# The Crystal Structure of the A-super Form of Lauric Acid

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The crystal structure of the A-super form of lauric acid has been determined. The structural parameters were refined by the block-diagonal least-squares method, and the final $R$ value was 0.094. Two types of molecular conformations of a lauric acid exist in the crystal; one is the ordinary type, as seen in the C-form or the $A_1$-form of the lauric acid, while the other is that rotating the carboxyl group about the Cl–C2 bond. This unusual structure was explained by the oxygen-oxygen distance of the adjacent molecule.

Even-numbered fatty acids are known by powder X-ray diffractions to exist in three crystalline forms, named A, B, and C.[1] In the case of lauric acid, the crystal structure of the C-form has been determined by Vand, Morley and Lomer.[2] This has an orthorhombic subcell of the hydrocarbon chain. Another crystal form, belonging to A, was studied by von Sydow[3] in only one projection. He showed that it has the triclinic subcell of the hydrocarbon chains. He named it the A-super form, because it could be regarded as a sixfold superstructure from the chain packing. Later, another crystal form, $A_1$, belonging to the A form, has been completely determined by Lomer.[4]

Three-dimensional results are required in order to discuss thoroughly the relations among polymorphic forms. We could obtain a single crystal of the A-super form of a sufficient size and studied its structure from a three-dimensional approach.

## Experimental

Lauric acid was purified according to the procedure described by Tsuchiya.[5] At first it crystallized in the C-form in an isooctane solution. After it had stood in the solution for about two weeks at room temperature, the C-form was gradually transformed into the A-super form with colorless, triclinic needle-like crystals elongated along the a-axis. The crystal data are listed in Table 1. The intensity data were collected by means of a Rigaku-Denki four-circle diffractometer by using graphite monochromated Cu $K\alpha$ radiation. Reflections with $2\theta$ values up to 60° were collected. The total number of observed reflections was 679.

TABLE 1. CRYSTAL DATA

| | |
|---|---|
| Lauric acid | A-super form |
| Molecular weight | 200.3 |
| Melting point | 44.0 °C |
| The unit cell was chosen as that of von Sydow. | |
| Triclinic; $A\bar{1}$ | |
| $Z=12$ | |
| $a=5.415(2)$Å | $\alpha=69.82°(4)$ |
| $b=25.964(11)$Å | $\beta=113.14°(4)$ |
| $c=35.183(13)$Å | $\gamma=121.15°(3)$ |
| $U=3829.9$ Å$^3$ | |
| $D_x=1.04$ g/cm$^3$ | |

## Structure Determination

The y and z co-ordinates of the atoms were assumed to be those given by von Sydow, and the approximate x co-ordinates were obtained by taking into account three-dimensional Patterson maps and the packing of the molecules.

The hydrogen atoms were placed at the calculated positions assuming the C–H length of 1.10 Å and a tetrahedral arrangement about the carbon atom. The hydrogen atoms of the end were assumed to be at the *gauche* position. The hydrogen atom of the carboxyl group was neglected. Refinements were carried out by the block-diagonal least-squares method using HBLS program (Ashida),[6] with anisotropic temperature factors for non-hydrogen atoms. The parameters of the hydrogen atoms were not refined. The $R$ value was reduced to 0.094.

The final atomic parameters are listed in Table 2.* The y and z co-ordinates did not differ significantly from those given by von Sydow.[3]

## Results and Discussion

The bond lengths, bond angles, and internal rotation angles are listed in Table 3. The arrangement of the molecules in the crystal is shown in Fig. 1. The chains are packed in a triclinic subcell with dimensions of $a=4.33$ Å, $b=5.42$ Å, $c=2.52$ Å, $\alpha=75.9°$, $\beta=108.9°$. $\gamma=122.1°$. Both carboxyl and methyl end groups appear in the same molecular layer.

An ORTEP (Johnson)[7] drawing of the three crystallographically independent molecules (I, II, and III) is shown in Fig. 2. The conformation of Molecule (III) is roughly equivalent to that of (II). There are two types of molecular conformations of lauric acid in an asymmetric unit; one type is (I), and the other, (II) and (III).

