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On the Crystal Structure of 2 DL-Methyloctadecanoic Acid

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2 DL-Methyloctadecanoic acid is triclinic with $a = 5{\cdot}07$, $b = 5{\cdot}76$, $c = 52{\cdot}5$ Å; $\alpha = 133° 45'$, $\beta = 87° 26'$, $\gamma = 109° 41'$. The racemic acid contains two molecules related by a centre of symmetry (space group C_i^1–$P\bar{1}$). From a crystallographic point of view the molecule is built up of the hydrocarbon octadecane with a carboxyl group in position 2 projecting out as a side chain. The polar groups are accommodated between the ends of the main chains by a suitable tilt of the molecules to the (001) planes (46°). The hydrocarbon tails of the molecules are then allowed to pack tightly in the common triclinic chain packing with all chain planes parallel. There are hydrogen-bonded dimers as is usual with higher fatty acids.

Introduction

In the series of methylsubstituted octadecanoic acids, the molecular arrangement in the solid state has been determined for acids branched in the middle of the chain and further away from the carboxyl group (Abrahamsson, 1956, 1958, 1959). For a systematic treatment of the series it was then necessary also to know the structure of an acid branched close to the polar group.

Preparation of crystals

The pure 2 DL-methyloctadecanoic acid was prepared by G. Ställberg (1958). Its melting point was 55·4–55·7 °C. The acid crystallized from acetone as beautiful thin plates. The crystals were very soft and therefore easily deformed; thus some difficulty was met with in obtaining good single crystals for the X-ray work. All crystals studied were biaxial positive and showed no twinning.

X-ray data

Rotation and Weissenberg photographs were taken with Cu K radiation using a calibrated camera. The following data were obtained:

Molecular formula: $C_{19}H_{38}O_2$.
Molecular weight: 298·49.
Unit cell: Triclinic.

$a = 5{\cdot}07 \pm 0{\cdot}02$, $b = 5{\cdot}67 \pm 0{\cdot}02$, $c = 52{\cdot}5 \pm 0{\cdot}3$ Å.
$\alpha = 133° 45' \pm 30'$, $\beta = 87° 26' \pm 30'$, $\gamma = 109° 14' \pm 30'$.
$U = 990 \pm 10$ Å^3.
$d(001) = 36{\cdot}5 \pm 0{\cdot}2$ Å.

Two molecules per unit cell.
Number of electrons: 336.
Density calculated: $1{\cdot}001 \pm 0{\cdot}010$ g.cm.$^{-3}$.
Density measured: 0·998 g.cm.$^{-3}$.
Space group: C_i^1–$P\bar{1}$.

The absence of the piezoelectric effect is consistent with the chosen space group.

The intensities of the ($0kl$) reflexions were estimated visually by two observers. The Lorentz and polarization factors were applied and a set of relative observed structure factors were evaluated. Absolute values were later obtained by comparison with calculated structure factors. No attempt was made to correct for absorption errors.

Subcell

The reciprocal lattice showed a marked sublattice revealing a periodic carbon chain. The following dimensions of the subcell were found:

$$a_s = 4{\cdot}33,\ b_s = 5{\cdot}27,\ c_s = 2{\cdot}50 \text{ Å};$$
$$\alpha_s = 72°,\ \beta_s = 109°,\ \gamma_s = 117°.$$

These data are in agreement with those found for the subcell of the triclinic packing of carbon chains (Vand & Bell, 1951; von Sydow, 1956) thereby fixing the relative positions of the carbon chains in the structure. The orientation of the subcell within the main cell determined the chain axis to be roughly parallel to the c-axis.

