On the Structure of the Crystal Form A' of n–Pentadecanoic Acid

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Form A' of n-pentadecanoic acid, $C_{14}H_{29}COOH$, is triclinic with $a = 4.25$ Å, $b = 5.01$ Å, $c = 42.76$ Å; $\alpha = 89° 50'$, $\beta = 111° 5'$, $\gamma = 112° 10'$.

The cell contains two molecules. The crystal shows no piezo-electric effect, indicating space group C_i^1–$P\bar{1}$. Fourier projections along the shortest axis were prepared. The packing of the hydrocarbon chains is triclinic, all the chain-planes being parallel. The planes are slightly twisted helically.

Introduction

As a continuation of a work by Stenhagen & von Sydow (1953) on the phase transitions in normal fatty acids it became necessary to study the different crystal forms in more detail to find the principal differences between them. Except for a great number of papers concerning long spacing, most of which are mentioned in the paper above, there have been few unit-cell determinations with X-rays: Müller (1927) (*B* form of stearic acid), Brill & Meyer (1928) (*C* form of lauric acid), Thibaud & Dupré la Tour (1932) (*C* form of palmitic acid and *B* form of stearic acid); and with electron diffraction: Trillat & v. Hirsch (1932) (the smallest axis-plane of each of three forms of stearic acid).

The first workers to use Fourier techniques on these compounds were Vand, Morley & Lomer (1951) in the determination of the structure of form *C* of lauric acid.

The unit-cell data from all these investigations can probably be derived from the unit-cell data of the orthorhombic packing of hydrocarbon chains determined by Bunn (1939) and Vainshtein & Pinsker (1950). In this packing the planes of alternate chains are almost perpendicular to each other.

This structure determination is the first Swedish contribution to this field and it will be followed by others at present in progress.

Preparation of crystals

The very pure specimen of n-pentadecanoic acid, $C_{14}H_{29}COOH$, obtained from Prof. E. Stenhagen and his collaborators, had a melting point of 52·3° C. compared with 52·26° C. and 52·1° C., according to Meyer & Reid (1933) and Francis, Piper & Malkin (1930), respectively.

According to Stenhagen & von Sydow (1953) the form *A'* of n-pentadecanoic acid is formed when crystallized from light petroleum and (together with form *B'*) from glacial acetic acid. With these solvents, however, the crystals formed are much too small and not very uniform. In addition to these solvents the following were tried under different conditions: benzene, toluene, pentane, hexane, heptane, ethanol, carbon disulfide, carbon tetrachloride, ethyl ether and benzyl alcohol. Carbon tetrachloride gave the best crystals of form *A'*, although they were not very large.

Optical studies of crystals

The crystals were rod-shaped with almost rectangular cross-section. The extinction in polarized light was very distinct and no twin formation could be seen under the microscope. The crystals were found to be biaxial with positive character. It was very helpful to know the direction of the acute bisectrix, i.e. the direction of the chains, when the crystals were later mounted for X-ray work. The crystals used for this purpose were cut from a rod, the cross-section of which had the dimensions 0.08×0.05 mm.

X-ray data

Rotation photographs about the *a* and *b* axes and zero- and n-layer Weissenberg photographs about the *a* axis, were taken, using Cu *K* radiation from a gas tube and a calibrated camera. The following data were obtained:

Molecular formula: $C_{15}H_{30}O_2$.
Molecular weight: 242·39.
Unit cell: triclinic.
$a = 4.25 \pm 0.02$, $b = 5.01 \pm 0.02$, $c = 42.76 \pm 0.17$ Å.
$\alpha = 89° 50' \pm 25'$, $\beta = 111° 5' \pm 20'$, $\gamma = 112° 10' \pm 20'$.
$d(001) = 39.43 \pm 0.16$ Å.
Two molecules per unit cell.
Numbers of electrons: 272.
Density calculated: 1.034 ± 0.016 g.cm.$^{-3}$.
Density measured: 1·02 g.cm.$^{-3}$.
Space group: C_1^1–$P1$ or C_i^1–$P\bar{1}$.

The absence of piezo-electric effect (I am indebted to Mr J. Baecklund for help with the measurements) indicates space group C_i^1–$P\bar{1}$, which has a centre of symmetry.

No twinning was observed.