The carbon atoms in each molecule are nearly coplanar, as is shown in Table 4. The dihedral angle between the plane of the carboxyl group and that of the carbon chain is 83° in Molecule (I), 10° in (II) and 25° in (III) respectively. The plane of the carboxyl group in Molecule (I) is almost perpendicular to the carbon chain, while in (II) and (III) the two planes are roughly parallel, as is found in the $A_1$ form of lauric acid. The conformation as found in Molecule (I) was also reported in the structure of *dl*-2-hydroxytetradecanoic acid,[8] which has a large substituent near the carboxyl group.

It is rare for two types of molecular conformation

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* The table of the observed and calculated structure factors has been submitted and is kept by the Office of the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo 101 (Document No 7804).

Table 2(a). Atomic co-ordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$ Å$^2$) for C and O atoms

The temperature factors are of the form:

$$T=\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)].$$

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C1 | 3357 | −100 | 483 | 835 | 45 | 3 | 160 | 23 | 11 |
| C2 | 5870 | −247 | 803 | 590 | 37 | 14 | 184 | −62 | −2 |
| C3 | 6427 | 28 | 1213 | 918 | 12 | 13 | 68 | 25 | −10 |
| C4 | 9072 | −161 | 1540 | 913 | 10 | 13 | 121 | 27 | −2 |
| C5 | 9600 | 72 | 1935 | 63 | 26 | 18 | 1 | −35 | −9 |
| C6 | 12036 | −120 | 2289 | 266 | 29 | 10 | 20 | 36 | −3 |
| C7 | 12930 | 118 | 2699 | 926 | 20 | 4 | 71 | −6 | −12 |
| C8 | 15516 | −62 | 3057 | 879 | 12 | 7 | 56 | 7 | −6 |
| C9 | 16250 | 207 | 3463 | 801 | 22 | 16 | 67 | 65 | 5 |
| C10 | 18566 | −10 | 3801 | 648 | 7 | 18 | 65 | 60 | −1 |
| C11 | 19358 | 257 | 4202 | 488 | 34 | 16 | 77 | −41 | −13 |
| C12 | 21828 | 64 | 4542 | 1058 | 50 | 7 | 119 | −91 | −26 |
| C13 | 1552 | 1552 | 459 | 958 | 6 | 26 | 28 | 92 | 9 |
| C14 | 4129 | 1402 | 814 | 685 | 31 | 15 | 118 | 15 | 4 |
| C15 | 4812 | 1679 | 1208 | 937 | 39 | 9 | 119 | 8 | −4 |
| C16 | 7252 | 1462 | 1554 | 419 | 40 | 13 | 126 | −29 | −15 |
| C17 | 8162 | 1746 | 1958 | 301 | 15 | 21 | −11 | 35 | 2 |
| C18 | 10510 | 1560 | 2293 | 664 | 2 | 8 | 73 | 53 | 7 |
| C19 | 11195 | 1776 | 2696 | 791 | 26 | 9 | 88 | 24 | 3 |
| C20 | 13702 | 1609 | 3058 | 906 | 19 | 12 | 79 | 16 | −2 |
| C21 | 14513 | 1871 | 3468 | 570 | 51 | 20 | 170 | 35 | −4 |
| C22 | 17046 | 1677 | 3800 | 849 | 32 | 25 | 46 | 85 | 1 |
| C23 | 17552 | 1878 | 4196 | 999 | 54 | 21 | 183 | 54 | 4 |
| C24 | 20195 | 1689 | 4548 | 1194 | 26 | 12 | 71 | 0 | −13 |
| C25 | 4368 | −1888 | 507 | 2069 | 10 | 47 | 165 | 280 | 36 |
| C26 | 7028 | −2022 | 827 | 1253 | 17 | 22 | 131 | 112 | 4 |
| C27 | 7765 | −1682 | 1219 | 611 | 25 | 11 | 102 | −3 | −6 |
| C28 | 10512 | −1850 | 1559 | 699 | 15 | 10 | 46 | 12 | −6 |
| C29 | 11336 | −1608 | 1958 | 870 | 28 | 12 | 78 | 45 | 0 |
| C30 | 13751 | −1806 | 2311 | 276 | 25 | 21 | 70 | 23 | −2 |
| C31 | 14743 | −1510 | 2708 | 592 | 28 | 21 | 120 | −11 | −10 |
| C32 | 17094 | −1720 | 3044 | 823 | 25 | 14 | 86 | 48 | −4 |
| C33 | 17994 | −1450 | 3452 | 334 | 27 | 16 | 42 | 36 | −1 |
| C34 | 20300 | −1730 | 3806 | 519 | 27 | 18 | 36 | 39 | −8 |
| C35 | 21090 | −1405 | 4197 | 308 | 16 | 22 | 39 | −4 | −11 |
| C36 | 23593 | −1583 | 4540 | 1175 | 63 | 14 | 206 | 22 | 7 |
| O1 | 3469 | −1546 | 490 | 522 | 15 | 8 | 32 | −55 | −10 |
| O2 | 744 | 1234 | 150 | 1187 | 26 | 22 | 101 | 13 | −19 |
| O3 | 3818 | 382 | 185 | 684 | 39 | 15 | 116 | −24 | 5 |
| O4 | 557 | −443 | 467 | 830 | 69 | 13 | 153 | 35 | 0 |
| O5 | 3530 | −2123 | 174 | 962 | 40 | 11 | 137 | −14 | −1 |
| O6 | 715 | 1849 | 445 | 909 | 47 | 10 | 121 | −40 | −16 |

