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On the Crystal Structure of 14 DL-Methyloctadecanoic Acid

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14 DL-methyloctadecanoic acid is triclinic with $a = 5{\cdot}06$, $b = 6{\cdot}01$ and $c = 54{\cdot}5$ Å; $\alpha = 135^\circ\,6'$, $\beta = 91^\circ\,42'$ and $\gamma = 107^\circ\,18'$. The cell contains two molecules related by a centre of symmetry (space group C_i^1–$P\bar{1}$). The structure represents a new molecular packing of long-chain fatty acids with a branching methyl group. From a crystallographic point of view the molecule is a butyl-branched pentadecanoic acid. The main chains can adopt a distorted triclinic chain packing by tilting 41° to the (001) planes to accomodate the butyl branches between the chain ends.

Introduction

The crystal structures of 9 DL- and 16 DL-methyloctadecanoic acid (Abrahamsson, 1956, 1958) have shown one possible molecular arrangement of long-chain fatty acids with a branching methyl group. From long-spacing, $d(001)$, measurements, however, 14 DL-methyloctadecanoic acid appeared to have a different structure and was, therefore, investigated by single crystal methods.

Preparation of crystals

The pure 14 DL-methyloctadecanoic acid was provided by Prof. E. Stenhagen and his collaborators. It had been synthesized by the Kolbe reaction from 3 DL-methylheptanoic acid and methyl hydrogen dodecan-1·12-dioate (cf. Ställberg-Stenhagen, 1950). Its melting point was 36·3–36·6 °C. Crystals were grown from acetone as transparent thin plates. They proved, however, to be twinned on the (001) planes when examined in polarized light and were, therefore, split parallel to these planes. Though this was done very carefully it was impossible to obtain good single crystals, and a certain spread of the X-ray reflexions could not be avoided. It is highly probable that single crystals of the acid always consist of somewhat disarranged, very thin plates. The crystals are biaxial positive.

X-ray data

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

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

$a = 5{\cdot}06 \pm 0{\cdot}03$, $b = 6{\cdot}01 \pm 0{\cdot}04$, $c = 54{\cdot}5 \pm 0{\cdot}5$ Å.
$\alpha = 135^\circ\,6' \pm 45'$, $\beta = 91^\circ\,42' \pm 45'$, $\gamma = 107^\circ\,18' \pm 45'$.
$d(001) = 35{\cdot}9 \pm 0{\cdot}2$ Å.

Two molecules per unit cell.
Number of electrons: 336.
Density calculated: $0{\cdot}95 \pm 0{\cdot}02$ g.cm.$^{-3}$.
Density measured: 0·94 g.cm.$^{-3}$.
Space group: C_i^1–$P\bar{1}$.

The crystals showed no piezo-electric effect, which is consistent with a centre of symmetry.

The intensities of the $(0kl)$ reflexions were estimated visually by two observers using the multiple-film technique. In spite of the spread of the spots the two observations were in good agreement. The usual Lorentz and polarization factors were applied and the evaluated relative structure factors were later brought to an absolute scale by comparison with calculated structure factors. No absorption correction was made.

Subcell

As usual with long-chain compounds with a periodic carbon chain a sublattice was found in the reciprocal lattice. The dimensions of the subcell were calculated to be:

$$a_s = 4{\cdot}47,\quad b_s = 5{\cdot}16,\quad c_s = 2{\cdot}57\ \text{Å};$$
$$\alpha_s = 72^\circ,\quad \beta_s = 109^\circ,\quad \gamma_s = 117^\circ.$$

These values correspond to those reported for the subcell of the triclinic packing of hydrocarbon chains (Vand & Bell, 1951; von Sydow, 1956). A chain packing of the common triclinic type was therefore expected to exist in this acid. The b_s edge of the subcell coincides with the a edge of the main cell and the c_s edge is parallel to the c edge but opposite in direction.

