one cycle is required even when the changes in coordinates are within their permitted range of exploration. The method does, however, converge rapidly with both centrosymmetric and non-centrosymmetric projections. In non-orthogonal projections there will be some interaction between the two positional parameters. This should not be serious provided the interaxial angle is not too different from 90°. The method has not yet been applied to such a projection so that the actual effect cannot be assessed.

The structures so far refined have not involved large variations in the individual temperature factors but in all the cases where the new method has been used the greater part of the refinement of the temperature factor refinement has been completed in a single cycle, provided the overall temperature factor and the scaling factor were correct. It might be expected that the new method would deal more easily with large variations than the existing least-squares methods, which tend to overestimate the reductions and underestimate the increases in temperature factors and necessarily need more than one cycle. Provided the coordinate refinement is well advanced there should be no problem of missing the 'hole'.

There is no reason why the methods could not be extended to deal with three-dimensional data and anisotropic temperature coefficients except that the existing methods may well be adequate.

It is considered that the methods will be most useful in two-dimensional work where there is a great deal of overlap which makes it very difficult to get the structure into the right 'hole' to start with.

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The Crystal and Molecular Structure of Lauric Acid (Form A_1)

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Form A_1 of lauric acid, $C_{12}H_{24}O_2$, is triclinic, with $a = 7{\cdot}45$, $b = 5{\cdot}40$, $c = 17{\cdot}47$ Å; $\alpha = 96°\ 53'$, $\beta = 113°\ 8'$, and $\gamma = 81°\ 7'$. The space group is $P\bar{1}$. The crystal is built of lauric acid dimers, which are packed together with the planes of all hydrocarbon chains parallel to each other (triclinic sub-cell), and with the carboxyl groups of one dimer adjacent to methyl groups of neighbouring dimers. The angle of tilt is 67° 20′.

Introduction

The polymorphism of the normal fatty acids is well known and the structures of most of the crystal forms have been reviewed by von Sydow (1956*a*). Form C (or α) which is obtained when lauric acid is crystallized from the melt or from ethyl alcohol solution at room temperature was described by Vand, Morley & Lomer (1951). Lomer (1955) described the slow, spontaneous transformation, in the solid state, of form C to the form A-super (or γ) and attempted to determine the unit cell dimensions of this latter form from powder photographs. Von Sydow (1956*b*) showed that Lomer's cell dimensions for the form

A-super were not accurate and that the cell was triclinic and not monoclinic as suggested by him. In the same paper von Sydow determined the crystal structure of the A-super form and described it in terms of a centred triclinic cell containing twelve molecules. He also mentioned the existence of another form (form A) which was recognized from its powder photograph as being similar to the form A-super, but probably having only two molecules per unit cell. More recently Lomer & Spanswick (1961) reported the unit cell dimensions of another form of lauric acid and it is the structure of this form which is described in the present paper. Because it, too, is very closely related to the A-super form it is now named form A_1.

Experimental

A small quantity of lauric acid, already in the A, A_1 or A-super form, was dissolved in diethyl ether and the solution was allowed to evaporate slowly to dryness at room temperature. The resulting material consisted of a tangle of fibres together with a few platelets. Powder photographs showed that the fibres consisted, at least partly, of the A-super form. Three of the platelets were selected for single-crystal examination and these proved to be in the A_1 form. Rotation and Weissenberg photographs were taken with the crystal rotating successively about [100] and [010]. The unit cell was found to be triclinic with

$$a=7{\cdot}45\pm0{\cdot}02,\ b=5{\cdot}40\pm0{\cdot}02,\ c=17{\cdot}47\pm0{\cdot}04\ \text{Å},$$
$$\alpha=96^\circ\,53',\ \beta=113^\circ\,8',\ \gamma=81^\circ\,7';$$

the long spacing ($=1/c^*$) was 16·02 Å and the calculated density was 1·04 g.cm^{-3} with two molecules of $C_{12}H_{24}O_2$ per unit cell.

The intensities of the ($h0l$) and ($0kl$) reflexions were estimated visually by the multiple film technique. The usual Lorentz and polarization factors were used in the calculation of the observed structure factors, which were subsequently brought to the absolute scale by comparison with calculated values.