Structure factors and electron-density projections

The length of the unit cell corresponds to a double molecular arrangement. The acid was therefore considered to exist as hydrogen-bonded dimers as is usual with higher fatty acids. As the branch is in the

Table 1. *Atomic coordinates*

Atom	y/b	z/c	Atom	y/b	z/c
O_1	0·053	0·4733	C_{10}	0·576	0·2311
O_2	0·340	0·4705	C_{11}	0·470	0·2005
C_1	0·085	0·4630	C_{12}	0·557	0·1812
C_2	0·674	0·4318	C_{13}	0·447	0·1519
C_3	0·528	0·3984	C_{14}	0·548	0·1332
C_4	0·609	0·3775	C_{15}	0·421	0·1017
C_5	0·516	0·3489	C_{16}	0·529	0·0846
C_6	0·606	0·3275	C_{17}	0·400	0·0525
C_7	0·497	0·2985	C_{18}	0·512	0·0367
C_8	0·592	0·2799	C_{19}	0·471	0·4370
C_9	0·481	0·2500			

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
000	—	336	018	18	19	0,1,$\bar{1}$8	8	−3	0,2,$\bar{4}$0	12	−15
001	—	−28	019	12	−10	0,1,$\bar{1}$9	9	1	0,2,$\bar{4}$1	13	−40
002	—	4	0,1,10	9	13	0,1,$\bar{2}$0	< 5	2	0,2,$\bar{4}$2	19	−20
003	—	−23	0,1,11	< 6	−5	0,1,$\bar{2}$1	11	−11	0,2,$\bar{4}$3	< 8	−2
004	—	−2	0,1,12	< 7	6	0,1,$\bar{2}$2	< 6	9			
005	12	−14	0,1,13	< 7	1				030	< 8	−8
006	10	−12	0,1,14	< 7	2	020	41	44	03$\bar{1}$	12	−12
007	3	−2	0,1,15	7	7	021	13	−8	03$\bar{2}$	12	10
008	18	−15	0,1,16	< 7	−1	022	9	8	03$\bar{3}$	< 8	3
009	9	4	0,1,17	8	9	023	< 7	−1	0,3,$\bar{2}$0	< 7	−6
0,0,10	23	−23	0,1,18	< 8	−2	02$\bar{1}$	13	14	0,3,$\bar{2}$1	23	27
0,0,11	10	10	0,1,19	11	14	02$\bar{2}$	21	−20	0,3,$\bar{2}$2	< 7	4
0,0,12	21	−23	0,1,20	10	−13	02$\bar{3}$	< 5	−5	0,3,$\bar{2}$3	10	−12
0,0,13	11	11	0,1,21	< 8	−6	02$\bar{4}$	11	−5	0,3,$\bar{2}$4	< 7	3
0,0,14	22	−21				02$\bar{5}$	< 5	−5	0,3,$\bar{2}$5	9	−12
0,0,15	13	7	01$\bar{1}$	37	−37	02$\bar{6}$	8	−2	0,3,$\bar{2}$6	< 7	5
0,0,16	20	−18	01$\bar{2}$	55	49	02$\bar{7}$	5	−3	0,3,$\bar{2}$7	9	−12
0,0,17	9	8	01$\bar{3}$	8	−4	02$\bar{8}$	8	−2	0,3,$\bar{2}$8	< 7	7
0,0,18	14	−15	01$\bar{4}$	25	21	02$\bar{9}$	5	−2	0,3,$\bar{2}$9	8	−10
0,0,19	7	3	01$\bar{5}$	6	8	0,2,$\bar{1}$0	9	−4	0,3,$\bar{3}$0	< 7	4
0,0,20	< 7	4	01$\bar{6}$	8	6	0,2,$\bar{1}$1	8	4	0,3,$\bar{3}$9	< 8	1
0,0,21	23	24	01$\bar{7}$	15	17	0,2,$\bar{1}$2	10	−6	0,3,$\bar{4}$0	9	−8
0,0,22	< 7	−8	01$\bar{8}$	6	−6	0,2,$\bar{1}$3	6	3	0,3,$\bar{4}$1	9	3
			01$\bar{9}$	25	28	0,2,$\bar{1}$4	6	−5	0,3,$\bar{4}$2	26	31
010	144	−132	0,1,$\bar{1}$0	15	−15	0,2,$\bar{1}$5	< 5	3	0,3,$\bar{4}$3	< 8	2
011	5	−7	0,1,$\bar{1}$1	29	31	0,2,$\bar{2}$0	< 5	−1	0,4,$\bar{2}$0	< 8	7
012	16	14	0,1,$\bar{1}$2	20	−19	0,2,$\bar{2}$1	34	−34	0,4,$\bar{2}$1	14	−22
013	25	−23	0,1,$\bar{1}$3	29	32	0,2,$\bar{2}$2	8	−7	0,4,$\bar{2}$2	< 8	−3
014	29	25	0,1,$\bar{1}$4	19	−20	0,2,$\bar{2}$3	< 6	12	0,4,$\bar{4}$1	< 8	2
015	25	−23	0,1,$\bar{1}$5	25	25	0,2,$\bar{2}$4	7	−5	0,4,$\bar{4}$2	22	−25
016	26	24	0,1,$\bar{1}$6	15	−15	0,2,$\bar{2}$5	< 6	10	0,4,$\bar{4}$3	< 8	−1
017	19	−18	0,1,$\bar{1}$7	18	15	0,2,$\bar{3}$9	< 8	−2			