Patterson projection

As the chain direction found from the orientation of the subcell within the main cell definitely excludes a molecular arrangement similar to that of the 9 DL- and 16 DL-methyloctadecanoic acids it was important to check this direction. Therefore, a Patterson projection along the shortest axis was calculated. The Fourier summations were performed partly with Beevers–Lipson strips (3°) and partly on the Hägg–Laurent machine (1946). The result confirmed the information

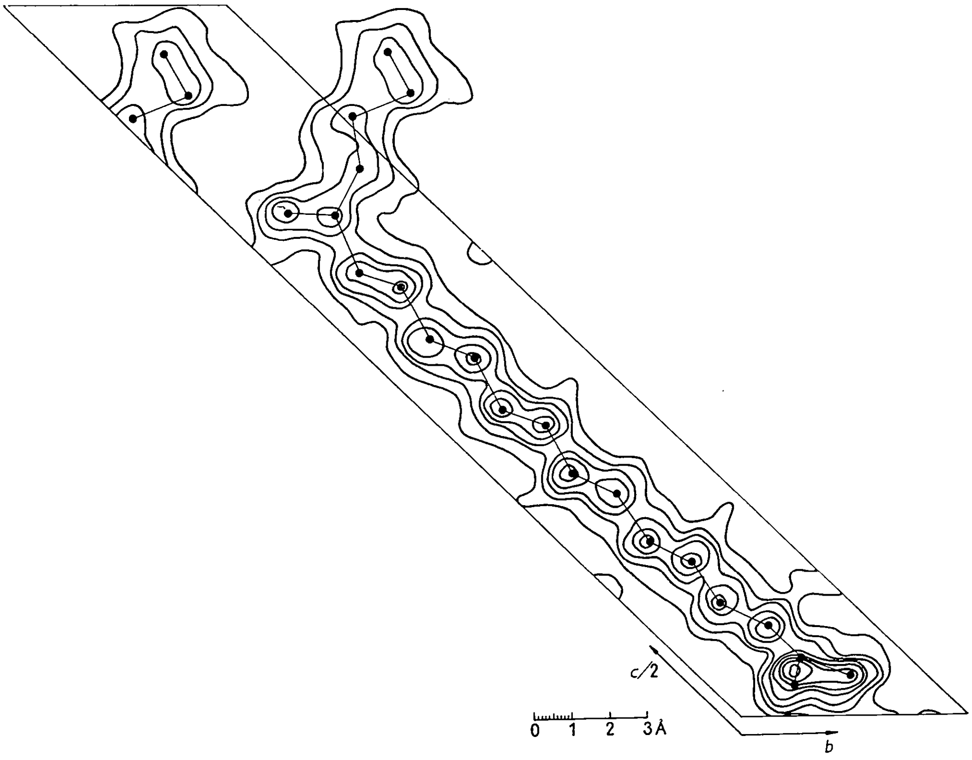

Fig. 1. Electron-density projection of 14 DL-methyloctadecanoic acid along the shortest axis. Contours are given at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

from the subcell determination that the direction of the periodic chain is approximately parallel to the chosen *c* axis.

Structure determination

At this stage the packing and the direction of the carbon chains was known. As the branching methyl group is at position 14 a trial structure was assumed with a regular carbon chain C_1–C_{14}. The rest of the carbon atoms were omitted in the first structure factor calculation but the two oxygen atoms were included. They were given positions consistent with the usual dimerization of long-chain fatty acids. A centre of symmetry was assumed on account of the racemic nature of the acid. Atomic scattering factors were taken from McWeeny (1951) and from Vand *et al.* (1957). In the later stages the structure-factor calculations were performed on the BESK-computer of the Swedish Board for Computing Machinery.

The first electron-density projection along the shortest axis, however, gave no further information about the structure. The oxygen atoms appeared on the map but for the rest only a repetition of the two subcell carbon atoms along the cell could be seen. Evidently atoms C_{15}–C_{19} contribute little to the structure factors used for the projection.

Considering again the packing and the direction of the carbon chain, a trial structure including the whole molecule was derived: the only possible arrangement seemed to be mainly as in Fig. 2. A structure factor calculation with all carbon and oxygen atoms determined 55 signs. The corresponding electron-density projection was satisfactory, allowing the usual refinement procedure to begin.