Determination of the structure

In nearly all the structures of saturated fatty acid crystals that have been determined the molecules

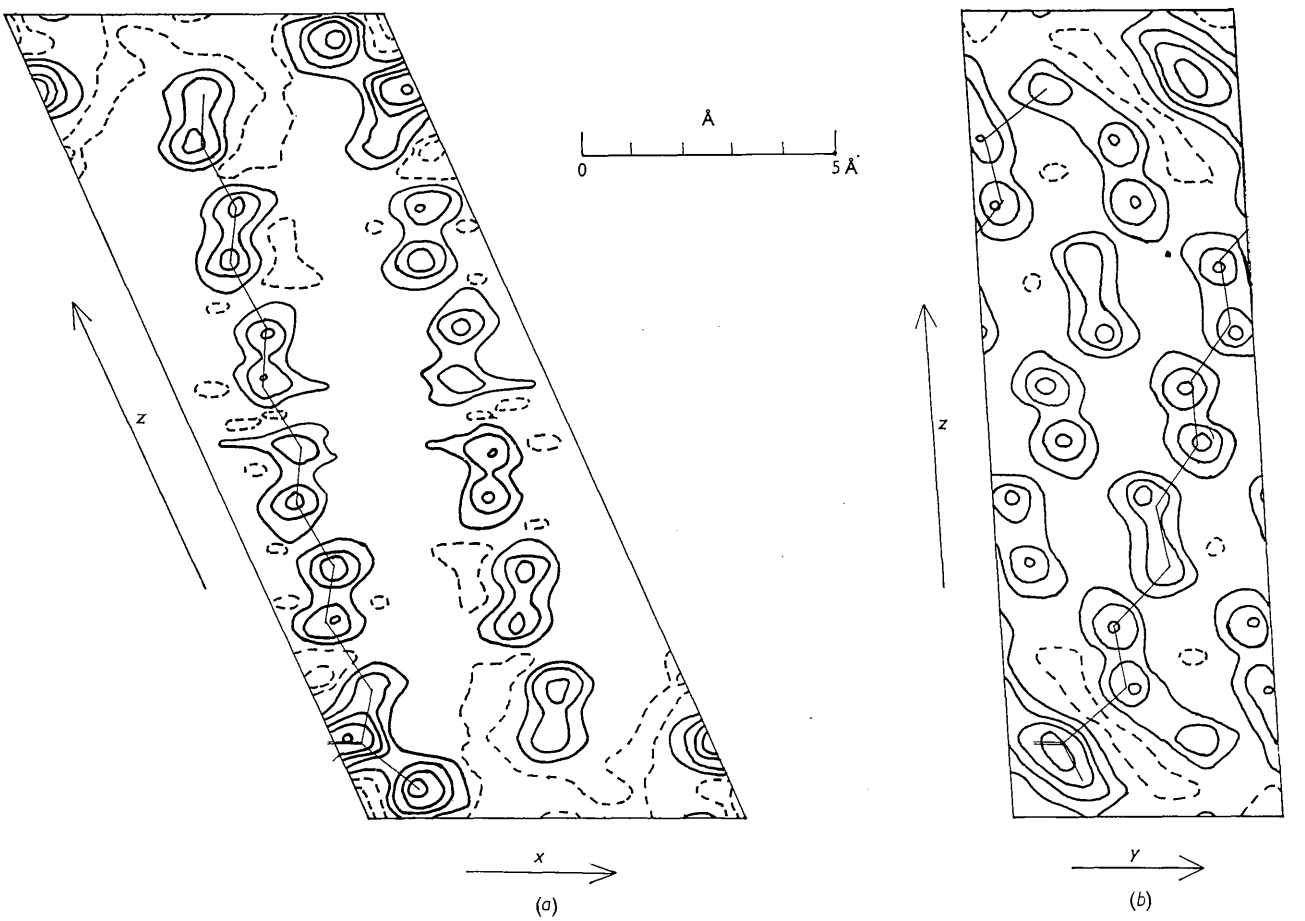

Fig. 1. Projections of electron density: (*a*) Along [010]. (*b*) Along [100]. Contours at intervals of 2 e.Å^{-2} with zero and negative contours broken.

are dimerized, by formation of two hydrogen bonds between the oxygen atoms of the carboxyl groups, and the dimers are centrosymmetrical. An example of this dimerization is shown in Fig. 2. It was assumed that such dimers existed in the A_1 crystal structure and, since there were only two molecules per unit cell, it was assumed that the crystal structure was also centrosymmetrical, the origin of the unit cell being chosen to coincide with the centre of symmetry of the dimers.

