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On the Structure of the Crystal Form A of Lauric Acid

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The A-form of lauric acid, $C_{11}H_{23}COOH$, is triclinic with space group $P\bar{1}$. For structural reasons the centered cell $A\bar{1}$ has been used. It has the dimensions $a = 5.41$ Å, $b = 26.27$ Å, $c = 35.42$ Å, $\alpha = 69° 36'$, $\beta = 113° 9'$, and $\gamma = 121° 21'$. The centered cell contains 12 molecules. The hydrocarbon chains are arranged in a triclinic packing and from this point of view the structure can be regarded as a sixfold superstructure. There are no layers in the crystals with only carboxyl groups or methyl groups, respectively. They appear together in the same layers in groups of six.

Like all the other crystal forms of normal fatty acids the crystalline A-form of acids with an even number of carbon atoms was first detected in a "long spacing" investigation [1]. Trillat and v. Hirsch [2] determined the smallest axis-plane of stearic acid with electron-diffraction. Lomer [3] has recently determined the unit cell dimensions of the A-forms (γ-form) of lauric acid and myristic acid from powder data. He suggests that the cells are monoclinic, which however seems to be wrong. For the A-form of lauric acid he gives a volume which is about 6 % less than the volume of the one described here. Lomers observed density data are also inconsistent with these results.

PREPARATION OF CRYSTALS

The very pure lauric acid used was prepared by Professor E. Stenhagen and his collaborators. It melts at 44.5—44.8° C.

According to Stenhagen and the author [4,5] lauric acid may crystallize exclusively in the form A from light petroleum, pentane, acetone, ethyl alcohol, and carbon disulfide. The best single crystals for the X-ray investigation were obtained from carbon disulfide.

Crystals of normal fatty acids are usually in form of thin plates, but the A-form of lauric acid crystallizes in elongated parallelepipeds with irregular shortsides. The crystals are biaxial positive. No twinning could be observed under the polarizing microscope.

X-RAY DATA

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

Molecular formula: $C_{12}H_{24}O_2$.
Molecular weight: 200.31.
Density calculated: 1.027 ± 0.013 g cm^{-3}.
Density observed: 1.033 g cm^{-3}.
Unit cell: triclinic (primitive).
Six molecules per unit cell.
Number of electrons: 672.
Space group: C_i^1—$P\ \bar{1}$.
For structural reasons the following cell will be used in the text:
Unit cell: triclinic (A-centered).
$a = 5.41 \pm 0.01$, $b = 26.27 \pm 0.07$, $c = 35.42 \pm 0.13$ Å.
$\alpha = 69° 36' \pm 30'$, $\beta = 113° 9' \pm 26'$, $\gamma = 121° 21' \pm 34'$.
d(001) $= 32.02 \pm 0.06$ Å.
Twelve molecules per unit cell.
Number of electrons: 1 344.
Absent reflexions: (hkl) when $(k+l)$ odd.
Space group: C_i^1—$A\ \bar{1}$.

The absence of the piezo-electric effect (I am indebted to Mr. J. Baecklund for help with the measurements) is consistent with a center of symmetry.

No twinning was observed.

The intensities were estimated by eye from two different sets of multiple films exposed for different times. They were corrected with the normal polarization and Lorentz factors, but no absorption corrections were applied. The relative, observed structure factors obtained were later brought to an absolute scale by comparison with the calculated structure factors. The intensities of the low angle reflexions (002), (011) and (01$\bar{1}$) were estimated from a powder photograph.

Subcell

In the triclinic reciprocal lattice strong reflexions appear periodically along (hkl) when $k = 6n$. They give rise to a larger reciprocal cell, which also is triclinic. Its dimensions agree very well with those of the cell having triclinic packing of hydrocarbon chains, described by Müller and Lonsdale[6] and Vand and Bell[7]. The triclinic subcell coincides approximately with the A-centered cell of the A-form of lauric acid having two axes equal to a and a value close to $b/6$. Considering the chainpacking the main crystal structure can be regarded as a sixfold superstructure.

Patterson projections

If the carbon atoms lie strictly according to the triclinic subcell, they contribute only to structure factors $F(hkl)$ with $k = 6n$. The oxygen atoms in the carboxylic groups, however, contribute to all structure factors and are the only cause of $F(hkl)$ with $k \neq 6n$.