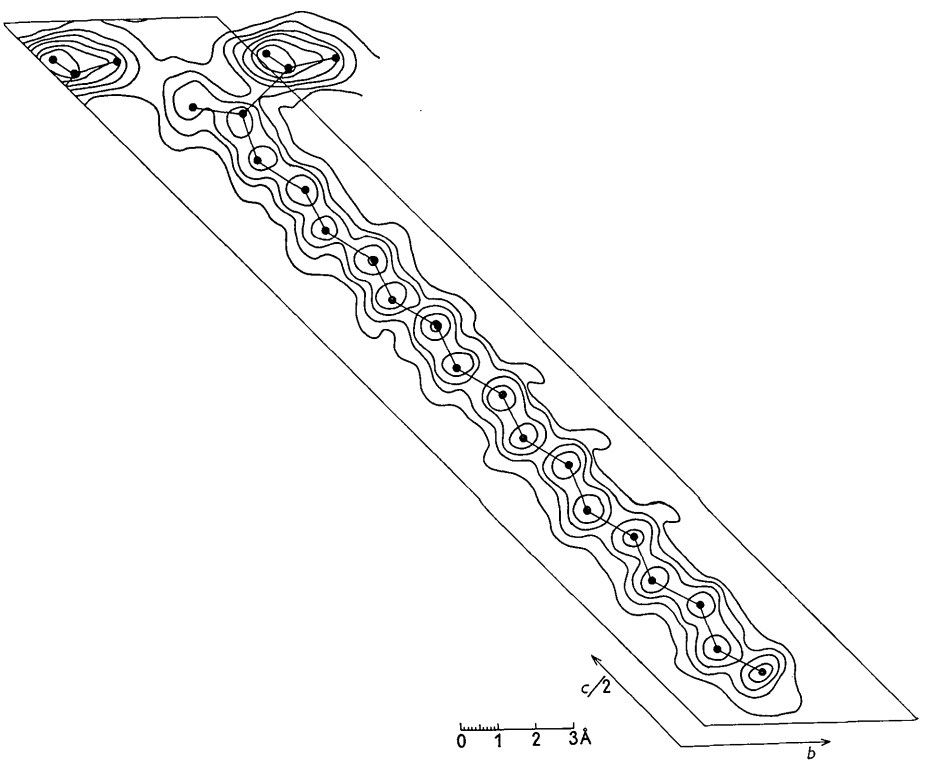

Fig. 1. Electron-density projection along the shortest axis of 2 DL-methyloctadecanoic acid. Contours are given at intervals of 1 e.Å^{-2}, starting with 1 e.Å^{-2}.