The average standard deviations are as follows:

$sx=200$, $sy=40$, $sz=30$, $sB_{11}=720$, $sB_{22}=40$, $sB_{33}=20$, $sB_{12}=160$, $sB_{13}=90$, $sB_{23}=20$, ($\times 10^4$).

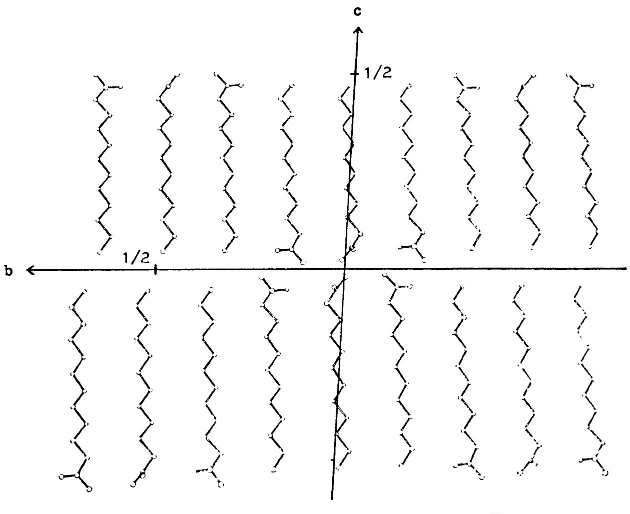
Table 2(b). Atomic co-ordinates ($\times 10^3$) for H atoms

The temperature factors are isotropic. $B=6.0$ Å$^2$

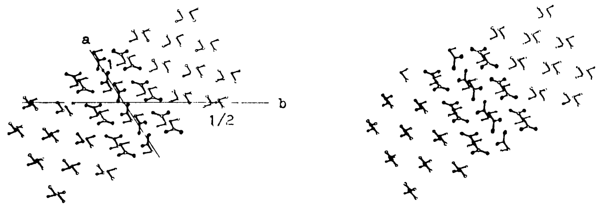
| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H2 | 788 | 2 | 68 | H20 | 1573 | 183 | 295 |
| H'2 | 509 | −74 | 88 | H'20 | 1286 | 111 | 314 |
| H3 | 733 | 53 | 113 | H21 | 1252 | 164 | 359 |
| H'3 | 442 | −24 | 133 | H'21 | 1545 | 237 | 339 |
| H4 | 1110 | 11 | 143 | H22 | 1907 | 193 | 368 |

