

The Crystal Structure of Propyl Stearate

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Propyl stearate has the monoclinic unit cell $a=5.59$, $b=7.39$, $c=30.0$, $\beta=119.2^\circ$. The cell contains 2 molecules and the space group is $P2_1$. The structure is solved and refined in 3 dimensions to an R -value of 0.129 with the least squares technique. The chains are arranged in the orthorhombic packing $O\perp(101)$. The molecules form sheets with the chains tilting 63° towards the end group planes. The alcohol chain forms a continuation of the main chain but a twist occurs at the carboxyl group. The atoms of the alcohol group seem to have a high degree of mobility.

In a series of investigations on esters of long-chain fatty acids two structures have earlier been reported, methyl stearate by Aleby and von Sydow¹ and ethyl stearate by Aleby.²

According to Malkin,³ propyl, as well as butyl and amyl esters of palmitic, margaric, and stearic acid exist in two crystal forms with a similar behaviour as ethyl esters. Cooling curves show two distinct plateaus corresponding to formation of α - and β -forms, respectively, while heating curves have two plateaus only in the case of margarates.

For palmitates and stearates the transformation $\alpha \rightarrow \beta$ is monotropic or the transition temperature for $\beta \rightarrow \alpha$ is very close to the melting point. The α -form gives only one side-spacing which is said to indicate that the chains rotate. The β -form shows two side-spacings like most long-chain compounds. With the nomenclature of Larsson⁴ the above β -form should be termed β' .

PREPARATION OF CRYSTALS

Propyl stearate (propyl octadecanoate) with m.p. $30.0^\circ - 30.6^\circ$ was crystallized from carbon disulphide, carbon tetrachloride and ethanol at room temperature (20°C) and at -14°C and from glacial acetic acid at room temperature. The room temperature crystallization from ethanol gave useful single crystals of the β' -form in the shape of long, thin plates. The crystals were optically biaxial and positive.

X-RAY DATA

Rotation and Weissenberg photographs were taken about the a and b axes at room temperature using CuK radiation. The following data were obtained:

Unit cell: monoclinic.

$a=5.59\pm 0.02$ Å, $b=7.39\pm 0.02$ Å, $c=30.0\pm 0.3$ Å, $\beta=119.2^\circ\pm 0.3^\circ$

$d(001)=26.3\pm 0.2$ Å (from Guinier powder photographs).

Two molecules per unit cell.

Number of electrons: 368.

Density calculated: 0.997 ± 0.014 g cm⁻³.

Density measured: 0.990 g cm⁻³.

Absent reflections: $h0l$, when h odd.

Space group: C_2^2-Pa .

The absent reflections indicate spacegroup Pa or $P2/a$. As the latter has 4 general positions and the density shows that the unit cell only contains two molecules the space group Pa was chosen. The intensities of the $h0l$ and $0kl$ -reflections were estimated visually by two observers using the multiple film technique. At a later stage also the $h1l$, $h2l$, $h3l$, $1kl$, and $2kl$ -reflections were included. The intensities were corrected for Lorentz and polarization factors but not for absorption. The resulting observed structure factors were later brought to an absolute scale by comparison with the calculated structure factors. The total number of reflections observed was 449 which corresponds to 18 % of the reflections inside 1/4 of the copper sphere. Within the layers used 28 % of the reflections were observed. This low value is caused by the low intensity for reflections between the subcell regions of reciprocal space.

STRUCTURE DETERMINATION AND REFINEMENT

The Weissenberg zero-layer films rotated around the a - and b -axes were both very similar to the corresponding films of ethyl stearate but without the A -centering of the latter. The subcell was of the common orthorhombic type (O_L , Bunn⁵).

In the yz -projection the stearic acid chain was given coordinates corresponding to ethyl stearate while the propoxy group was presumed to be a continuation of the main chain but with its plane parallel to the ac -plane. From the reflections $20\bar{1}$, 200, and 201 x -coordinates were found. Structure factors $0kl$ and $h0l$ were calculated with atomic scattering factors according to Berghuis *et al.*⁶ and McWeeny⁷ for hydrogen. The agreement with the observed F 's was reasonable and refinement was started with cycles of structure factor calculations and difference syntheses in the two projections. In the later stages hydrogen atoms were included at distances 1.10 Å from the carbons and 110° angles from carbon-carbon bonds. Individual temperature factors $\exp(-B \sin^2\theta/\lambda^2)$ were used. The calculations were performed on a Ferranti "Mercury" computer using programs described by Mills and Rollett.⁸

When the R -values for the $0kl$ - and $h0l$ -reflections were 0.24 and 0.20, respectively, the higher layers mentioned above were included in the data.