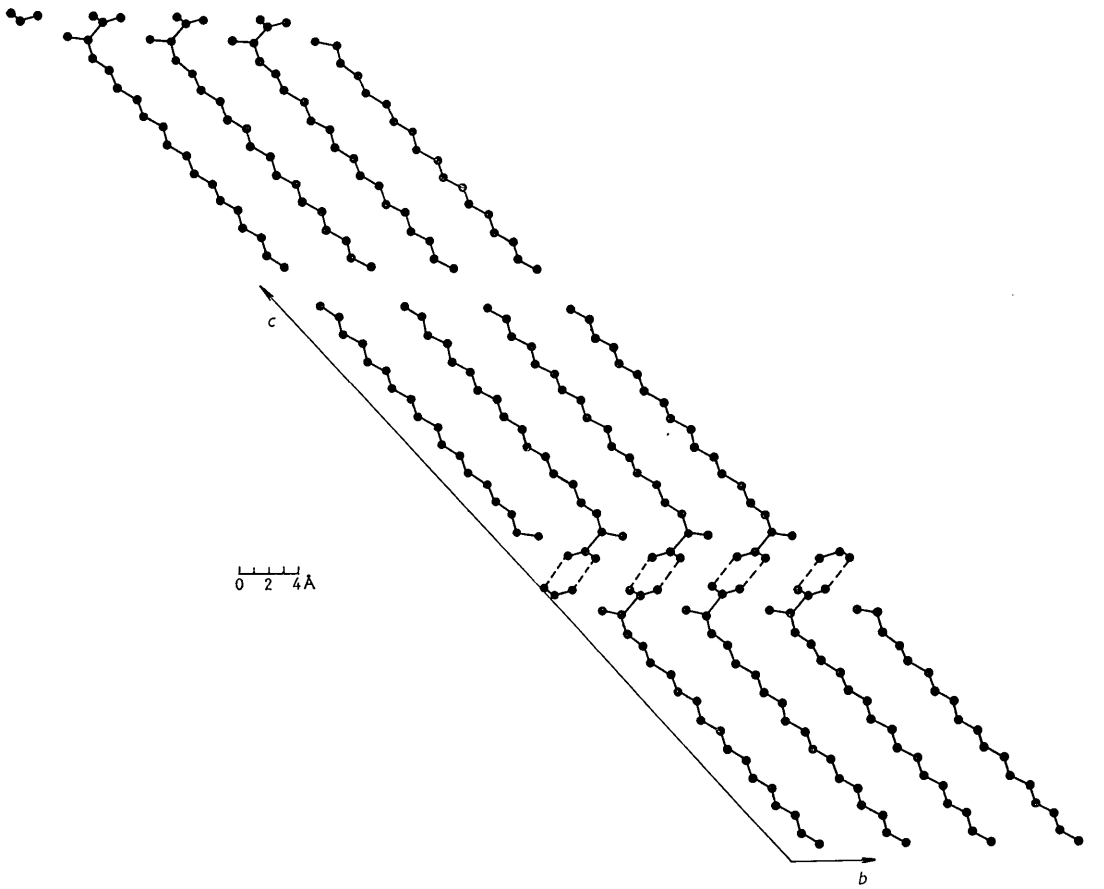

Fig. 2. Molecular arrangement of 2 DL-methyloctadecanoic acid as viewed along the shortest axis.

vicinity of the carboxyl group, the hydrocarbon tails of the molecules were assumed to be regular, forming the expected triclinic chain packing.

A trial structure along these lines was adopted with the methyl group ends of the chains separated by the usual van der Waals distances. The arrangement of the carboxyl region was more difficult to predict but from spatial considerations it was evident that a structure mainly as shown in Fig. 2 should be possible.

Cycles of structure-factor calculations and electron-density maps were performed for the (y, z) projection. The structure factors were computed on the BESK computer of the Swedish Board for Computing Machinery using the atomic scattering values of Vand *et al.* (1957). The electron-density projections were prepared with Beevers–Lipson strips (3°) and the Hägg–Laurent machine (1946).

The final refinement was accomplished by several difference syntheses. In the later stages of the structure determination the hydrogen atoms were included in the structure-factor calculations. Their positions relative to the carbon atoms were derived from the data of Vainshtein & Pinsker (1950). A temperature factor was applied: $\exp(-B\sin^2\theta/\lambda^2)$ with the final value of $R = 5{\cdot}4$ Å^2. The reliability index R_1 is 0·16, omitting non-observed reflexions. The coordinates of the carbon and oxygen atoms are given in Table 1, and observed and calculated structure factors in Table 2. The final electron-density projection is shown in Fig. 1.

