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On the Crystal Structure of 16DL-Methyloctadecanoic Acid

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16 DL-Methyloctadecanoic acid is triclinic with $a = 5{\cdot}40$ Å, $b = 7{\cdot}54$ Å, $c = 51{\cdot}8$ Å; $\alpha = 145°\ 38'$, $\beta = 105°\ 42'$, $\gamma = 60°\ 18'$. The cell contains two molecules related by a centre of symmetry (space group C_i^1–$P\bar{1}$) owing to the racemic nature of the compound. The carbon chains are arranged in the triclinic packing in which all chain planes are parallel. The tight side packing is made possible by accommodating the branching groups between the chain ends. The molecules are therefore tilted 33° to the (001) planes. Distortions found are due to the carboxyl groups forced into the chain packing and to the limited space provided for the substituted methyl groups. The whole chain packing is thereby disturbed.

Introduction

The crystal structure of 16DL-methyloctadecanoic acid has been determined as a part of the investigation of the solid-state behaviour of long-chain carboxylic acids with a branching methyl group. In an earlier paper (Abrahamsson, 1956) the structure of 9DL-methyloctadecanoic acid has been described.

Previous X-ray studies of the acid have given the unit-cell dimensions (Clark & Chu, 1951) and the long spacing (Velick, 1944).

Preparation of crystals

The 16DL-methyloctadecanoic acid (m.p. 49·9–50·6 °C.) was synthesized by Cason & Prout (1944). It crystallizes in thin plates. The crystals are nearly always imperfect, twinning being very common. From a sample crystallized from methanol, however, a good, though very small, single crystal could be selected under polarized light and used for the X-ray work.

The crystals studied were all biaxial positive, in agreement with the structure of parallel carbon chains (see below). Clark & Chu (1951) found a negative optic sign, which seems unlikely. As they have reported cell dimensions roughly corresponding to a unit cell obtained from the one of the present investigation by the transformation

$$\begin{bmatrix} 1 & 0 & 0 \\ \bar{1} & 1 & 0 \\ 0 & \bar{6} & \bar{1} \end{bmatrix}$$

the crystals investigated in both cases seem to have had the same structure.

X-ray data

Rotation and Weissenberg photographs were taken with Cu K radiation from a gas tube, using a calibrated camera. The following data were obtained, selecting the c axis parallel to the chain direction:

Molecular formula: $C_{19}H_{38}O_2$.
Molecular weight: 298·49.
Unit cell: triclinic.
$a = 5{\cdot}40 \pm 0{\cdot}02$ Å, $b = 7{\cdot}54 \pm 0{\cdot}03$ Å, $c = 51{\cdot}8 \pm 0{\cdot}3$ Å;
$\alpha = 145°\ 38' \pm 30'$, $\beta = 105°\ 42' \pm 30'$, $\gamma = 60°\ 18' \pm 30'$.
$d(001) = 27{\cdot}8 \pm 0{\cdot}1$ 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 piezo-electric effect is consistent with a centre of symmetry.

Owing to the smallness of the crystal used, only 76 ($0kl$) reflexions were recorded in a 230 hr. exposure. Two observers estimated the intensities visually, using the multiple-film technique. After correction for the Lorentz and polarization factors, a set of relative observed structure factors was evaluated. Absolute values were obtained at the later stages of the investigation by comparison with calculated structure factors. Absorption errors were not corrected for.

Subcell

The sublattice regions of strong reflexions in the reciprocal lattice due to the periodic carbon chain were rather large, indicating distortions in the chain packing. The following dimensions of the subcell were found:

$$a_s = 4{\cdot}49 \text{ Å},\quad b_s = 5{\cdot}40 \text{ Å},\quad c_s = 2{\cdot}56 \text{ Å};$$
$$\alpha_s = 73°,\quad \beta_s = 107°,\quad \gamma_s = 123°.$$

These data correspond to the subcell described by Vand & Bell (1951) and von Sydow (1956) for the triclinic packing of hydrocarbon chains. Thus, the main features of the side packing of the chains are known. The orientation of this subcell within the main cell is such that b_s coincides with a and c_s is parallel to c but opposite in direction.