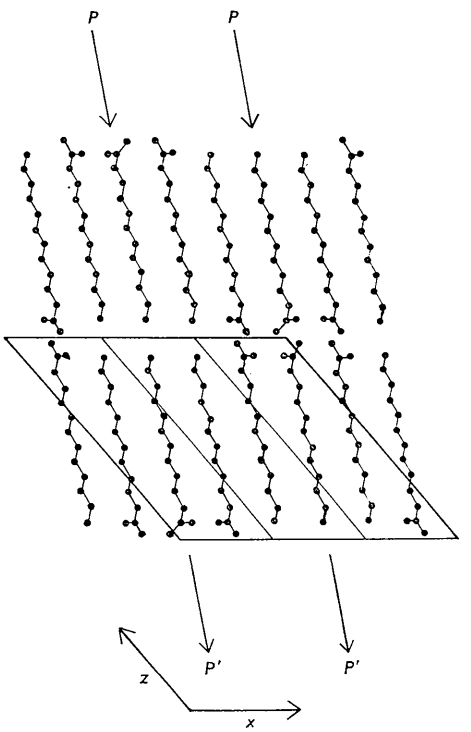

Fig. 2. The structure of the A-super phase, with one unit cell indicated. The three smaller cells are those of the A_1 phase. It is the 'alternative cells' (see text) that are shown. Shifts of molecules along the lines PP′ produce the A_1 structure.

The [010] projection was solved first. The $20\bar{1}$ reflexion was very intense and thus gave the approximate direction of the chain axes, and a consideration of a few other strong reflexions allowed the positions of the carbon atoms to be determined. The hydrocarbon chains were all parallel to each other, and as shown in Fig. 1(*a*), were separated from each other by exactly one half of the *a* cell dimension. It thus followed that the carbon atoms (and most of the hydrogen atoms) could make no contribution to the structure factors of *h*0*l* reflexions with *h* odd, and that the appreciable observed intensity of the 10*l* and 30*l* reflexions was due chiefly to scattering from the oxygen atoms. Consideration of the magnitude of these latter intensities showed that the carboxyl groups necessarily lay at opposite ends of adjacent hydrocarbon chains, and since only two atoms of the asymmetric unit were involved, it was not difficult to place them so that good agreement was obtained between the observed and calculated structure factors for these reflexions. Precisely the same reasoning was used to obtain the trial structure for the [100] projection, the strong $02\bar{2}$ reflexion being used to give the approximate direction of the chain axes. Electron density maps were calculated using the signs of the structure factors determined from the trial structure, and the coordinates of the atoms determined from these maps were further refined by the least-squares method; McWeeny's (1951) scattering factor data were used and the calculations were done on the Manchester University 'Mercury' computer with Curtis's (1959) program. This program can refine the scale factor on F_o, and the anisotropic temperature parameters simultaneously with the atomic coordinates, but in this investigation only isotropic temperature parameters were used because of the relatively small number of reflexions that were observed. It was soon apparent that the hydrogen atoms, which had been neglected completely, were contributing an appreciable fraction to some of the observed structure factors. This contribution was calculated by assuming that the hydrogen atoms were in tetrahedral positions round the carbon atoms with bond lengths of 1·03 Å, and was subtracted from the observed structure factors. The calculated value of the structure factor for the $20\bar{1}$ reflexion was persistently too great; it was assumed that this was due to extinction and this reflexion was omitted from the final cycles of refinement. The isotropic temperature factors for all atoms were the same within experimental error and so the same average value ($B=8\pi^2u_s^2=3{\cdot}6$) was assigned to all atoms in the final calculation. The final values of the reliability index ($R=\Sigma||F_o|-|F_o||/\Sigma|F_c|$ for all observed reflexions except $20\bar{1}$) were 0·138 for the *h*0*l* reflexions and 0·141 for the 0*kl* reflexions. These low values of R justify the assumption that the structure is centrosymmetrical. The fractional coordinates of the carbon and oxygen atoms are given in Table 1; the standard deviations of these coordinates correspond to ±0·08 Å