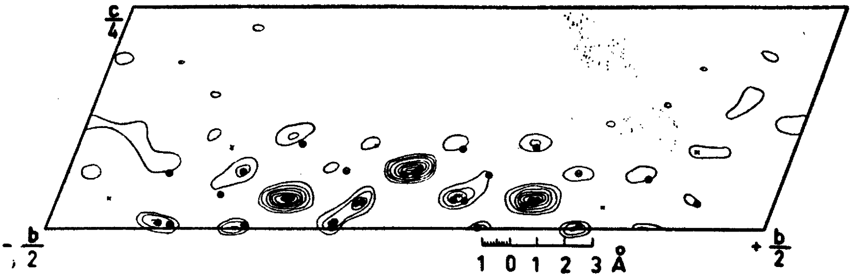

Fig. 1. Patterson projection with $F^2(0kl)$ *values for* $k \neq 6n$. *Origo: 15 contours.* × *single,* ⊗ *double oxygen-oxygen vectors calculated with the final oxygen coordinates.*

A Patterson synthesis with $F^2(hkl)$ for which $k = 6n$ should thus give interatomic distances in the hydrocarbon chains and a synthesis with F^2 (hkl) for which $k \neq 6n$ should give peaks which either represent at least approximate oxygen-oxygen vectors or have no significance at all. The latter is due to the fact that the contribution from the oxygen atoms to $F(hkl)$ with $k = 6n$ is not taken into consideration. This contribution may be comparatively large as there are two oxygen atoms bonded to each of the twelve hydrocarbon chains in the centered cell.

Two Patterson projections were carried out, one with $F^2(0kl)$ where $k = 6n$ and the other with $F^2(0kl)$ where $k \neq 6n$. Both were sharpened by multiplication by the function

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 \exp\left(-\frac{\pi^2}{p} S^2\right) \text{ with } p = 7.25$$

as suggested by Lipson and Cochran [9, p. 172].

The first gave carbon-carbon distances which fitted well with the subcell data given by Vand and Bell [7]. The second projection (Fig. 1) consisted of many peaks concentrated round (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$ in agreement with the centering. It was treated by Buergers vector set method [10] and a set of relative positions was obtained. The carboxylic group and the hydrogen bonding between two acid molecules was supposed to be very similar to those in the other crystal forms of normal fatty acids, *e. g.* the C-form of lauric acid investigated by Vand, Morley and Lomer [8]. With this assumption it could be seen that some of the positions obtained by the vector set method were impossible and thus caused by the fact that the oxygen contribution to $F(0kl)$ with $k = 6n$ had not been accounted for. The remaining positions were supposed to be relative oxygen positions and agreed well with the assumptions above. From the knowledge of other crystal forms (*e. g.* Refs.[8, 13, 14]) they were placed relative to the carbon atoms.

Structure factors and electron-density projections

If all carbon atoms are assumed to be situated strictly according to the triclinic subcell, the structure factors can be calculated using the coordinates

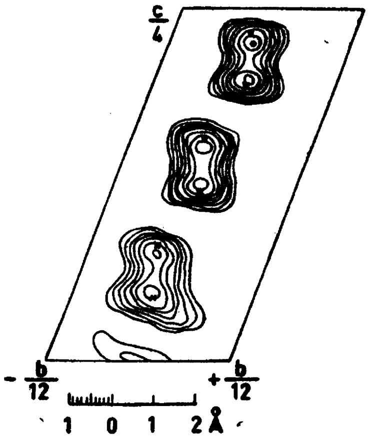

Fig. 2. Fourier projection along the shortest axis with 27 F*(0*kl*) where* k = 6n. *Arbitrary contour scale. The correct positions of the carbon atoms are marked with crosses.*

of only six carbon atoms (later with two hydrogen atoms each) and six oxygen atoms. This will cause small errors in the structure factors due to the non-existence of hydrogen atoms at the carbon atom in the carboxylic group, the existence of a hydrogen atom in the hydroxyl group and of a third hydrogen atom in the methyl group. This effect is, however, insignificant and has been ignored.

With the information obtained from the Patterson projections, structure factors were calculated without the hydrogens. Atomic scattering factors were taken from McWeeny[11] using for oxygen $f = \frac{1}{3}(f^{\perp} + 2f^{\parallel})$ and for carbon the values for "valence states".