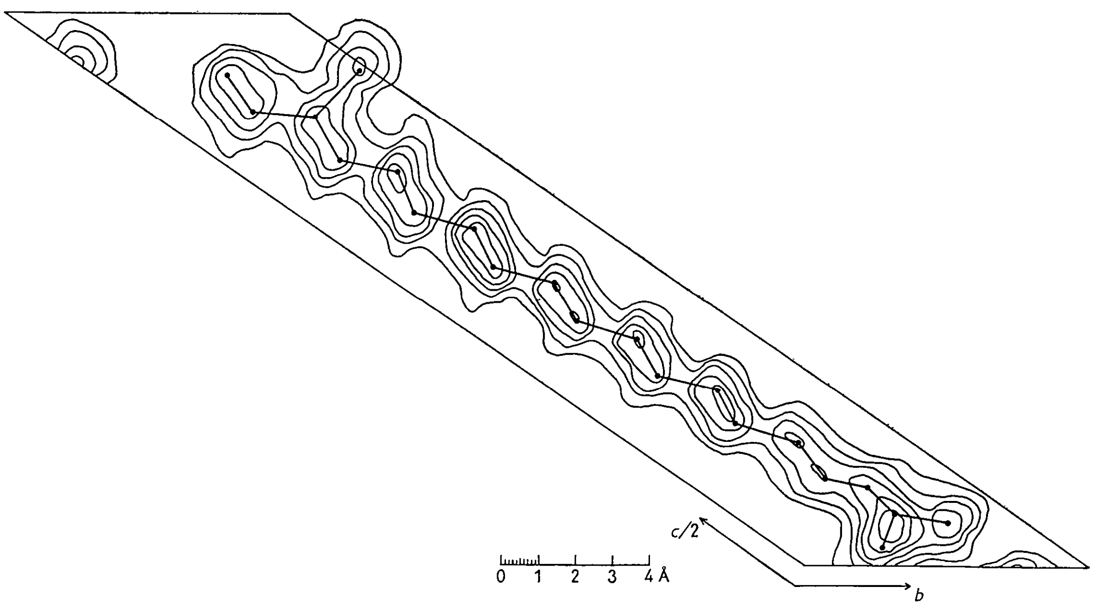

Fig. 1. Electron-density projection along the shortest axis of 16DL-methyloctadecanoic acid. Contours are given at intervals of 1 e.Å^{-2}, starting with 1 e.Å^{-2}.

Structure factors and electron-density projections

The racemic acid must have a centre of symmetry in the triclinic cell (space group C_i^1–$P\bar{1}$). Knowing the structure of 9DL-methyloctadecanoic acid, a trial structure was postulated with a similar molecular arrangement.

Though irregularities in the carbon chain were expected, the subcell theory (Müller, 1927; Vand, 1951; Vand & Bell, 1951) was used for the first structure-factor calculation. Atomic scattering curves were taken from McWeeny (1951), using for oxygen $f = \frac{1}{3}(f^{\perp}+2f^{\parallel})$ and for carbon the values for 'valence states'.

The signs determined were used for an electron-density projection along the shortest axis. The Fourier summations were performed partly with Beevers–Lipson strips (3°) and partly on the Hägg–Laurent machine (1946). The projection revealed the expected distortions in the chain and it was possible to assign new coordinates to the atoms. As the carbon chain was now deformed the subcell theory could not be used for the succeeding structure-factor calculations.

The subcell has centres of symmetry at (0, 0, 0) and (0, 0, $\frac{1}{2}$) and both can, of course, be taken as origin for the subcell structure. Only one of these, however, will give the correct structure when building up the whole carbon chain (cf. Vand & Bell, 1951, and Shearer & Vand, 1956).