Conclusions from the unit cell

If the unit-cell data are compared with the data of the triclinic subcell in trilaurin (Vand & Bell, 1951) some interesting similarities will be seen. The triclinic subcell in question has the following data:

$$a_s = 4\cdot287, \ b_s = 5\cdot40, \ c_s = 2\cdot45 \text{ Å};$$
$$\alpha_s = 74° \ 45', \ \beta_s = 108° \ 2', \ \gamma_s = 117° \ 24'.$$

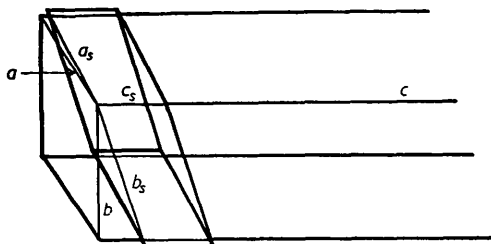In Fig. 1 the two cells are placed with their c axes

Fig. 1. Part of the main cell and the triclinic subcell.

and bc planes coincident. The a axes will then coincide approximately. The distance in the main cell along b_s,

$$b'_s \sim b/\cos \ (\alpha - \alpha_s) \sim 5\cdot20 \text{ Å} ,$$

is rather close to b_s. From these facts one can conclude with some certainty that the A' form of n-pentadecanoic acid has the same triclinic packing of the hydrocarbon chains as trilaurin.

Structure factors and electron-density projection

Owing to the smallness of the available crystal rather few reflexions were registered: with a 120 hr. exposure there were only 38 ($0kl$) reflexions.

Two observers estimated the intensities by eye, using the multiple-film technique of de Lange, Robertson & Woodward (1939). The strongest reflexion was 250 times stronger than the weakest one observed. The intensities were corrected with the normal polarization and Lorentz factors. No absorption corrections were applied. A set of relative, observed structure factors were calculated. These were later brought on an absolute scale by comparison with calculated structure factors.

For the first calculation of structure factors atomic coordinates were taken from the triclinic subcell in trilaurin (Vand & Bell, 1951). The subcell theory for long-chain compounds, first suggested by Müller (1927) and later developed by Vand (1951) and used by Vand & Bell (1951), was used here. At this stage the CH_2 groups were considered as single atoms with $f=f_C+2f_H$. The carboxylic group was given probable coordinates.

Atomic scattering factors were taken from McWeeny (1951), using for oxygen $f = \frac{1}{3}(f^\perp + 2f^{||})$ and for carbon the values for 'valence states'.

For the Fourier summation both Beevers–Lipson

strips (3°) and a machine designed by Hägg & Laurent (1946) were used.

Successive electron-density projections along the shortest axis were prepared, alternating with structure-factor calculations. The first summation was made with only 18 structure factors and gave a remarkably good resolution. This is of course due to the periodicity in the hydrocarbon chains.

In the later structure-factor calculations the carbon and hydrogen atoms were separated. The coordinates of the two hydrogen atoms relative to the corresponding carbon atom were determined from data given by Vainshtein & Pinsker (1950). As both hydrogen atoms had about the same y and z coordinates they were placed on the centre of gravity and considered as one atom having $f = 2f_H$.

From the sixth projection (Fig. 2) it can be seen that the chains are not planar. The carbon atoms are still lying on two straight lines, which now, however, diverge. As the distance between the carbon atoms in each row in the projection is constant, within experimental error, the subcell theory can still be applied, but two different subcell regions must be considered, each representing one row of carbon atoms with their hydrogen atoms.

The last structure-factor calculation was carried out with data from the projection in Fig. 2 and the oxygen
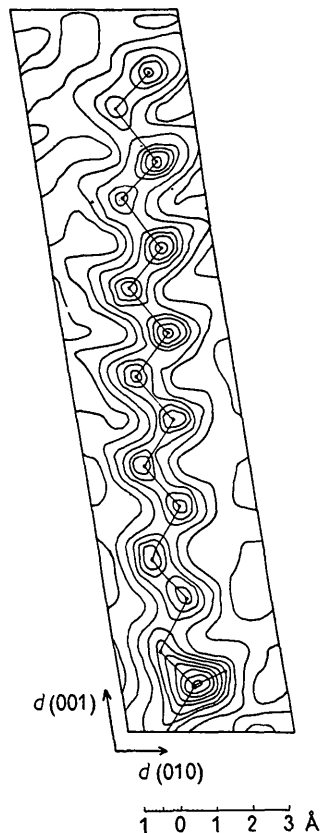

Fig. 2. Electron-density projection along the a axis.