Table 2(b). (Continued)

| | x | y | z | | x | y | z |
|---|---|---|---|---|---|---|---|
| H'4 | 821 | −66 | 161 | H'22 | 1611 | 117 | 386 |
| H5 | 752 | −17 | 203 | H23 | 1553 | 162 | 430 |
| H'5 | 1053 | 58 | 187 | H'23 | 1842 | 238 | 413 |
| H6 | 1404 | 7 | 218 | H24 | 1942 | 119 | 460 |
| H'6 | 1112 | −62 | 236 | H'24 | 2078 | 182 | 485 |
| H7 | 1094 | −9 | 281 | H''24 | 2223 | 193 | 443 |
| H'7 | 1378 | 62 | 263 | H26 | 893 | −178 | 69 |
| H8 | 1752 | 16 | 295 | H'26 | 625 | −252 | 94 |
| H'8 | 1462 | −56 | 314 | H27 | 582 | −192 | 135 |
| H9 | 1422 | 0 | 357 | H'27 | 864 | −119 | 111 |
| H'9 | 1730 | 71 | 339 | H28 | 968 | −235 | 164 |
| H10 | 1753 | −51 | 388 | H'28 | 1244 | −162 | 143 |
| H'10 | 2060 | 20 | 369 | H29 | 934 | −180 | 207 |
| H11 | 1734 | 4 | 431 | H'29 | 1230 | −110 | 188 |
| H'11 | 2029 | 76 | 412 | H30 | 1571 | −163 | 219 |
| H12 | 2092 | −44 | 461 | H'30 | 1275 | −231 | 239 |
| H'12 | 2250 | 23 | 483 | H31 | 1279 | −169 | 282 |
| H''12 | 2380 | 26 | 443 | H'31 | 1578 | −101 | 262 |
| H14 | 618 | 164 | 70 | H32 | 1905 | −154 | 293 |
| H'14 | 346 | 91 | 91 | H'32 | 1604 | −223 | 312 |
| H15 | 275 | 146 | 131 | H33 | 1600 | −162 | 356 |
| H'15 | 582 | 218 | 113 | H'33 | 1914 | −95 | 338 |
| H16 | 922 | 166 | 143 | H34 | 2234 | −151 | 370 |
| H'16 | 623 | 96 | 163 | H'34 | 1915 | −220 | 389 |
| H17 | 914 | 225 | 188 | H35 | 1910 | −162 | 431 |
| H'17 | 618 | 155 | 208 | H'35 | 2203 | −91 | 411 |
| H18 | 1255 | 177 | 219 | H36 | 2427 | −141 | 482 |
| H'18 | 957 | 105 | 236 | H'36 | 2268 | −209 | 462 |
| H19 | 916 | 157 | 280 | H''36 | 2552 | −140 | 442 |
| H'19 | 1203 | 228 | 262 | | | | |



1) A perspective view along the **b**×(**b**×**ā**) direction drawn by ORTEP.⁷⁾



2) Stereoscopic view along the **b**×(**b**×**c̄**) direction drawn by ORTEP.

Fig. 1. Drawings of the crystal structure.

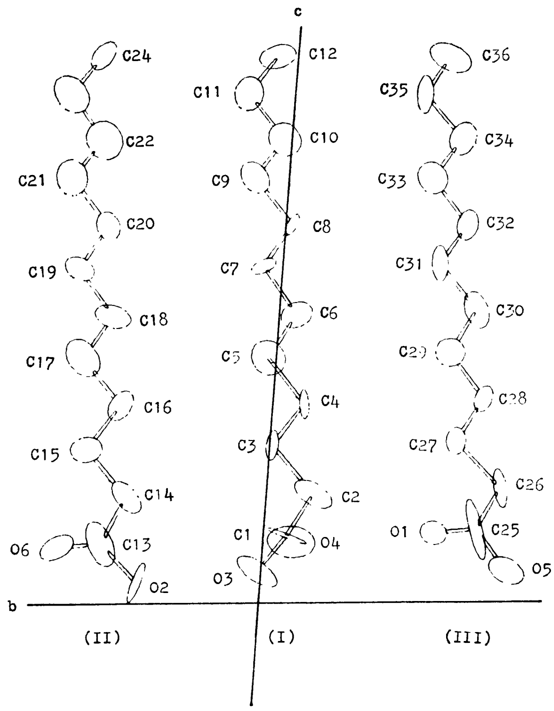


Fig. 2. Three molecules in an asymmetric unit. The atoms are drawn with ellipsoids of thermal vibration of 50% probability.