A Fourier synthesis was carried out with relative, observed $F(0kl)$ values for $k = 6n$ using 27 signs from the first structure factor calculation. The projection obtained is given in Fig. 2 and shows clearly the six carbon atoms.

In order to obtain the oxygen positions another synthesis with relative, observed $F(0kl)$ values for $k \neq 6n$ was performed using 105 calculated signs (none of these was later found to be wrong). This projection can be seen in Fig. 3. For comparison the final coordinates of the atoms are marked with crosses in both figures.

Structure factors were now calculated again and a total electron-density projection along the shortest axis was prepared. The coordinates were refined using several (F_o—F_c)-syntheses and the hydrogen atoms were included in the

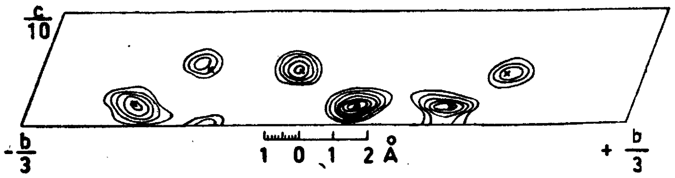

Fig. 3. Fourier projection along the shortest axis with 105 F*(0*kl*) where* k $\neq$ 6n. *Arbitrary contour scale. The correct positions of the oxygen atoms are marked with crosses.*

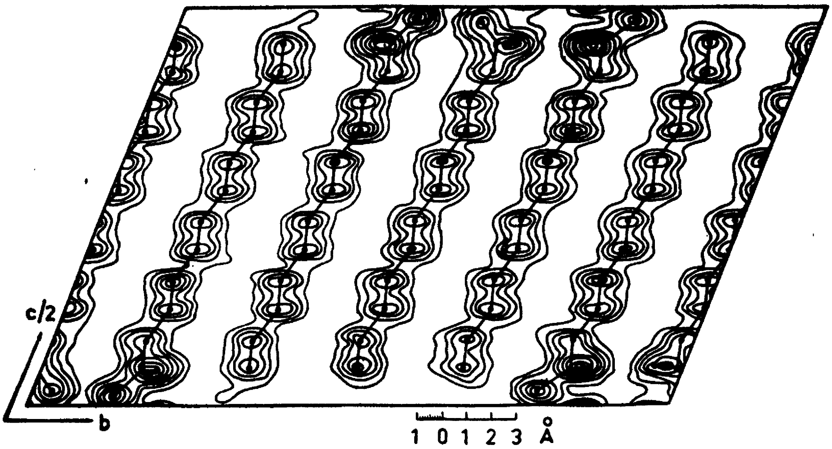

Fig. 4. The A-form of lauric acid. Electron-density projection along the shortest axis. Contour scale: 1 e Å^{-2}.

structure factor calculations as was mentioned above. Their positions relative to the carbon atoms were calculated from data given by Vainshtein and Pinsker[12]. A temperature factor, $\exp\left(-B\,\frac{\sin^2\Theta}{\lambda^2}\right)$ with $B = 4.2$, was applied.

The final coordinates are collected in Table 1, and observed and calculated structure factors in Table 2. The electron-density projection prepared with the values from Table 2 is shown in Fig. 4. The reliability index $R_1 = 0.15$

Table 1. Coordinates of the atoms.

Atom	y/b	z/c	Atom	y/b	z/c
O_1^1	0.0323	0.0180	C_1	$0.9922 + n \cdot \frac{1}{6}$	0.0445
O_2^1	0.9555	0.0475	C_2	$0.9795 + n \cdot \frac{1}{6}$	0.0803
O_1^2	0.1337	0.0128	C_3	$0.9979 + n \cdot \frac{1}{6}$	0.1196
O_2^2	0.1820	0.0435	C_4	$0.9850 + n \cdot \frac{1}{6}$	0.1553
O_1^3	0.3663	0.4872	C_5	$0.0035 + n \cdot \frac{1}{6}$	0.1947
O_2^3	0.3180	0.4565	C_6	$0.9908 + n \cdot \frac{1}{6}$	0.2302
O_1^4	0.4677	0.4820	C_7	$0.0092 + n \cdot \frac{1}{6}$	0.2698
O_2^4	0.5445	0.4525	C_8	$0.9965 + n \cdot \frac{1}{6}$	0.3053
O_1^5	0.7142	0.4834	C_9	$0.0150 + n \cdot \frac{1}{6}$	0.3447
O_2^5	0.6449	0.4530	C_{10}	$0.0021 + n \cdot \frac{1}{6}$	0.3804
O_1^6	0.7858	0.0166	C_{11}	$0.0205 + n \cdot \frac{1}{6}$	0.4197
O_2^6	0.8551	0.0470	C_{12}	$0.0078 + n \cdot \frac{1}{6}$	0.4555

Table 2. Observed and calculated structure factors.