At this stage a program system for the DATASAAB D21 computer described by Abrahamsson *et al.*⁹ was available and was used for the remaining work.

Before the start of the 3-dimensional refinement the correlations between the parameters were studied. With all parameters included in the refinement there was an average correlation of 0.72 between the *x*-coordinates and of 0.86 between the *z*-coordinates. Between the *y*- and *B*-parameters the correlation was close to 0. The situation was the same as in ethyl stearate² and was handled in the same way by refining only part of the molecule at a time.

The 3-dimensional refinement was performed with a full-matrix program described by Abrahamsson¹⁰ and Aleby.¹¹ The molecule was treated in two parts, one comprised of the atoms C(18)...C(2) of the main chain and the other of the atoms of the group $-\text{C}(=\text{O})-\text{O}\cdot\text{C}_3\text{H}_7$. Hydrogen atoms were attached to the carbons at distances of 1.09 Å and in tetrahedral angles. Individual, isotropic temperature factors were used (the amount of data and their quality was not considered to make anisotropic refinement meaningful).

Of the measured reflections 28 strong ones showed poor agreement and were excluded from the refinement. During the refinement the atoms of the propoxy group turned out to have very high *B*-values indicating an uncertainty in their positions. Difference maps gave no safe information except for the position of C(23). Several different arrangements were tried, all refining to high *B*-values and with only small differences in the values of *R* and $\sum w(|F_o| - |F_c|)^2$. Finally O(1) was placed so as to form a normal carboxyl group, then C(21) was located by putting it in as 6 atoms with *B*=9, each with an individual weight ("occupation number", denoted by *n*) of 1/6 in the

Table 1. Coordinates and temperature factors.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
C(18)	0.411	0.212	0.9111	9.26 Å ²
C(17)	0.536	0.318	0.8792	6.03
C(16)	0.413	0.197	0.8323	4.74
C(15)	0.533	0.287	0.7978	5.14
C(14)	0.383	0.201	0.7413	3.82
C(13)	0.500	0.284	0.7056	5.09
C(12)	0.372	0.200	0.6537	4.52
C(11)	0.478	0.288	0.6203	7.06
C(10)	0.365	0.207	0.5701	1.89
C(9)	0.467	0.277	0.5374	5.46
C(8)	0.323	0.209	0.4778	4.34
C(7)	0.434	0.287	0.4451	4.07
C(6)	0.318	0.208	0.3968	4.37
C(5)	0.420	0.278	0.3608	3.64
C(4)	0.297	0.215	0.3108	3.31
C(3)	0.398	0.284	0.2784	5.07
C(2)	0.241	0.214	0.2214	2.58
C(1)	0.377	0.250	0.1963	5.43
O(1)	0.229	0.231	0.1451	8.01
O(2)	0.569	0.328	0.2069	9.59
C(21)	0.352	0.257	0.1072	7.44
C(22)	0.160	0.232	0.0664	14.96
C(23)	0.236	0.260	0.0249	9.26

structure factor calculations, the 6 positions separated by a 60° turning around the C(1)—O(1) bond. Refinement showed C(21) to be in one (or both) of the positions in the plane O(2)—C(1)—O(1), these having $B=1.4$ and -0.8 after one cycle while the other positions had $B>16$, >16 , 14.3 , and 10.5 . These two positions were given the weight $1/2$ and two cycles of refinement then gave $\bar{B}=3.4$ and 11.8 which was considered to exclude the latter position thus placing C(21) *cis* relative to O(2), which is the usual conformation of the ester group (*e.g.* Lumbroso and Schuijl¹² and Owen¹³). With C(23) fixed from difference maps and never shifted much during refinement the position of C(22) remained to be determined. With normal bond lengths and angles only two positions were possible for C(22), one below and one above the plane through O(1), C(21), and C(23) (meaning that the y coordinate is smaller and larger resp., than the coordinate of the plane which was considered roughly perpendicular to the b -axis). C(22) was distributed over these two positions with different occupation numbers and in some cases also one part was placed in a position in the plane O(1)—C(21)—C(23). Refinement of coordinates and B -values tended to shift the in-plane position away and to keep the two others with $n\approx 0.3$ and $B\approx 9$. Refinement of the occupation numbers also gave $n\approx 0.3$ for the two out-of-plane positions but also indicated a contribution with $n\approx 0.6$ for the in-plane position. From the B -values (6.2 and 12.0) it appeared that the position below the plane was more important than the one above. C(22) was placed completely below the plane and on continued refinement it was shifted up to the plane but got a very high $B=15$. It must be concluded that this represents an average position of a highly movable atom or that disorder is causing this uncertainty of the position in the "superposition" structure.