After ten cycles of difference syntheses the reliability index R_1 was reduced to 0·17 (non-observed reflexions omitted). In the later structure-factor calculations the contributions from the hydrogen atoms of the more regular part of the chain, C_2–C_{13} (see below) were included. A temperature factor: $\exp(-B\sin^2\theta/\lambda^2)$ with the final value of $B = 5{\cdot}9$ Å^2 was applied. The positions of the hydrogen atoms relative to the carbon atoms were calculated from the data of Vainshtein & Pinsker (1950). The electron-density map is shown in

Table 1. *Atomic coordinates*

Atom	*y*/*b*	*z*/*c*	Atom	*y*/*b*	*z*/*c*
O_1	0·375	0·0205	C_{10}	0·472	0·2515
O_2	0·666	0·0272	C_{11}	0·361	0·2655
C_1	0·537	0·0405	C_{12}	0·475	0·3020
C_2	0·535	0·0635	C_{13}	0·353	0·3125
C_3	0·430	0·0800	C_{14}	0·511	0·3525
C_4	0·493	0·1085	C_{15}	0·835	0·3850
C_5	0·405	0·1235	C_{16}	0·055	0·4215
C_6	0·469	0·1560	C_{17}	0·400	0·4365
C_7	0·377	0·1715	C_{18}	0·489	0·4655
C_8	0·474	0·2045	C_{19}	0·305	0·3535
C_9	0·354	0·2155			

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	0,1,19	< 2	−2	026	5	−8	0,2,$\overline{43}$	< 3	3
001	—	41	0,1,20	8	−11	027	3	−1			
002	—	−6	0,1,21	8	11	028	5	−7	03$\bar{6}$	< 3	−2
003	24	18	0,1,22	12	12	029	< 3	1	03$\bar{7}$	6	8
004	3	1	0,1,23	< 3	−5	02$\bar{1}$	18	−21	03$\bar{8}$	< 3	3
005	12	9				02$\bar{2}$	< 3	1	03$\bar{9}$	< 3	1
006	< 1	−2	01$\bar{1}$	7	−6	02$\bar{3}$	< 2	−7	0,3,$\overline{10}$	5	8
007	< 1	2	01$\bar{2}$	11	9	02$\bar{4}$	5	3	0,3,$\overline{11}$	< 3	−2
008	5	−10	01$\bar{3}$	18	−15	02$\bar{5}$	< 2	−3	0,3,$\overline{19}$	< 3	4
009	7	9	01$\bar{4}$	27	−28	02$\bar{6}$	8	−4	0,3,$\overline{20}$	17	−16
0,0,10	15	−16	01$\bar{5}$	17	23	02$\bar{7}$	2	2	0,3,$\overline{21}$	17	−19
0,0,11	3	5	01$\bar{6}$	30	−34	02$\bar{8}$	7	−10	0,3,$\overline{22}$	< 3	1
0,0,12	15	−14	01$\bar{7}$	9	12	02$\bar{9}$	4	3	0,3,$\overline{23}$	< 3	−9
0,0,13	9	−10	01$\bar{8}$	< 2	4	0,2,$\overline{10}$	< 2	−5	0,3,$\overline{24}$	10	−10
0,0,14	9	−7	01$\bar{9}$	21	−27	0,2,$\overline{11}$	8	−9	0,3,$\overline{25}$	< 3	−4
0,0,15	16	−14	0,1,$\overline{10}$	31	34	0,2,$\overline{12}$	< 2	−2	0,3,$\overline{26}$	6	−10
0,0,16	6	−6	0,1,$\overline{11}$	30	−30	0,2,$\overline{13}$	< 2	−5	0,3,$\overline{27}$	3	−2
0,0,17	12	−9	0,1,$\overline{12}$	31	34	0,2,$\overline{14}$	12	−14	0,3,$\overline{28}$	< 3	−7
0,0,18	16	−19	0,1,$\overline{13}$	< 2	−1	0,2,$\overline{15}$	< 2	5	0,3,$\overline{29}$	7	−5
0,0,19	8	6	0,1,$\overline{14}$	6	9	0,2,$\overline{16}$	10	−15	0,3,$\overline{30}$	< 3	−5
0,0,20	5	−4	0,1,$\overline{15}$	21	22	0,2,$\overline{17}$	5	6	0,3,$\overline{31}$	< 3	−5
0,0,21	24	−21	0,1,$\overline{16}$	4	4	0,2,$\overline{18}$	8	−9	0,3,$\overline{32}$	6	−9
0,0,22	20	−22	0,1,$\overline{17}$	14	14	0,2,$\overline{19}$	12	3	0,3,$\overline{33}$	< 3	1
0,0,23	< 3	5	0,1,$\overline{18}$	15	17	0,2,$\overline{20}$	< 2	3	0,3,$\overline{34}$	3	−4
			0,1,$\overline{19}$	< 3	−1	0,2,$\overline{21}$	< 2	10	0,3,$\overline{35}$	< 3	3
010	119	−125	0,1,$\overline{20}$	17	19	0,2,$\overline{22}$	9	8	0,3,$\overline{38}$	< 3	4
011	72	−73	0,1,$\overline{21}$	48	46	0,2,$\overline{23}$	8	−8	0,3,$\overline{39}$	7	−4
012	< 2	1	0,1,$\overline{22}$	16	8	0,2,$\overline{24}$	< 2	−2	0,3,$\overline{40}$	12	4
013	11	5	0,1,$\overline{23}$	5	−3	0,2,$\overline{32}$	< 3	4	0,3,$\overline{41}$	22	19
014	13	−9	0,1,$\overline{24}$	16	16	0,2,$\overline{33}$	4	3	0,3,$\overline{42}$	23	19
015	16	15	0,1,$\overline{25}$	< 3	−3	0,2,$\overline{34}$	5	2	0,3,$\overline{43}$	< 3	−2
016	< 2	1	0,1,$\overline{26}$	10	12	0,2,$\overline{35}$	< 3	5			
017	< 2	1	0,1,$\overline{27}$	< 3	5	0,2,$\overline{36}$	7	8	0,4,$\overline{19}$	< 3	7
018	14	11				0,2,$\overline{37}$	< 3	−2	0,4,$\overline{20}$	16	17
019	5	−1	020	24	27	0,2,$\overline{38}$	< 3	2	0,4,$\overline{21}$	< 3	5
0,1,10	9	6	021	30	29	0,2,$\overline{39}$	< 3	4	0,4,$\overline{40}$	< 3	−5
0,1,11	3	3	022	< 2	1	0,2,$\overline{40}$	8	2	0,4,$\overline{41}$	24	−25
0,1,12	< 3	2	023	6	−9	0,2,$\overline{41}$	< 3	−1	0,4,$\overline{42}$	21	−18
0,1,13	3	3	024	6	−5	0,2,$\overline{42}$	15	−15	0,4,$\overline{43}$	< 3	8
0,1,14	< 3	4	025	7	−9						