$h\,k\,l$	$\frac{1}{2} F_o$	$\frac{1}{2} F_c$	$h\,k\,l$	$\frac{1}{2} F_o$	$\frac{1}{2} F_c$	$h\,k\,l$	$\frac{1}{2} F_o$	$\frac{1}{2} F_c$
0, 0, 0	336		0, 3, 15	12	−12	0, 6, 10	21	−23
0, 0, 2	12	12	0, 3, 17	12	−12	0, 6, 12	59	−55
0, 0, 4	< 2	1	0, 3, 19	10	−10	0, 6, 14	35	26
0, 0, 6	11	−12	0, 3, 21	8	− 7	0, 6, 16	15	7
0, 0, 8	20	−22	0, 3, 23	< 3	− 3	0, 6, 18	8	5
0, 0, 10	24	−27				0, 6, 20	7	4
0, 0, 12	27	−31	0, 3, $\bar{1}$	14	−15	0, 6, 22	< 3	4
0, 0, 14	5	3	0, 3, $\bar{3}$	12	−14	0, 6, 24	< 3	3
0, 0, 16	< 3	− 4	0, 3, $\bar{5}$	7	− 9	0, 6, 26	33	28
0, 0, 18	< 3	2	0, 3, $\bar{7}$	3	− 1	0, 6, 28	9	− 6
0, 0, 20	5	3	0, 3, $\bar{9}$	8	7	0, 6, 30	8	− 5
0, 0, 22	< 3	4	0, 3, $\overline{11}$	13	12	0, 6, 32	7	− 4
0, 0, 24	6	6	0, 3, $\overline{13}$	16	14	0, 6, 34	< 4	− 4
0, 0, 26	28	27	0, 3, $\overline{15}$	11	12	0, 6, 36	< 4	− 3
0, 0, 28	20	−17	0, 3, $\overline{17}$	8	8	0, 6, 38	4	− 4
0, 0, 30	10	−10	0, 3, $\overline{19}$	< 3	3	0, 6, 40	6	5
0, 0, 32	5	− 7				0, 6, 42	< 4	0
0, 0, 34	< 4	− 5	0, 4, 10	< 3	− 1			
			0, 4, 12	5	− 6	0, 6, $\bar{2}$	43	−41
0, 1, 1	30	30	0, 4, 14	11	−10	0, 6, $\bar{4}$	19	−16
0, 1, 3	24	25	0, 4, 16	12	−11	0, 6, $\bar{6}$	14	−12
0, 1, 5	15	15	0, 4, 18	10	−10	0, 6, $\bar{8}$	13	−11
0, 1, 7	6	5	0, 4, 20	7	− 8	0, 6, $\overline{10}$	9	− 9
0, 1, 9	< 3	− 3	0, 4, 22	< 3	− 5	0, 6, $\overline{12}$	6	− 6
						0, 6, $\overline{14}$	17	−23
0, 1, $\bar{1}$	29	29	0, 4, $\bar{8}$	< 3	2	0, 6, $\overline{16}$	< 4	− 4
0, 1, $\bar{3}$	21	21	0, 4, $\overline{10}$	6	6			
0, 1, $\bar{5}$	11	12	0, 4, $\overline{12}$	7	8	0, 6, $\overline{22}$	< 4	4
0, 1, $\bar{7}$	4	2	0, 4, $\overline{14}$	7	8	0, 6, $\overline{24}$	5	6
0, 1, $\bar{9}$	< 3	− 4	0, 4, $\overline{16}$	7	7	0, 6, $\overline{26}$	13	15
			0, 4, $\overline{18}$	4	4	0, 6, $\overline{28}$	16	−16
0, 2, 8	< 3	− 2	0, 4, $\overline{20}$	< 3	1	0, 6, $\overline{30}$	< 4	− 4
0, 2, 10	6	− 5						
0, 2, 12	9	− 7	0, 5, 1	12	13	0, 7, 1	4	3
0, 2, 14	9	− 7	0, 5, 3	12	13	0, 7, 3	< 3	1
0, 2, 16	6	− 6	0, 5, 5	9	10			
0, 2, 18	4	− 4	0, 5, 7	< 3	6	0, 7, 17	< 4	0
0, 2, 20	< 3	− 1				0, 7, 19	5	2
			0, 5, $\bar{1}$	11	11	0, 7, 21	4	2
0, 2, $\bar{8}$	< 3	0	0, 5, $\bar{3}$	4	6	0, 7, 23	< 4	2
0, 2, $\overline{10}$	6	3	0, 5, $\bar{5}$	< 3	2			
0, 2, $\overline{12}$	9	7	0, 5, $\bar{7}$	4	− 2	0, 7, $\bar{1}$	4	3
0, 2, $\overline{14}$	9	7	0, 5, $\bar{9}$	6	− 4	0, 7, $\bar{3}$	5	3
0, 2, $\overline{16}$	6	6	0, 5, $\overline{11}$	6	− 4	0, 7, $\bar{5}$	4	2
0, 2, $\overline{18}$	< 3	4	0, 5, $\overline{13}$	3	− 3	0, 7, $\bar{7}$	4	2
			0, 5, $\overline{15}$	3	− 2	0, 7, $\bar{9}$	3	2
0, 3, 1	11	−12	0, 5, $\overline{17}$	< 3	− 1	0, 7, $\overline{11}$	4	2
0, 3, 3	6	− 7				0, 7, $\overline{13}$	5	3
0, 3, 5	4	− 2	0, 6, 0	157	157	0, 7, $\overline{15}$	5	3
0, 3, 7	< 3	− 1	0, 6, 2	28	27	0, 7, $\overline{17}$	< 4	2
0, 3, 9	4	− 2	0, 6, 4	9	7			
0, 3, 11	6	− 6	0, 6, 6	3	− 5	0, 8, 10	< 3	− 2
0, 3, 13	13	−10	0, 6, 8	11	−14	0, 8, 12	3	− 5

