The crystal structure of *trans* D, L 9–10 methylene octadecanoic acid projected down [b].

approximately coplanar: (i) C_{18} to C_{11}; (ii) the ring, C_9, C_{19}, C_{10}; (iii) C_8 to C_4; (iv) the carboxyl end of the chain C_3, C_2, C_1; (v) the carboxyl group C_1, O_1, O_2.

(3) In projection the chain axes of (i) and (iii) are nearly parallel with a relative lateral displacement of 0·3 Å at the ring. The planes of (i) and (iii) makes angles of about 45° and 35° respectively with (010). The sense of these angles cannot be determined, and it is not known whether the planes of the two chains are approximately 10° or 80° to each other.

(4) If the cyclopropane ring is an equilateral triangle, the sides are about 1·4 Å, and it is inclined at 55° to (010). The experimental evidence is insufficient to establish whether the cyclopropane ring bond lengths are significantly shorter than the standard C–C lengths of 1·54 Å. Examination of a model shows that the *trans* substituted ring introduces only a small bend in the axis of the molecule of about 10°, which is not apparent in this projection and presumably will correspond to a small difference in angle of tilt of the axes of (i) and (iii) to the plane of (010).

(5) The plane of the carboxyl end (iv) is tilted more sharply to (010) at an angle of about 60°. Again it is not known whether this is a twist of 25° or 95° at the C_3–C_4 bond. While it is not unusual in fatty acids for the oxygen atoms to be out of the plane of the chain carbon atoms, this extension of the twist further back up the chain appears to be a novel feature.

(6) Assuming a carboxyl acid group with bond lengths 1·25 Å and a 120° angle, the C_1 and oxygen atoms lie in a plane inclined at an angle of 55° to the (010) plane.

The stereochemistry of this acid is considerably more complicated than that of the normal straight-chain compounds of comparable length. Without a complete three-dimensional analysis it is not possible to distinguish between a number of possibilities. One of these will be a nearly planar alignment of the chain carbon atoms with an elliptical cross-section, as represented diagrammatically in Fig. 7(*a*), while another is that of Fig. 7(*b*), which would have an average circular cross-section.

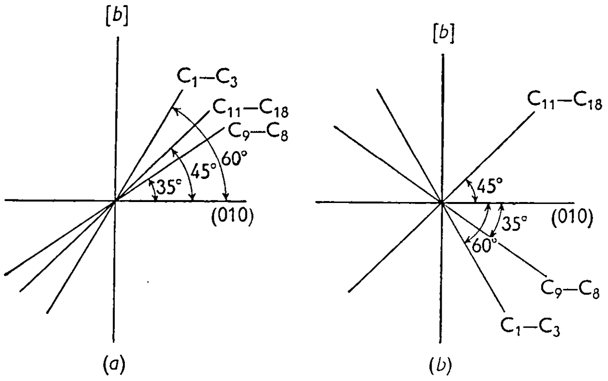


Fig. 7. Possible orientation of the methylene carbon atom planes giving rise to (*a*) an average elliptical cross-section, (*b*) an average circular cross-section.

In this connection it is relevant to note that the ratio of the unit-cell dimensions normal to the chain axis, i.e., $a \sin 57^\circ/b$, is 1·63. This is much closer to $\sqrt{3}$, which is associated with the hexagonal closest packing of cylindrical rods, than the cross-sectional ratio for the normal fatty acids, e.g., lauric acid, 1·47; palmitic acid, 1·44: stearic acid, 1·49.

The hydrogen bonding is shown in Fig. 6. It is not possible from the projection to distinguish whether this is dimerisation across the center of symmetry or a spiral infinite chain about the screw axis.

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