Fig. 1 and the coordinates of the heavier atoms are listed in Table 1. Observed and calculated structure factors are in Table 2.

Discussion of the results

The molecular arrangement is shown in Fig. 2. It represents a new packing of long-chain fatty acids with a branching methyl group. From a crystallographic point of view the molecule can be described as a butyl-branched pentadecanoic acid with the branch in position ($\omega-1$).

By a suitable tilt of the acid molecules to the (001) planes, the butyl branches are accommodated between the ends of the main chains and these can pack tightly together in the common triclinic chain packing with all chain planes parallel. The necessary angle of tilt is 41°, calculated from the average difference of z-coordinates between alternate carbon atoms in the main chain (C_2–C_{13}) and the subcell dimension 2·57 Å. The acid molecule is thus tilted more than in normal chain acids (60°, von Sydow, 1956) but less than in 16 DL- and 9 DL-methyloctadecanoic acid (33° and 18° respectively).

The chain packing is severely distorted. No part of the main chain is quite regular and the chain axis is clearly bent. Some of this deformation is caused by the carboxyl groups as they have less favourable positions than in normal chain acids due to the tilt of the molecules. Their disturbing effect is not so pronounced, however, as in 16 DL- and 9 DL-methyloctadecanoic acid where the carboxyl groups are effectively forced into the chain packing.