Table 2. Continued

h k l	$\frac{1}{4} F_o$	$\frac{1}{4} F_c$	*h k l*	$\frac{1}{4} F_o$	$\frac{1}{4} F_c$	*h k l*	$\frac{1}{4} F_o$	$\frac{1}{4} F_c$
0, 8, 14	6	− 8	0, 10, 20	5	− 6	0, 12, $\bar{2}$	32	−37
0, 8, 16	7	− 9	0, 10, 22	4	− 4	0, 12, $\bar{4}$	8	− 9
0, 8, 18	8	− 9	0, 10, 24	$<$ 4	− 1	0, 12, $\bar{6}$	4	− 2
0, 8, 20	7	− 7				0, 12, $\bar{8}$	$<$ 4	1
0, 8, 22	$<$ 4	− 4	0, 10, $\bar{8}$	$<$ 4	1	0, 12, $\overline{10}$	$<$ 4	2
			0, 10, $\overline{10}$	5	4	0, 12, $\overline{12}$	$<$ 4	− 1
0, 8, $\bar{6}$	$<$ 3	3	0, 10, $\overline{12}$	6	6	0, 12, $\overline{14}$	13	−17
0, 8, $\bar{8}$	6	8	0, 10, $\overline{14}$	$<$ 4	5	0, 12, $\overline{16}$	$<$ 4	2
0, 8, $\overline{10}$	10	11						
0, 8, $\overline{12}$	12	14	0, 11, 1	10	−12	0, 12, $\overline{26}$	$<$ 5	8
0, 8, $\overline{14}$	12	12	0, 11, 3	11	−11	0, 12, $\overline{28}$	6	−11
0, 8, $\overline{16}$	7	9	0, 11, 5	10	− 9	0, 12, $\overline{30}$	$<$ 5	1
0, 8, $\overline{18}$	$<$ 4	6	0, 11, 7	5	− 6			
			0, 11, 9	$<$ 4	− 3	0, 13, 1	5	− 6
0, 9, 1	3	− 2				0, 13, 3	5	− 8
0, 9, 3	$<$ 3	4	0, 11, $\bar{1}$	9	−10	0, 13, 5	5	− 8
0, 9, 5	6	8	0, 11, $\bar{3}$	6	− 6	0, 13, 7	4	− 1
0, 9, 7	9	9	0, 11, $\bar{5}$	$<$ 4	− 3	0, 13, 9	$<$ 4	2
0, 9, 9	6	6						
0, 9, 11	5	0	0, 12, 0	27	35	0, 13, $\bar{1}$	4	− 3
0, 9, 13	3	− 6	0, 12, 2	$<$ 4	0	0, 13, $\bar{3}$	$<$ 4	1
0, 9, 15	8	−11	0, 12, 4	5	− 8			
0, 9, 17	13	−13	0, 12, 6	7	−10	0, 18, 0	10	10
0, 9, 19	10	−12	0, 12, 8	8	−10	0, 18, 2	$<$ 5	3
0, 9, 21	8	− 9	0, 12, 10	8	− 9			
0, 9, 23	$<$ 4	− 5	0, 12, 12	36	−35	0, 18, 10	$<$ 6	2
			0, 12, 14	12	11	0, 18, 12	20	−24
0, 9, $\bar{5}$	$<$ 3	− 2	0, 12, 16	8	5	0, 18, 14	$<$ 6	4
0, 9, $\bar{7}$	3	3	0, 12, 18	4	3			
0, 9, $\bar{9}$	8	9	0, 12, 20	$<$ 4	1	0, 18, $\bar{2}$	13	−17
0, 9, $\overline{11}$	13	13	0, 12, 22	$<$ 4	− 1	0, 18, $\bar{4}$	$<$ 5	− 1
0, 9, $\overline{13}$	11	13	0, 12, 24	$<$ 4	− 4			
0, 9, $\overline{15}$	7	11	0, 12, 26	15	18	0, 18, $\overline{12}$	$<$ 6	− 1
0, 9, $\overline{17}$	$<$ 4	7	0, 12, 28	$<$ 5	1	0, 18, $\overline{14}$	10	−12
						0, 18, $\overline{16}$	$<$ 6	5
0, 10, 14	$<$ 4	− 4	0, 12, 36	$<$ 5	− 1			
0, 10, 16	5	− 7	0, 12, 38	5	− 5			
0, 10, 18	4	− 7	0, 12, 40	$<$ 5	5			