Table 1. *Atomic coordinates*

Atom	*y*/*b*	*z*/*c*
O_1	0·727	0·0390
O_2	0·370	0·0165
C_1	0·580	0·0470
C_2	0·611	0·0700
C_3	0·511	0·0775
C_4	0·600	0·1115
C_5	0·469	0·1270
C_6	0·583	0·1590
C_7	0·443	0·1710
C_8	0·558	0·2050
C_9	0·438	0·2215
C_{10}	0·567	0·2580
C_{11}	0·425	0·2720
C_{12}	0·550	0·3055
C_{13}	0·417	0·3200
C_{14}	0·579	0·3580
C_{15}	0·428	0·3680
C_{16}	0·562	0·4050
C_{17}	0·371	0·4105
C_{18}	0·466	0·4435
C_{19}	0·956	0·4475

When using the subcell concept in the beginning of a structure determination most signs determined belong to the strong reflexions of the reciprocal sublattice. This means that the arbitrary choice of subcell origin might impart some ambiguity to the interpretation of the electron-density projections. Thus, in the present investigation signs were calculated with the wrong subcell origin. The corresponding projection was quite satisfactory, distinctly showing the complete molecule of the acid translated $\frac{1}{2}c_s$ from the correct position. Now in this case the molecular arrangement excluded this choice of origin, but, in other cases where a translation of $\frac{1}{2}c_s$ is not forbidden from spatial considerations, some care is evidently needed as to subcell origin.

The coordinates were refined by successive approximations and finally by several difference syntheses. The hydrogen atoms were included in the structure-factor calculations at the later stages of the refine-

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	$01\bar{7}$	13	11	$0,2,\overline{11}$	8	− 5	$0,3,\overline{25}$	< 7	3
003	25	−24	$01\bar{8}$	11	12	$0,2,\overline{12}$	14	−19			
004	11	−11	$01\bar{9}$	7	−10	$0,2,\overline{13}$	< 5	0	$0,4,\overline{18}$	< 9	3
005	19	−20	$0,1,\overline{10}$	13	13	$0,2,\overline{14}$	8	− 7	$0,4,\overline{19}$	27	27
006	19	−16	$0,1,\overline{11}$	19	−20	$0,2,\overline{15}$	9	8	$0,4,\overline{20}$	13	18
007	13	−10	$0,1,\overline{12}$	8	5	$0,2,\overline{16}$	< 6	0	$0,4,\overline{21}$	23	−25
008	13	−12	$0,1,\overline{13}$	20	−22	$0,2,\overline{17}$	16	18	$0,4,\overline{22}$	9	7
009	< 5	6	$0,1,\overline{14}$	< 5	9	$0,2,\overline{18}$	< 6	7	$0,4,\overline{23}$	< 8	−11
0,0,10	11	−13	$0,1,\overline{15}$	15	−22	$0,2,\overline{19}$	27	24	$0,4,\overline{24}$	13	13
0,0,11	< 6	6	$0,1,\overline{16}$	16	16	$0,2,\overline{20}$	7	9	$0,4,\overline{25}$	< 8	− 1
0,0,12	10	− 9	$0,1,\overline{17}$	12	−12	$0,2,\overline{21}$	7	− 9	$0,4,\overline{26}$	13	14
0,0,13	8	6	$0,1,\overline{18}$	18	21	$0,2,\overline{22}$	< 7	−11	$0,4,\overline{27}$	12	−10
0,0,14	< 8	− 1	$0,1,\overline{19}$	10	− 8	$0,2,\overline{23}$	12	19	$0,4,\overline{28}$	12	12
			$0,1,\overline{20}$	15	23	$0,2,\overline{24}$	< 7	− 5	$0,4,\overline{29}$	13	−13
010	148	−152	$0,1,\overline{21}$	21	−21				$0,4,\overline{30}$	< 9	5
011	22	21	$0,1,\overline{22}$	13	10	$03\bar{8}$	< 8	10	$0,4,\overline{31}$	10	− 8
012	42	40	$0,1,\overline{23}$	< 8	− 8	$03\bar{9}$	8	− 9	$0,4,\overline{32}$	< 9	− 5
013	< 6	2				$0,3,\overline{10}$	8	11	$0,4,\overline{39}$	<10	− 2
014	25	28	020	36	39	$0,3,\overline{11}$	8	− 7	$0,4,\overline{40}$	17	18
015	< 6	0	021	< 8	11	$0,3,\overline{12}$	8	11	$0,4,\overline{41}$	11	14
016	12	12	022	22	−19	$0,3,\overline{13}$	< 7	− 1	$0,4,\overline{42}$	12	−11
017	< 7	− 3	023	10	11	$0,3,\overline{18}$	< 7	− 5	$0,4,\overline{43}$	<10	3
$01\bar{1}$	35	35	024	< 9	−13	$0,3,\overline{19}$	37	−33			
$01\bar{2}$	11	5	$02\bar{1}$	< 7	7	$0,3,\overline{20}$	18	−15	$0,5,\overline{39}$	<10	3
$01\bar{3}$	47	39	$02\bar{7}$	< 6	3	$0,3,\overline{21}$	52	48	$0,5,\overline{40}$	17	−10
$01\bar{4}$	7	12	$02\bar{8}$	15	−13	$0,3,\overline{22}$	16	13	$0,5,\overline{41}$	16	−11
$01\bar{5}$	27	27	$02\bar{9}$	8	− 5	$0,3,\overline{23}$	11	13	$0,5,\overline{42}$	11	12
$01\bar{6}$	6	11	$0,2,\overline{10}$	19	−22	$0,3,\overline{24}$	12	5	$0,5,\overline{43}$	<10	− 7