The refinement converged to an R -value of 0.129 . In the final cycles the average shifts in positions were 0.08 of the average standard deviation and the maximum shift was 0.21 of the corresponding standard deviation. A final difference syntheses showed no significant peaks (all being $< 0.2 \text{ e}\cdot\text{\AA}^{-3}$). When the 28 strong reflections were included the R -value became 0.153 . Some cycles of refinement using all the reflections did not produce any significant changes in the parameters. The maximum shift was 0.043 \AA for C(22) and the average shift was 0.016 \AA . The R -value dropped to 0.151 .

RESULTS AND DISCUSSION

The final parameters (from the refinement without the strong reflections) are given in Table 1. The observed and calculated structure factors (including the strong ones marked with — after the phase angle) are shown in Table 2 (where h and l are interchanged because the calculations were performed in space group Pc). Table 3 gives the bond lengths and angles. The average length of the C—C bonds between C(2) and C(18) is 1.53 \AA and the average angle at the same atoms is 113° . The average standard deviation (estimated from the elements of the inverse of the normal equation matrix) is 0.031 \AA for the position coordinates and 0.7 \AA^2 for the isotropic temperature factors. The standard deviation in the bond lengths is on the average 0.044 \AA and for

Table 2. Continued.

H	K	L	Fo	Fc	FI	H	K	L	Fo	Fc	FI	H	K	L	Fo	Fc	FI	H	K	L	Fo	Fc	FI	
10	-3	-2	7	8	0.927	1	-3	-3	15	8	0.575	11	5	0	18	19	0.316	24	-4	-2	15	12	0.919	
9	-3	-2	4	5	0.794	0	-3	-3	15	8	0.907	11	5	0	24	23	0.853	23	-4	-2	9	7	0.437	
8	-3	-2	4	4	0.511	10	-3	-3	7	0.007	12	5	0	7	8	0.007	13	-4	-2	6	7	0.777		
7	-3	-2	5	5	0.207	11	-3	-3	15	15	0.025	24	5	0	4	4	0.496	12	-4	-2	13	11	0.356	
6	-3	-2	6	7	0.076	24	-3	-4	9	0.375	12	7	0	10	12	0.840	2	-4	-2	6	6	0.786		
5	-3	-2	4	4	0.903	13	-3	-4	9	0.331	12	7	0	11	13	0.331	1	-4	-2	15	17	0.648		
5	-3	-2	4	5	0.661	12	-3	-4	5	0.831	12	-4	-1	36	37	0.720	0	4	2	16	14	0.723		
3	-3	-2	4	4	0.458	3	-3	-4	5	0.314	11	-4	-1	17	17	0.153	11	4	2	6	14	0.898		
3	-3	-2	7	8	0.398	2	-3	-4	6	0.185	1	-4	-1	9	8	0.557	13	-5	-2	10	10	0.584		
2	-3	-2	20	18	0.446	1	-3	-4	18	0.691	0	4	1	22	24	0.848	12	-5	-2	29	26	0.080		
1	-3	-2	27	27	0.090	0	0	0	6	0.332	11	4	1	19	18	0.443	11	-5	-2	8	9	0.500		
1	-3	-2	5	5	0.159	24	-3	-5	3	0.035	12	4	1	13	11	0.993	1	-5	-2	15	15	0.940		
2	-3	-2	6	6	0.604	14	-3	-5	5	0.241	23	4	1	10	9	0.122	0	0	2	18	18	0.583		
2	-3	-2	6	6	0.734	26	-3	-6	6	0.906	1	-5	-1	13	16	0.739	11	-5	-2	10	10	0.059		
2	-3	-2	4	4	0.801	25	-3	-6	6	0.605	0	5	1	20	19	0.550	13	-7	-2	6	7	0.042		
1	-3	-2	10	11	0.558	0	0	0	221	180	0.500	-	11	11	7	0.763	12	-7	-2	16	15	0.586		
22	-3	-2	4	5	0.720	1	4	0	66	53	1.000	-	12	-6	-1	22	25	0.216	11	-7	-2	5	5	0.049
23	-3	-2	4	4	0.250	1	4	0	12	11	0.360	-	11	-6	-1	13	13	0.678	1	7	2	10	1	0.184
24	-3	-2	16	15	0.796	2	2	0	2	6	0.357	0	6	1	12	13	0.465	11	7	2	10	10	0.061	
23	-3	-2	6	6	0.253	9	4	0	4	4	0.210	11	6	1	14	14	0.959	0	7	2	4	6	0.565	
14	-3	-2	9	9	0.777	11	4	0	10	9	0.112	12	6	1	10	9	0.464	11	7	2	4	6	0.051	
13	-3	-2	18	16	0.658	12	4	0	11	9	0.565	12	-8	-1	8	11	0.705	11	7	2	4	6	0.565	
12	-3	-2	21	18	0.194	23	4	0	7	6	0.231	11	-8	-1	6	7	0.222							