Table 1. *Coordinates of the atoms*

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1)	0·0727	0·2067	0·0928
C(2)	0·1597	0·4509	0·1598
C(3)	0·1256	0·4174	0·2429
C(4)	0·2138	0·6293	0·3138
C(5)	0·1802	0·5974	0·3862
C(6)	0·2664	0·7433	0·4625
C(7)	0·2364	0·7443	0·5373
C(8)	0·3199	0·9135	0·6093
C(9)	0·3029	0·8857	0·6905
C(10)	0·3834	0·0958	0·7617
C(11)	0·3619	0·0592	0·8385
C(12)	0·4320	0·2804	0·8981
O(1)	0·1661	0·2665	0·0381
O(2)	0·9866	0·0841	0·0927

Table 2. *Observed and calculated structure factors*

h k l	Fo	Fc	h k l	Fo	Fc	h k l	Fo	Fc	h k l	Fo	Fc	h k l	Fo	Fc	h k l	Fo	Fc
0 0 1	--	12	2 0 0	28	-30	-3 0 6	9	-8	5 0 8	*6	1	0 1 20	*7	2	0 3 0	*6	2
0 0 2	--	3	2 0 1	15	-14	-3 0 7	*5	-3	5 0 9	*6	2				0 3 1	*6	-4
0 0 3	8	-6	2 0 2	11	-13	-3 0 8	*5	0	5 0 10	*6	0	0 -1 1	12	11	0 3 2	*6	0
0 0 4	14	-15	2 0 3	16	-14	-3 0 9	5	5	5 0 11	*6	1	0 -1 2	13	12	0 3 3	*6	-1
0 0 5	19	-19	2 0 4	16	-16	-3 0 10	8	7	5 0 12	*6	2	0 -1 3	11	9	0 3 4	*7	-1
0 0 6	21	-15	2 0 5	13	-12	-3 0 11	8	7				0 -1 4	5	6	0 3 5	*7	3
0 0 7	*5	-4	2 0 6	24	-22	-3 0 12	6	6	-5 0 1	*6	5	0 -1 5	*4	6	0 3 6	*7	10
0 0 8	*5	0	2 0 7	5	-5	-3 0 13	*6	4	-5 0 2	*6	-3	0 -1 6	*4	1	0 3 7	*8	9
0 0 9	*5	1	2 0 8	*4	-2	-3 0 14	*7	1	-5 0 3	*6	-6	0 -1 7	*5	3	0 3 8	*8	5
0 0 10	*5	2	2 0 9	4	4	-3 0 15	*7	2	-5 0 4	*6	-6	0 -1 8	*5	4	0 3 9	*8	6
0 0 11	*5	2	2 0 10	*4	5	-3 0 16	*7	1	-5 0 5	*6	-6	0 -1 9	*5	4	0 3 10	*8	1
0 0 12	*5	2	2 0 11	*4	7	-3 0 17	*6	2	-5 0 6	*6	-4	0 -1 10	*6	7	0 3 11	*8	-2
0 0 13	22	17	2 0 12	7	11	-3 0 18	*6	0	-5 0 7	*6	-2	0 -1 11	*6	4	0 3 12	*8	-4
0 0 14	23	-17	2 0 13	10	-13	-3 0 19	*6	-2	-5 0 8	*6	-1	0 -1 12	*7	4	0 3 13	*8	-3
0 0 15	7	-9	2 0 14	*6	-2	-3 0 20	*6	0	-5 0 9	*6	-4	0 -1 13	*7	2	0 3 14	*8	-3
0 0 16	*5	-6	2 0 15	*7	0	-3 0 21	*6	0	-5 0 10	*6	-2	0 -1 14	*8	0	0 3 15	*7	0
0 0 17	*5	-3	2 0 16	*7	1	-3 0 22	*5	0	-5 0 11	*6	-1	0 -1 15	*8	-1	0 3 16	*7	0
0 0 18	*5	-1	2 0 17	*6	1	-3 0 23	*5	0	-5 0 12	*6	-2	0 -1 16	*8	-3	0 3 17	*7	0
0 0 19	*5	2	2 0 18	*6	2	-3 0 24	*4	0	-5 0 13	*6	-1	0 -1 17	*7	-1	0 3 18	*7	0
0 0 20	*5	2	2 0 19	*6	0				-5 0 14	*6	-2	0 -1 18	*7	-2			
0 0 21	*5	1				4 0 0	5	-4	-5 0 15	*6	-3	0 -1 19	*7	-3	0 -3 1	*6	2
0 0 22	*5	0	-2 0 1	69	104	4 0 1	*5	1				0 -1 20	*7	-1	0 -3 2	*6	5
			-2 0 2	15	13	4 0 2	*5	2	6 0 0	*6	4				0 -3 3	*6	5
1 0 0	16	15	-2 0 3	*3	1	4 0 3	*5	2	6 0 1	*6	4	0 2 0	11	-11	0 -3 4	*7	-1
1 0 1	13	12	-2 0 4	5	-6	4 0 4	*5	1	6 0 2	*6	4	0 2 1	11	-12	0 -3 5	*7	-4
1 0 2	9	8	-2 0 5	13	-13	4 0 5	6	-10	6 0 3	*7	1	0 2 2	17	-17	0 -3 6	*7	-7
1 0 3	*4	-1	-2 0 6	16	-16	4 0 6	*6	5	6 0 4	*7	-9	0 2 3	32	-32	0 -3 7	*8	-9
1 0 4	10	-11	-2 0 7	31	-32	4 0 7	*6	4	6 0 5	*7	8	0 2 4	46	-42	0 -3 8	*8	-7
1 0 5	14	-14	-2 0 8	30	31	4 0 8	*7	5	6 0 6	*7	2	0 2 5	37	34	0 -3 9	*8	-6
1 0 6	17	-16	-2 0 9	17	18	4 0 9	*7	5	6 0 7	*6	1	0 2 6	14	12	0 -3 10	*8	-2