ment. They were given approximate parameters calculated from the data of Vainshtein & Pinsker (1950). During the difference syntheses a temperature factor exp $(-B\sin^2\theta/\lambda^2)$ was applied with the final value of $B = 4{\cdot}1$ Å^2. The electron-density projection is shown in Fig. 1. The coordinates of the oxygen and carbon atoms are collected in Table 1, and observed and calculated structure factors in Table 2. The reliability index, R_1, is 0·14, omitting non-observed reflexions.

Discussion of the results

The molecular arrangement is in general agreement with the structure of 9DL-methyloctadecanoic acid. A tight side packing of the carbon chains is possible only if the branching groups can be accommodated between the chain ends (Fig. 2). This is accomplished by the acid molecules being tilted to the carboxyl group planes more than normal chain acids. The angle of tilt is 33°, calculated from the average difference of z coordinates between alternate carbon atoms in the middle of the chain (C_6–C_{13}) and the subcell dimension $c_s = 2{\cdot}56$ Å. 9DL-Methyloctadecanoic acid, which is branched in the middle of the chain, is of course still more tilted (18°), whereas normal chain acids have angles of tilt of approximately 60° (von Sydow, 1956).

The hydrocarbon chain is very much distorted. No part of it is quite regular, the largest deformations being found in the vicinity of the carboxylic group and the branching methyl group. Disregarding the irregularities, all chain planes are parallel, as required by the triclinic chain packing.

The carboxyl groups forced into the chain packing cause most of the distortions in the chain (Fig. 2). The oxygen atoms exert a pressure on the neighbouring chains which must separate a little. This deformation influences the following chains, and the whole chain packing is disturbed. A comparison with 9DL-methyloctadecanoic acid is interesting. In the chain direction the carboxyl groups are in that case on a level with the branching groups and consequently also with the chain ends. The pressure of the oxygen atoms therefore results in a bending of the neighbouring chains into the space between the chain ends, leaving other chains almost unaffected. The distortions are here large but local, whereas those of 16DL-methyloctadecanoic acid are smaller but disturb the whole chain packing.

The large deformations at the end of the chain must be due to the branching methyl groups. The space provided for them between the chain ends is evidently not large enough, and again distortions result.

The distorted chain packing is certainly responsible for the difficulty in growing perfect crystals of the acid. The common twinning on the (001) planes and the cleavage properties along these planes are also consistent with the structure: the methyl group ends of the acid dimers are only held together by weak van der Waals forces.