the angles between bonds 3.6°. Two of the bonds in the chain [C(7)—C(6) and C(5)—C(4)] seem to be significantly shorter than the average. As this is improbable the conclusion would be that the standard deviations given above are underestimated. This is also indicated by the value of $[\sum w(|F_o| - |F_c|)^2 / m - n]^{1/2} = 1.3$ instead of 1 (see, e.g., Taylor *et al.*¹⁴). Some bonds in the polar part of the molecule also show large deviations from their normal values, in this case obviously depending on the above mentioned difficulty of defining the positions of the atoms.

An electron density map was calculated using all the reflections and Fig. 1 shows a composite drawing of this with sections parallel to the *ac*-plane and close to the C and O atoms.

Table 3. Bond lengths and angles.

C(18)—C(17)	1.64 Å	C(18)—C(17)—C(16)	97°
C(17)—C(16)	1.52	C(17)—C(16)—C(15)	102
C(16)—C(15)	1.62	C(16)—C(15)—C(14)	110
C(15)—C(14)	1.61	C(15)—C(14)—C(13)	112
C(14)—C(13)	1.62	C(14)—C(13)—C(12)	113
C(13)—C(12)	1.50	C(13)—C(12)—C(11)	111
C(12)—C(11)	1.53	C(12)—C(11)—C(10)	113
C(11)—C(10)	1.45	C(11)—C(10)—C(9)	116
C(10)—C(9)	1.45	C(10)—C(9)—C(8)	119
C(9)—C(8)	1.64	C(9)—C(8)—C(7)	117
C(8)—C(7)	1.51	C(8)—C(7)—C(6)	113
C(7)—C(6)	1.39	C(7)—C(6)—C(5)	116
C(6)—C(5)	1.54	C(6)—C(5)—C(4)	119
C(5)—C(4)	1.39	C(5)—C(4)—C(3)	117
C(4)—C(3)	1.44	C(4)—C(3)—C(2)	115
C(3)—C(2)	1.58	C(3)—C(2)—C(1)	112
C(2)—C(1)	1.33	C(2)—C(1)—O(1)	115
C(1)—O(1)	1.35	C(2)—C(1)—O(2)	133
C(1)—O(2)	1.12	O(1)—C(1)—O(2)	110
O(1)—C(21)	1.60	C(1)—O(1)—C(21)	124
C(21)—C(22)	1.18	O(1)—C(21)—C(22)	103
C(22)—C(23)	1.51	C(21)—C(22)—C(23)	111

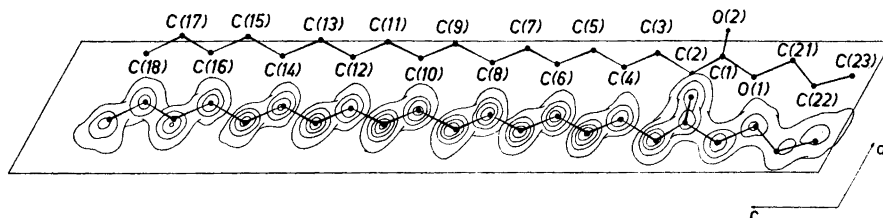


Fig. 1. Electron density in sections close to the atoms. Contours at intervals of $1 \text{ e} \cdot \text{\AA}^{-3}$ starting with $1 \text{ e} \cdot \text{\AA}^{-3}$.