Table 1. Co-ordinates of the atoms

Atom	y/b	z/c	Atom	y/b	z/c
O_1H_1	0·265	0·002	H_2+H_3	0·129	0·060
C_1	0·450	0·0320	H_4+H_5	0·651	0·093
O_2	0·630	0·046	H_6+H_7	0·171	0·123
C_2	0·277	0·0562	H_8+H_9	0·697	0·153
C_3	0·496	0·0926	$H_{10}+H_{11}$	0·213	0·185
C_4	0·318	0·1188	$H_{12}+H_{13}$	0·743	0·214
C_5	0·542	0·1532	$H_{14}+H_{15}$	0·255	0·248
C_6	0·360	0·1814	$H_{16}+H_{17}$	0·789	0·274
C_7	0·588	0·2138	$H_{18}+H_{19}$	0·297	0·310
C_8	0·402	0·2439	$H_{20}+H_{21}$	0·835	0·335
C_9	0·634	0·2743	$H_{22}+H_{23}$	0·339	0·373
C_{10}	0·444	0·3065	$H_{24}+H_{25}$	0·882	0·396
C_{11}	0·681	0·3349	$H_{26}+H_{27}$	0·381	0·435
C_{12}	0·486	0·3691	$H_{28}+H_{29}$	0·928	0·456
C_{13}	0·727	0·3955	H_{30}	0·634	0·482
C_{14}	0·528	0·4317			
C_{15}	0·773	0·4561			

atoms were moved until the best resemblance to observed structure factors was obtained. No new signs were obtained. The atomic coordinates are collected in Table 1 and observed and calculated structure factors in Table 2. The reliability index $R = \Sigma|F_o-F_c| \div \Sigma|F_o|$ is 0·21.

Discussion of the results

As has been pointed out already, no twinning has been observed. This is remarkable as this effect seems to be very common among the fatty acids and also among other long-chain compounds (see for instance Müller (1927) and Stenhagen, Vand & Sim (1952)).

As pointed out by Vand & Bell (1951), the triclinic packing of hydrocarbon chains with all chain-planes parallel, which appears in this crystal form and in trilaurin, also appears in the low-temperature form of hydrocarbons described by Müller & Lonsdale (1948) and in silver soaps described by Vand, Aitken & Campbell (1949). The difference in the dimensions of the smallest axis-plane is partly due to the chain length and partly to the nature of the end group.

The increment of long spacing for this crystal form, according to Stenhagen & von Sydow (1953), is 2·39 Å. Thus the angle of tilt is between 71° and 66° if the distance between alternate carbon atoms has a value between 2·521 Å, found in lauric acid by Vand, Morley & Lomer (1951), and 2·610 Å, found in strontium laurate by Morley & Vand (1949).

From the electron-density map shown in Fig. 2 it can be seen that the chains are not planar.* The plane is probably helically twisted round the centreline of the chain. The centreline may be somewhat bent, too, in that case in a direction perpendicular to the chain plane. In the projection one can also see that the thermal motion is bigger in the end of the hydrocarbon chain than in the carboxylic group, which is held more tightly with hydrogen bonds.

* This is probably not an effect due to series termination as the projection proceeding the last one did not show this effect, having the rows of carbon atoms approximately parallel.