I wish to thank Dr E. von Sydow for much advice during this work. I also thank Prof. G. Hägg and Prof. E. Stenhagen for their constant interest. Finally I am indebted to Prof. J. Cason of the University of California for a sample of the acid and to Mr S. Aleby,

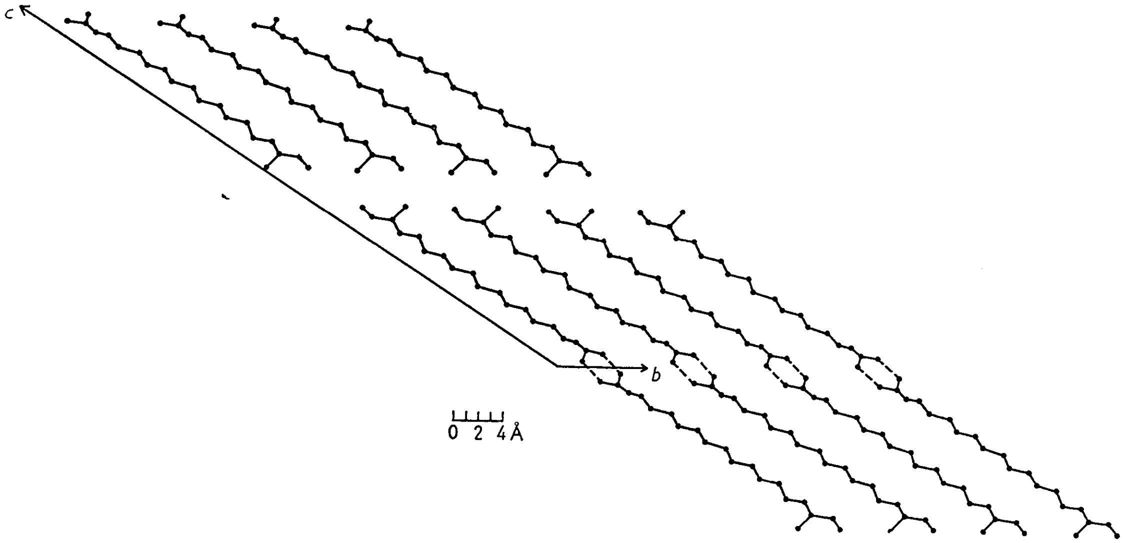

Fig. 2. Molecular arrangement of 16DL-methyloctadecanoic acid, as viewed along the shortest axis.

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References

Abrahamsson, S. (1956). *Acta Cryst.* **9**, 663.
Cason, J. & Prout, F. S. (1944). *J. Amer. Chem. Soc.* **66**, 46.
Clark, G. J. & Chu, C.-C. (1951). *Acta Cryst.* **4**, 470.
Hägg, G. & Laurent, T. (1946). *J. Sci. Instrum.* **23**, 155.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Müller, A. (1927). *Proc. Roy. Soc.* A, **114**, 542.
Shearer, H. M. M. & Vand, V. (1956). *Acta Cryst.* **9**, 379.
Sydow, E. von (1956). *Ark. Kemi*, **9**, 231.
Vainshtein, B. K. & Pinsker, Z. G. (1950). *Dokl. Akad. Nauk. SSSR.* **72**, 53.
Vand, V. (1951). *Acta Cryst.* **4**, 104.
Vand, V. & Bell, I. P. (1951). *Acta Cryst.* **4**, 465.
Velick, S. F. (1944). *J. Biol. Chem.* **156**, 101.

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The Crystal Structure of Dicalcium Phosphate Dihydrate, $CaHPO_4 . 2H_2O$

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The structure of $CaHPO_4 . 2H_2O$ has been determined, and refined to a moderate accuracy (standard deviation of oxygen positions about 0·03 Å, R approximately 26%). The structure is similar to that of gypsum, but there is a definite change of cell dimensions and a small shift in atomic parameters. The hydrogen atoms are probably situated between pairs of water molecules. The structure contains corrugated sheets of composition $CaPO_4$, with the waters in layers between them.

Introduction

Dicalcium phosphate is of interest as a mineral (brushite) which is isomorphous with the corresponding arsenate (pharmacolite). The crystals are very similar to those of gypsum, with which, indeed, it forms a mixed series (Hill & Hendricks, 1936; O'Daniell, 1939; Smith, Lehr & Brown, 1955). It can be grown into very fine large crystals, and we are obliged to the Research Department of the Tennessee Valley Authority for specimens which were used for the cutting of crystal plates for Geiger-counter spectrometry. Smaller crystals were grown for this work by the Research Department of Scottish Agricultural Industries Limited.