Discussion of the results

The molecular arrangement is shown in Fig. 2. From a crystallographic point of view the molecule is built up of the hydrocarbon octadecane with a carboxyl group in position 2 projecting out as a side chain.

The long hydrocarbon tails of the molecules tend to arrange in a tight side packing, in this case triclinic with all chain planes parallel. The disturbing effect of the carboxyl branch is made as small as possible by tilting the molecules with respect to the (001) planes so that the polar groups are accommodated between the neighbouring methyl-group ends of the main chains (Fig. 2). The angle of tilt is 46°, calculated from the average difference of z-coordinates between alternate carbon atoms in the regular part of the chain (C_4–C_{18}, see below) and the subcell dimension $c_s = 2{\cdot}50$ Å. By this arrangement the formation of hydrogen-

bonded dimers is still possible and takes place around a centre of symmetry as usual. Double molecular sheets result which are held together by weak van der Waals forces only. This leads to the soft flaky crystals. Fatty acid crystals built up of sheets of molecules do often exhibit twinning. No twins were found, however, in this investigation.

Distortions are found in the chain packing in the vicinity of the carboxyl group where space problems exist. The long tails (C_4–C_{18}) of the molecules, however, are free to arrange in an almost regular chain packing. The main deviation seems to be a certain twist of the chain plane as the two rows of carbon atoms of one molecule are not quite parallel in the projection (Fig. 1).

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On the Crystal Structure of 2 D-Methyloctadecanoic Acid

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2 D-methyloctadecanoic acid is monoclinic with $a = 9{\cdot}08$, $b = 5{\cdot}01$, $c = 24{\cdot}0$ Å; $\beta = 116°\ 37'$. It belongs to the space group C_2^2–$P2_1$. From a crystallographic point of view the molecule is built up of the hydrocarbon octadecane with a carboxyl group in position 2 projecting out as a side chain. The branches are as usual accommodated between the tails of the main chains. A new packing of hydrocarbon chains is found. It resembles the common orthorhombic chain packing but the symmetry elements are interchanged with respect to the subcell axes which are identical in both cases. The molecules are linked together in chains by infinite helices of hydrogen bonds.

Introduction

In connexion with synthetic work on 2-methyloctadecanoic acid (G. Ställberg, 1958) the optically active forms of the acid were found to exhibit polymorphism. As the high melting modification showed an unusual infrared spectrum for long-chain fatty acids in the solid state, a crystal structure investigation was started as a part of studies of other branched-chain acids (Abrahamsson, 1956, 1958, 1959*a*, *b*).

Preparation of crystals

One crystal form (m.p. 54·7–55·0 °C.) of the enantiomers is obtained by crystallization from solution and another (m.p. about 43 °C.) by cooling the melted acid. Crystals of the high melting form were grown from glacial acetic acid. They were well developed, long and lath-shaped and showed no twinning. Their optic sign was positive.

X-ray data

Rotation and Weissenberg photographs were taken with Cu K radiation using a calibrated camera. The following data were found:

Molecular formula: $C_{19}H_{38}O_2$.
Molecular weight: 298·49.
Unit cell: monoclinic.

$a = 9{\cdot}08 \pm 0{\cdot}03$, $b = 5{\cdot}01 \pm 0{\cdot}02$, $c = 24{\cdot}0 \pm 0{\cdot}2$ Å.
$\beta = 116°\ 37' \pm 30'$.
$U = 977 \pm 10$ Å^3.
$d(001) = 21{\cdot}46 \pm 0{\cdot}10$ Å.

Two molecules per unit cell.
Number of electrons: 336.
Density calculated: $1{\cdot}015 \pm 0{\cdot}010$ g.cm.$^{-3}$.
Density measured: 1·015 g.cm.$^{-3}$.
Absent reflexions: $(0k0)$ for k odd.
Space group: $P2_1$ or $P2_1/m$.