Table 2. Observed and calculated structure factors

hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c
000	272	—	0,1,12	< 10·2	− 2·6	026	< 12·0	− 1·5
001	30·7	33·2	0,1,13	< 10·5	2·9	027	< 12·2	4·2
002	5·9	6·1	0,1,14	< 10·9	−11·0	028	< 12·4	− 1·2
003	25·6	28·3	0,1,15	50·8	58·8	029	< 12·6	5·7
004	< 4·9	0·0	0,1,16	24·1	33·1	0,2,10	< 12·9	1·4
005	16·4	20·4	0,1,17	20·8	−27·4	0,2,11	< 13·1	6·2
006	< 6·0	− 7·1				0,2,12	< 13·4	5·8
007	6·5	12·1	$01\bar1$	44·3	−30·0	0,2,13	< 13·6	11·0
008	8·9	−12·5	$01\bar2$	75·1	64·2	0,2,14	21·9	23·6
009	< 7·4	5·0	$01\bar3$	< 7·3	− 9·2	0,2,15	31·6	−32·8
0,0,10	9·7	−16·0	$01\bar4$	24·3	20·8	$0,2,16$	16·1	−20·3
0,0,11	< 8·3	4·2	$01\bar5$	< 7·7	− 8·4			
0,0,12	13·8	−15·8	$01\bar6$	13·8	13·1	$02\bar1$	< 11·1	− 2·4
0,0,13	< 9·1	4·4	$01\bar7$	< 8·0	− 5·7	$02\bar2$	17·4	−11·9
0,0,14	14·4	−15·3	$01\bar8$	16·1	12·8	$02\bar3$	< 10·9	4·5
0,0,15	< 10·0	0·1	$01\bar9$	< 8·6	− 0·8	$02\bar4$	< 10·9	− 6·2
0,0,16	11·6	12·2	$0,1,\overline{10}$	17·2	12·2	$02\bar5$	< 10·9	− 2·8
0,0,17	< 10·9	− 0·4	$0,1,\overline{11}$	9·2	6·0	$02\bar6$	< 10·9	− 4·0
			$0,1,\overline{12}$	19·9	12·6	$02\bar7$	< 11·0	− 8·1
010	116·6	−107·9	$0,1,\overline{13}$	9·8	9·4	$02\bar8$	< 11·1	− 3·0
011	18·5	−14·6	$0,1,\overline{14}$	19·1	15·0	$02\bar9$	< 11·2	−14·0
012	32·4	−24·3	$0,1,\overline{15}$	12·4	10·3	$0,2,\overline{10}$	< 11·3	− 1·3
013	14·5	− 6·0	$0,1,\overline{16}$	26·7	−35·5	$0,2,\overline{11}$	< 11·5	− 9·1
014	10·9	− 7·8	$0,1,\overline{17}$	67·5	73·5	$0,2,\overline{12}$	< 11·7	0·6
015	< 8·2	− 5·7				$0,2,\overline{13}$	< 12·0	−13·0
016	< 8·4	− 3·9	020	< 11·1	− 0·2	$0,2,\overline{14}$	< 12·3	2·6
017	< 8·6	− 4·9	021	< 11·3	1·5	$0,2,\overline{15}$	< 12·6	−11·6
018	< 8·9	− 3·4	022	< 11·4	0·6	$0,2,\overline{16}$	< 12·9	4·7
019	< 9·2	− 3·5	023	< 11·5	2·1	$0,2,\overline{17}$	19·2	−32·6
0,1,10	< 9·5	− 4·1	024	< 11·7	− 0·5	$0,2,\overline{18}$	40·8	−53·1
0,1,11	< 9·8	− 1·9	025	< 11·8	2·5	$0,2,\overline{19}$	18·8	18·8

I am most thankful to Dr V. Vand, who taught me the fundamentals of this sort of work, and to Prof. G. Hägg and Prof. E. Stenhagen for their advice and interest. Mr S. E. Flygar has carried out much of the computations and I am indebted to him for his careful work.

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The Crystal Structure of Samarium*

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The crystal structure of samarium is rhombohedral; $a = 8.996$ Å, $\alpha = 23° 13'$, $Z = 3$. The atomic positions are 0, 0, 0; $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$; and $\frac{1}{9}, \frac{1}{9}, \frac{1}{9}$. Single-crystal data require a disordered (or submicroscopically twinned) structure where half of the unit cells are rotated 180° about the threefold axis with respect to the other half. The hexagonal lattice constants are $a = 3.621 \pm 0.007$ Å, $c = 26.25 \pm 0.05$ Å; $Z = 9$.

Introduction

The method of preparation and the large, rhombohedral unit cell for samarium were reported recently by Daane, Dennison & Spedding (1953). Single crystals showed clearly that some sort of disorder was present in the structure, and an investigation of the structure and nature of the disorder was made. Since the completion of this work a report of the structure derived from powder data has been published by Ellinger & Zachariasen (1953). We report here a brief confirmation of the structure from single-crystal data, together with the nature of the disorder, which was not discovered from the powder data.

Experimental data

Weissenberg and precession photographs were taken with Cu $K\alpha$ and Mo $K\alpha$ radiation, respectively, using single crystals picked from a sample of 99% purity. Precession data, using small crystals and Mo radiation, indicated a Laue symmetry D_{6h}.

The reflections were indexed on a hexagonal cell with lattice constants

$$a = 3.621 \pm 0.007 \text{ Å}, \quad c = 26.25 \pm 0.05 \text{ Å}.$$

(These values were obtained from a precession photograph of $(h0.l)$ data with a calcite diffraction pattern superimposed on the film.) The observed bulk density is 7.53 g.cm.$^{-3}$, while the calculated X-ray density is 7.54 g.cm.$^{-3}$ assuming 9 atoms per unit cell.

The observed reflections may be divided into two types:

Type I: $(hk.l)$—for $h-k = 3n$, only with $l = 9n$;
Type II: $(hk.l)$—for $h-k \neq 3n$, only with $l \neq 3n$.

In addition it was observed that the intensities of reflections of Type I are the same, except for the normal decline due to reduced scattering power of the

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