The structure is of the same type as the earlier investigated esters and most other long-chain compounds with the molecules arranged in layers with all chain axes parallel. The side packing of the chains can be described by the subcell $O_{\perp}(101)$. The dimensions of the subcell are $a_s = 4.99 \text{ \AA}$, $b_s = 7.39 \text{ \AA}$, $c_s = 2.52 \text{ \AA}$. The tilt of the chains relative to the end group planes is 63° . The shortest distance between carbon atoms across the end group layer is 4.00 \AA .

The molecular geometry is outlined in Fig. 2 which shows the molecule as seen in the direction of the c -axis (which is pointing down from the plane of the paper). The lines of intersection between the a^*b -plane and the best least-squares planes through the main chain [atoms C(2)...C(18)], the carboxyl group [atoms C(2), C(1), O(1), O(2)] and the propoxy group [atoms O(1), C(21), C(22), C(23)] are shown and their angles to the b -axis indicated. All these planes are nearly parallel to the c -axis. The projections of the centroids of the different groups are also shown. The angles between the planes and the bc -plane are 45° for the chain plane, 65° for the carboxyl plane and 77° for the propoxy plane.

The atoms of the main chain lie within 0.08 \AA from the plane except C(2) and C(17) which are 0.13 and 0.17 \AA , respectively, out of the plane, C(2)

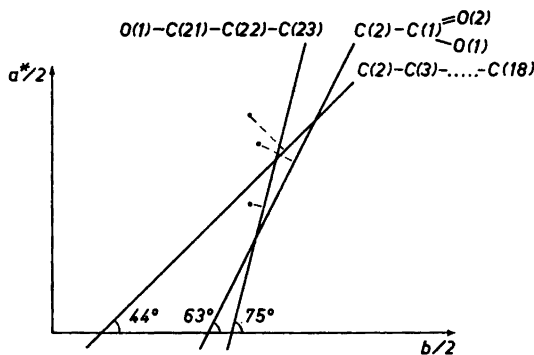


Fig. 2. Least-squares planes through different parts of the molecule (the intersections between the planes and the a^*b -plane are shown as well as the projections of the centroid of the group of atoms).

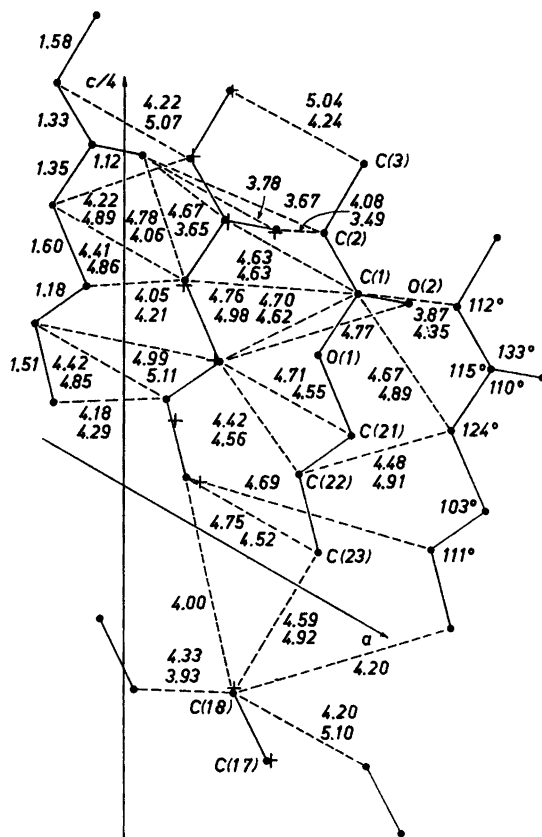


Fig. 3. Detail of the ester group region (where two distances are given they refer to atoms displaced one b -axis from each other).

tending to the more "vertical" arrangement of the carboxyl group. There is an indication of a twist of the chain plane so that the part nearer to the methyl end is more parallel to the bc -plane. The same direction of twisting continues through the carboxyl group to the propoxy group. The carboxyl group is planar within the limits of error, the sum of the bond angles is 358° and the maximum deviation from the plane is 0.08 \AA . The propoxy group is planar within 0.02 \AA .

In Fig. 3 details of the ester group region are shown with distances and angles indicated. It is obvious that the poor definition of the atoms of the propyl group has led to some abnormal distances. It can be noted that the distances between the peak centres of the electron density (marked with crosses in the figure) differ appreciably from the corresponding distances calculated from the refined positions: for $O(1)-C(21)$ 1.48 and 1.60 , respectively, for $C(21)-C(22)$ 1.36 and 1.18 , and for $C(22)-C(23)$ 1.24 and 1.51 \AA , respectively.

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