1 0 7	13	-13	-2 0 10	15	13	4 0 10	*6	5	6 0 8	*6	-1	0 2 7	12	9	0 -3 11	*8	0
1 0 8	*6	-7	-2 0 11	8	9	4 0 11	*6	6	6 0 9	*6	-1	0 2 8	13	11	0 -3 12	*8	0
1 0 9	*6	-5	-2 0 12	*6	4	4 0 12	*6	-8	6 0 10	*6	-1	0 2 9	9	7	0 -3 13	*8	2
1 0 10	*6	0	-2 0 13	*6	2							0 2 10	*7	3	0 -3 14	*7	0
1 0 11	*6	4	-2 0 14	29	21	-4 0 1	25	-25	-6 0 1	*6	3	0 2 11	21	-19	0 -3 15	*7	1
1 0 12	*6	1	-2 0 15	8	-11	-4 0 2	24	26	-6 0 2	7	-10	0 2 12	8	9	0 -3 16	*7	1
1 0 13	*6	0	-2 0 16	7	-6	-4 0 3	*5	0	-6 0 3	*6	8	0 2 13	*8	2	0 -3 17	*7	0
1 0 14	*7	-1	-2 0 17	*6	-5	-4 0 4	7	-9	-6 0 4	*6	3	0 2 14	*8	2	0 -3 18	*7	1
1 0 15	*7	-1	-2 0 18	*6	-3	-4 0 5	10	-11	-6 0 5	*6	1	0 2 15	*7	1			
1 0 16	*7	-2	-2 0 19	*6	-2	-4 0 6	10	-11	-6 0 6	*6	2	0 2 16	*7	-1	0 4 0	*8	0
1 0 17	*7	-3	-2 0 20	*6	-1	-4 0 7	11	-10	-6 0 7	*6	2	0 2 17	*7	0	0 4 1	*8	8
1 0 18	*6	0	-2 0 21	*5	5	-4 0 8	29	-31	-6 0 8	*6	3	0 2 18	7	5	0 4 2	23	18
1 0 19	*6	0	-2 0 22	*5	1	-4 0 9	13	10	-6 0 9	18	-21	0 2 19	*7	0	0 4 3	16	-11
1 0 20	*6	1	-2 0 23	*5	-1	-4 0 10	12	9	-6 0 10	*6	3	0 2 20	*7	0	0 4 4	*8	0
						-4 0 11	*6	6	-6 0 11	*7	2				0 4 5	*8	-2
-1 0 1	17	21	3 0 0	*5	-1	-4 0 12	*6	4	-6 0 12	*7	0	0 -2 1	5	5	0 4 6	*8	-2
-1 0 2	16	17	3 0 1	*5	2	-4 0 13	*6	1				0 -2 2	38	-38	0 4 7	*8	1
-1 0 3	13	12	3 0 2	*5	-1	-4 0 14	*7	-4	0 1 0	11	10	0 -2 3	18	19	0 4 8	*8	-3
-1 0 4	8	7	3 0 3	*5	-4	-4 0 15	10	13	0 1 1	5	6	0 -2 4	10	7	0 4 9	*8	1
-1 0 5	4	-1	3 0 4	6	-7	-4 0 16	*7	-3	0 1 2	6	-6	0 -2 5	*5	2	0 4 10	*8	-4
-1 0 6	*4	-1	3 0 5	7	-8	-4 0 17	*7	-1	0 1 3	15	-14	0 -2 6	*6	-4	0 4 11	*8	0
-1 0 7	*4	5	3 0 6	*6	-8	-4 0 18	*6	0	0 1 4	22	-20	0 -2 7	*6	-1	0 4 12	*8	-3
-1 0 8	4	3	3 0 7	*6	-1	-4 0 19	*6	0	0 1 5	24	-21	0 -2 8	*6	3	0 4 13	*8	-1
-1 0 9	7	7	3 0 8	*7	-1	-4 0 20	*5	0	0 1 6	18	-16	0 -2 9	18	-28			
-1 0 10	7	4	3 0 9	*7	3	-4 0 21	*5	-2	0 1 7	10	-9	0 -2 10	*7	-2	0 -4 1	*8	0
-1 0 11	6	3	3 0 10	*7	7	-4 0 22	6	7	0 1 8	6	-6	0 -2 11	*7	11	0 -4 2	*8	6
-1 0 12	*6	3	3 0 11	*7	4	-4 0 23	*4	2	0 1 9	*6	2	0 -2 12	*8	9	0 -4 3	*8	0
-1 0 13	*6	0	3 0 12	*7	3	-4 0 24	*3	0	0 1 10	*6	6	0 -2 13	*8	7	0 -4 4	*8	7
-1 0 14	*7	-2	3 0 13	*7	3				0 1 11	*6	2	0 -2 14	*8	7	0 -4 5	*8	0
-1 0 15	*7	-4	3 0 14	*7	2	5 0 0	*6	7	0 1 12	*7	2	0 -2 15	*7	-5	0 -4 6	*8	6
-1 0 16	*7	-3	3 0 15	*7	0	5 0 1	*6	7	0 1 13	*7	1	0 -2 16	*7	8	0 -4 7	*8	-1
-1 0 17	*7	-4				5 0 2	*6	5	0 1 14	*7	-1	0 -2 17	*7	-1	0 -4 8	*8	-1
-1 0 18	*6	-5	-3 0 1	8	-7	5 0 3	*6	2	0 1 15	*8	-3	0 -2 18	*7	-1	0 -4 9	*8	-2
-1 0 19	*6	-1	-3 0 2	8	-9	5 0 4	*7	0	0 1 16	*8	-2	0 -2 19	*7	-1	0 -4 10	*8	-5
-1 0 20	*6	-1	-3 0 3	8	-9	5 0 5	*7	2	0 1 17	*7	1	0 -2 20	*7	0	0 -4 11	8	10
-1 0 21	*5	0	-3 0 4	10	-11	5 0 6	*7	1	0 1 18	*7	1				0 -4 12	*8	-3
-1 0 22	*5	1	-3 0 5	10	-9	5 0 7	*6	-1	0 1 19	*7	2				0 -4 13	*8	-6