The large butyl branches do not easily fit in the arrangement and cause most of the distortions in the chain. It is impossible to pack the branches tightly and a rather open structure is found in the branch region. This is clearly shown by the low density of the acid, 0·95 g.cm.$^{-3}$, as compared with the values 0·991 and 1·001 g.cm.$^{-3}$ of 16 DL- and 9 DL-methyloctadecanoic acid respectively. The shape of the branch is such that its last two atoms constitute a continuation of the neighbouring main chain, (Fig. 1), though an exact fit in the subcell repetition of this chain is not obtained.

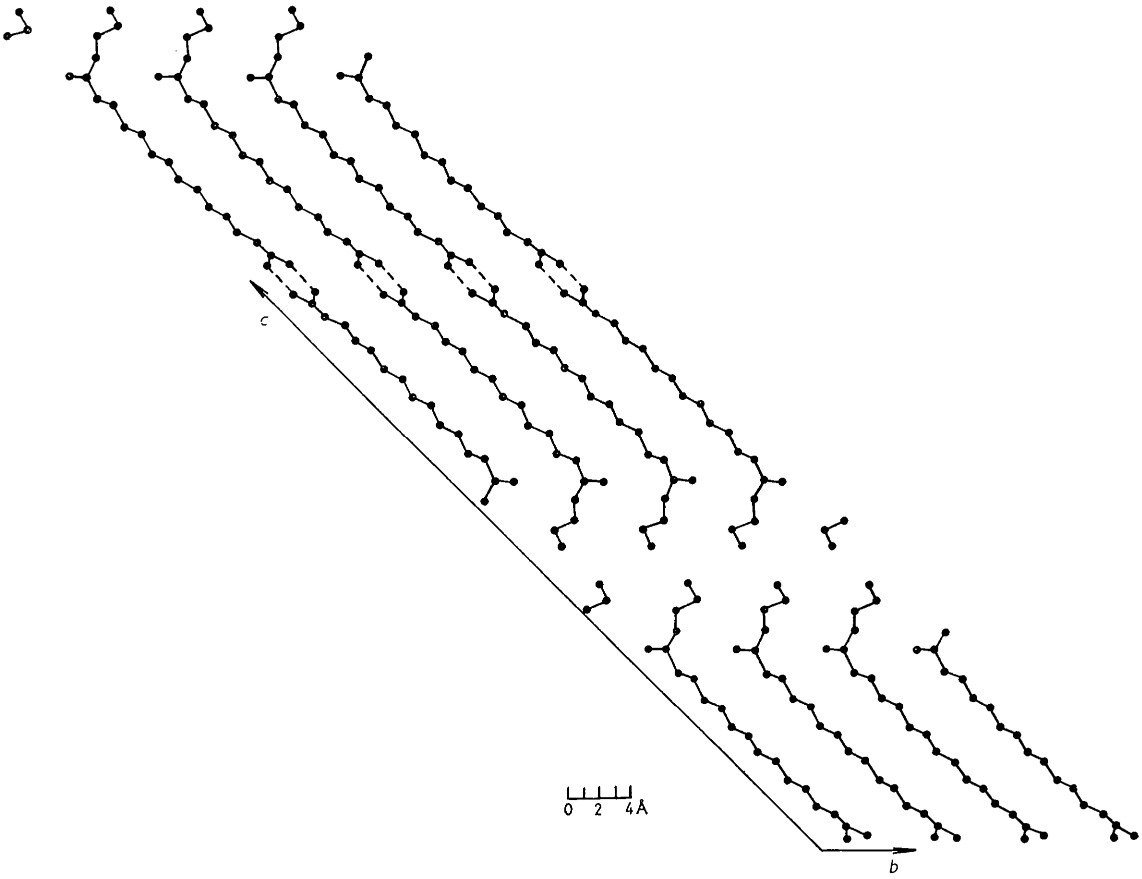

Fig. 2. Molecular arrangement of 14 DL-methyloctadecanoic acid as viewed along the shortest axis.

The acid dimers are held together by weak van der Waals forces between the methyl group layers of the branches. This causes the crystals to grow as thin plates and allows the frequent twinning on the (001) planes.

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