for all observed (0*kl*) reflexions and $R_1 = 0.16$ for observed (0*kl*) reflexions with $k \neq 6n$.

The 66 vectors between the oxygen atoms in six adjacent carboxylic groups calculated from the final coordinates are marked in the Patterson projection with $F^2(0kl)$ and $k \neq 6n$ in Fig. 1.

DISCUSSION OF THE RESULTS

The hydrocarbon chains of the A-form of lauric acid are arranged in the triclinic packing first found by Müller and Lonsdale[6] in a low-temperature form of a paraffin. In this packing all chain-planes are parallel. Form A′ of acids with an odd number of carbon atoms [13, 14] has the same hydrocarbon chain packing.

The dimers of the A-form of lauric acid are, however, entirely differently arranged, as compared with the A′-form. From the chain-packing point of view the structure of the A-form of lauric acid is a sixfold superstructure (Fig. 4). The carboxylic groups and the methyl groups are situated together in the same layers in the crystal in groups of six units (Fig. 4) giving rise to equal binding forces in every such layer (hydrogen bonds and van der Waals bonds). This is not the case with the other crystal forms of normal fatty acids where the carboxylic groups and the methyl groups, respectively, are situated in alternate layers. The binding forces are then much weaker in the methyl group layers (van der Waals bonds) than in the carboxylic group layers (hydrogen bonds). These different molecular arrangements affect the macrocrystalline shape as well as the cleavage properties. As was stated earlier normal fatty acids usually crystallize in thin plates, which can easily be split up into thinner plates, but the A-form of lauric acid grows in parallelepiped-shaped crystals, which do not split up in the same regular way as the crystals of the other polymorphic forms. The absence of twinning is also in accordance with the molecular arrangement.

The carboxylic groups fit so well into the chain-packing that none of the carbon atoms need be moved from its position in the subcell to allow hydrogen bonding between two carboxylic groups.

The increment of long spacing for this crystal form of acids with an even number of carbon atoms is 2.36 Å according to Stenhagen and the author [4]. Thus the angle of tilt will be between 69° and 65° if the distance between alternate carbon atoms is between 2.521 Å, given by Vand, Morley and Lomer [8], and 2.610 Å, given by Morley and Vand [15].

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