in x and z and $\pm 0{\cdot}10$ Å in y. The electron density maps for the two projections are reproduced in Fig. 1, and the calculated and observed structure factors are recorded in Table 2.

Discussion of the results

The dimensions of the molecule of lauric acid determined from the atomic coordinates in Table 1 do not show any surprising features. The average distance between alternate carbon atoms is $2{\cdot}538 \pm 0{\cdot}025$ Å, and the average C–C bond in the chain is $1{\cdot}505 \pm 0{\cdot}025$ Å. The C–OH and C=O distances are respectively $1{\cdot}45 \pm 0{\cdot}08$ Å and $0{\cdot}99 \pm 0{\cdot}08$ Å. The crystal is built of pairs of molecules, dimerized by hydrogen bonds of length $2{\cdot}77 \pm 0{\cdot}08$ Å between oxygen atoms. Although the values of the x coordinates of the carbon atoms suggest that the molecule may be slightly helically deformed, it was found that the carbon atoms in any one molecule were coplanar within the limits of experimental error. The greatest deviation of an atom from the calculated 'best' plane was 0·125 Å and the r.m.s. deviation of all the carbon atoms was 0·066 Å. The perpendicular distance of the origin from the calculated best plane is $0{\cdot}107 \pm 0{\cdot}022$ Å: thus the two chains which constitute a dimer are not quite coplanar in this crystal form. The oxygen atoms are appreciably displaced from the plane of the carbon atoms, O(1) by $-0{\cdot}39 \pm 0{\cdot}06$ Å and O(2) by $0{\cdot}27 \pm 0{\cdot}06$ Å. These displacements may be regarded as resulting from a rotation of the plane of the carboxyl group about the C(2)–C(1) bond of $16 \pm 3°$.