Table 3. Structural parameter

| | | | | | |
|---|---|---|---|---|---|
| (a) Interatomic distances[a] (Å) | | | | | |
| C1-C2 | 1.52 | C13-C14 | 1.54 | C25-C26 | 1.52 |
| C2-C3 | 1.69 | C14-C15 | 1.61 | C26-C27 | 1.70 |
| C3-C4 | 1.63 | C15-C16 | 1.61 | C27-C28 | 1.65 |
| C4-C5 | 1.58 | C16-C17 | 1.63 | C28-C29 | 1.55 |
| C5-C6 | 1.59 | C17-C18 | 1.53 | C29-C30 | 1.58 |
| C6-C7 | 1.57 | C18-C19 | 1.56 | C30-C31 | 1.60 |
| C7-C8 | 1.63 | C19-C20 | 1.59 | C31-C32 | 1.55 |
| C8-C9 | 1.62 | C20-C21 | 1.62 | C32-C33 | 1.56 |
| C9-C10 | 1.55 | C21-C22 | 1.59 | C33-C34 | 1.61 |
| C10-C11 | 1.58 | C22-C73 | 1.53 | C34-C35 | 1.60 |
| C11-C12 | 1.59 | C23-C24 | 1.66 | C35-C36 | 1.57 |
| O3-C1 | 1.31 | O2-C13 | 1.34 | O5-C25 | 1.32 |
| O4-C1 | 1.29 | O6-C13 | 1.14 | O1-C25 | 1.20 |
| (b) Bond angles[b] (°) | | | | | |
| O3-C1-O4 | 117 | O6-C13-O2 | 123 | O1-C25-O5 | 121 |
| C2-C1-O3 | 121 | C14-C13-O2 | 110 | C26-C25-O5 | 108 |
| C3-C2-C1 | 101 | C15-C14-C13 | 107 | C27-C26-C25 | 101 |
| C4-C3-C2 | 98 | C16-C15-C14 | 101 | C28-C27-C26 | 99 |
| C5-C4-C3 | 100 | C17-C16-C15 | 105 | C29-C28-C27 | 106 |
| C6-C5-C4 | 104 | C18-C17-C16 | 106 | C30-C29-C28 | 108 |
| C7-C6-C5 | 109 | C19-C18-C17 | 106 | C31-C30-C29 | 107 |
| C8-C7-C6 | 110 | C20-C19-C18 | 109 | C32-C31-C30 | 106 |
| C9-C8-C7 | 106 | C21-C20-C19 | 109 | C33-C32-C31 | 106 |
| C10-C9-C8 | 104 | C22-C21-C20 | 104 | C34-C33-C32 | 106 |
| C11-C10-C9 | 105 | C23-C22-C21 | 103 | C35-C34-C33 | 102 |
| C12-C11-C10 | 105 | C24-C23-C22 | 104 | C36-C35-C34 | 104 |
| (c) Internal rotation angles (°) | | | | | |
| C3-C2-C1-O3 | 99 | C15-C14-C13-O2 | −178 | C27-C26-C25-O5 | 179 |
| C4-C3-C2-C1 | 178 | C16-C15-C14-C13 | 175 | C28-C27-C26-C25 | 178 |
| C5-C4-C3-C2 | −179 | C17-C16-C15-C14 | 178 | C29-C28-C27-C26 | −177 |
| C6-C5-C4-C3 | 177 | C18-C17-C16-C15 | −180 | C30-C29-C28-C27 | 175 |
| C7-C6-C5-C4 | 177 | C19-C18-C17-C16 | −176 | C31-C30-C29-C28 | 177 |
| C8-C7-C6-C5 | −178 | C20-C19-C18-C17 | −179 | C32-C31-C30-C29 | 179 |
| C9-C8-C7-C6 | 180 | C21-C20-C19-C18 | 178 | C33-C32-C31-C30 | −178 |
| C10-C9-C8-C7 | 177 | C22-C21-C20-C19 | −179 | C34-C33-C32-C31 | 177 |
| C11-C10-C9-C8 | 180 | C23-C22-C21-C20 | −176 | C35-C34-C33-C32 | −180 |
| C12-C11-C10-C9 | −178 | C24-C23-C22-C21 | −179 | C36-C35-C34-C33 | −175 |

a) The average of the values of the standard deviation is 0.14 Å. b) The average of the standard deviation is 7.