The chains are packed together in accordance with the triclinic subcell described by Vand & Bell (1951).

Table 3. *Dimensions of the triclinic sub-cell*

Compound	a	b	c	α	β	γ
Tri-laurin β-form (Vand & Bell)	4·287 Å	5·40 Å	2·45 Å	74° 45′	108° 2′	117° 24′
n-Pentadecanoic acid, A′ form (von Sydow, 1954)	4·25 Å	5·82 Å	2·61 Å	66°	106°	122°
Lauric acid, A form (von Sydow, 1956)	4·42 Å	5·41 Å	2·63 Å	74°	109°	122°
Lauric acid, A_1 form	4·25 Å	5·41 Å	2·54 Å	74·9°	108·4°	120°

The dimensions of the subcell are given in Table 3 together with the corresponding dimensions in other compounds. Some care must be exercised in comparing these dimensions since other authors quote dimensions determined from the positions of strong spots on photographs of the compound, while in the present work the dimensions have been calculated from the atomic coordinates. Although the Fourier transform of the whole crystal can have large values only where the subcell transform has large values, an X-ray diffraction photograph samples that transform only at the reciprocal-lattice points of the whole crystal. Thus while a strong spot on a photograph must lie near a maximum in the transform of the subcell it does not in general lie *at* that maximum and therefore the dimensions and orientation of the subcell determined directly from diffraction photographs may not be accurate. It is thus dangerous to conclude (von Sydow, 1956*a*) that the distance between alternate carbon atoms is greater in the triclinic packing than in the orthorhombic packing of hydrocarbon chains. In form A_1 of lauric acid this distance is $2·54 \pm 0·02$ Å which is quite normal; the greater value of 2·60 Å found by Vand, Lomer & Lang (1949) in potassium caprate is more probably due to strong binding in the ionic layers of that crystal than to any effect of chain packing.

The A-super form of lauric acid crystallizes in the form of needles, whereas most other forms of the fatty acids and paraffins crystallize as plates. It has been suggested that this is due to its unusual structure, in which carboxyl and methyl groups appear in the same layers in the crystal, but the few crystals of the A_1 form which were available to the author, and which have the same unusual arrangement of carboxyl and methyl groups, crystallized as plates. The well developed surfaces of these plates are (001) and presumably contain both methyl and carboxyl groups. These crystals might therefore have some unusual surface properties. The relationship between the structures of the forms A_1 and A-super is most clearly demonstrated by choosing unit cells different from those so far reported. The A-super lattice may be referred to an uncentred cell of dimensions

$$a=22·32,\ b'=5·41,\ c=21·68 \text{ Å};$$
$$\alpha'=98·3°,\ \beta'=132·1°,\ \gamma'=82·2°$$

and the form A_1 lattice to a cell of dimensions

$$a''=7·46,\ b''=5·40,\ c''=21·52 \text{ Å};$$
$$\alpha''=98·8°,\ \beta''=131·8°,\ \gamma''=81·0°.$$

Within the limits of experimental error these cells are the same except that a' is just three times as great as a''. The structure of A-super relative to these cells is shown in Fig. 2, which also indicates how this structure is related to that of the A_1 form. The A-super structure results from that of the A_1 form by a translation of every third dimer (counting along the x axis) combined with some rotation of the carboxyl groups in those dimers. The translation is parallel to the dimer axis and of magnitude one half the 'length' of a dimer.

The movements of the molecules which occur during the transition from form A_1 to form C are more complex. Translations of half a dimer length accompanied by a 90° rotation of the whole dimer, applied to every second dimer (counting along the x axis), produce a structure very similar to that of the C form but with an angle of tilt of 67° instead of 55°. Additional small systematic translations of the dimers parallel to their axes could correct the angle of tilt. It would be interesting to know more of the mechanism by which this transformation is effected in the solid state.

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