Table 4. Atomic displacements from the least-squares planes of hydrocarbon chains

The equation expressed in the orthogonal Cartesian system:

Z//**c**, X//**a***, Y//**c**×**a*** in Å unit.

C1-C12 $0.362X+0.870Y-0.336Z=0.210$

C13-C24 $0.365X+0.867Y-0.340Z=1.756$

C25-C36 $0.380X+0.843Y-0.380Z=-1.390$

| | | | | | |
|---|---|---|---|---|---|
| C1 | −0.06 | C13 | −0.09 | C25 | −0.18 |
| C2 | 0.02 | C14 | 0.00 | C26 | −0.03 |
| C3 | 0.01 | C15 | 0.03 | C27 | 0.01 |
| C4 | 0.06 | C16 | −0.02 | C28 | 0.12 |
| C5 | 0.01 | C17 | 0.07 | C29 | 0.07 |
| C6 | −0.03 | C18 | 0.04 | C30 | 0.03 |
| C7 | 0.00 | C19 | −0.01 | C31 | 0.09 |
| C8 | 0.00 | C20 | 0.00 | C32 | 0.05 |
| C9 | 0.03 | C21 | 0.03 | C33 | 0.04 |
| C10 | −0.04 | C22 | 0.04 | C34 | −0.10 |
| C11 | 0.00 | C23 | −0.06 | C35 | −0.07 |
| C12 | −0.01 | C24 | −0.04 | C36 | −0.05 |
| O3 | 1.00 | O2 | −0.27 | O5 | −0.21 |
| O4 | −1.16 | O6 | 0.11 | O1 | −0.02 |

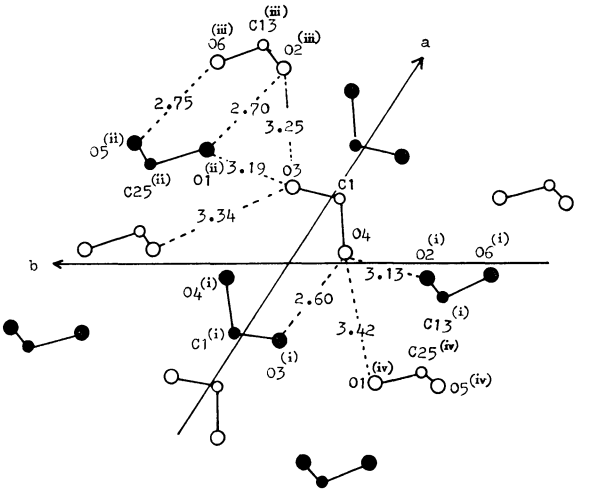


Fig. 3. A projection along the c*-axis.
○: Upper layer atoms, ●: lower layer atoms.
Symmetry code (i) −x, −y, −z, (ii) −x+1, −y, −z, (iii) x+1, y, z, (iv) x−1, y, z.

to appear in a crystal of the simple fatty acid. The larger thermal parameters of the atoms in the carboxyl group, listed in Table 2, might be due to this unusual arrangement of molecules.

The arrangement of the end groups is shown in Fig. 3. As is commonly found in fatty acids, the molecules are bound together to form dimers through hydrogen bonds between the carboxyl groups. The hydrogen-bond lengths are 2.60 Å between $O3\text{–}O4^{(i)}$, 2.70 Å between $O2^{(iii)}\text{–}O1^{(ii)}$, and 2.75 Å between $O6^{(iii)}\text{–}O5^{(ii)}$.

If Molecule (I) took the same conformation as (II), the $O4\text{–}O2^{(i)}$ distance would be 2.34 Å, too close to form a hydrogen bond between the molecules. This short contact is relieved by rotating the carboxyl group about the C1–C2 bond, resulting in a particular conformation of Molecule (I).

In the C-form of lauric acid, carboxyl groups appear in the same layer, but in the A-form, both the A-super form and the $A_1$-form, they do not. In the $A_1$-form the carboxyl group is adjacent to the methyl group of the neighboring molecule, and the short contact mentioned above is relieved.

The structure in which the carboxyl groups of the same conformation appear in the same layer, as is seen in the C-form, might be unfavorable in the A-form of lauric acid.

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