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The Crystal Structure of Methyl Stearate

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Methyl stearate, $C_{17}H_{35}COOCH_3$, is monoclinic with

$$a=5\cdot61,\ b=7\cdot33,\ c=106\cdot6\ \text{Å};\ \beta=116^\circ\ 47'.$$

The cell contains eight molecules and the space group is $A2/a$. The carbon chains are arranged in the orthorhombic packing $0\perp$ (101). The molecules form double sheets (dimerization) like the acids. The structure is related to the structure of the *B*-form of stearic acid apart from the *A*-centering which permits better molecular interaction.

Introduction

As a continuation of investigations on the molecular packing of normal fatty acids (von Sydow, 1954*a*, *b*; 1955*a*, *b*, *c*; 1956*a*, *b*) and branched-chain fatty acids (Abrahamsson, 1956, 1958, 1959*a*, *b*, *c*, *d*, *e*, and von Sydow, 1958) at this University, we have started investigations on the structural behaviour of esters of normal fatty acids. This paper is the first contribution.

The structural information on the methyl esters of the normal fatty acids in the literature is the result of long-spacing investigations on crystalline powders of the esters prepared and treated in different ways, carried out by Malkin (1931), and also of thermal investigations by King & Garner (1936) and Francis & Piper (1939).

Malkin found that methyl esters of even-numbered fatty acids have only one crystal form—a dimeric form with the chains tilted 63° relative to the base plane, i.e. the plane containing the end groups of the molecules. Methyl esters of the odd-numbered acids, however, have two forms—one similar to that of the even numbered acids but with a slightly higher angle of tilt, $67\frac{1}{2}^\circ$, and one monomeric form with the chains tilted to 75°. For comparison, the angle of tilt for the various crystal forms of normal fatty acids is close to 60° (von Sydow, 1956*b*). This is in agreement with the thermal data given by King & Garner (1936) with the exception of the monomeric form which has the thermal properties of a structure with vertical, oscillating hydrocarbon chains. King & Garner (1936) also point out that there are some peculiarities near the melting points of methyl palmitate and methyl eicosanate. This is confirmed in the work by Francis & Piper (1939) where they state that methyl esters of even-numbered fatty acids also have two crystal forms with different melting points only a few tenths of a degree apart, the formation being dependent on the rate of crystallization. This will be discussed later in this paper.

Preparation of crystals

Very pure methyl stearate (methyl octadecanoate) with m.p. 39·1–39·4 °C. was crystallized from glacial acetic acid, ethanol, acetone, carbon tetrachloride, chloroform and carbon disulfide at room temperature (20 °C.) and −14 °C. The low-temperature crystallization from carbon disulfide gave large single crystals (m.p. 39·1–39·4 °C.) in the form of rhombic plates with the acute angle 74°. The crystals are optically biaxial and positive. Twinning on the (001) plane was frequently observed under the microscope. In order to avoid absorption errors, crystals for the X-ray measurements were cut from the plates, thereby obtaining small cross-sections.

X-ray data

Rotation and Weissenberg photographs were taken at 22 °C. using Cu $K\alpha$ radiation. The following data were obtained:

Molecular formula: $C_{19}H_{38}O_2$.
Molecular weight: 298·49.
Unit cell: monoclinic.

$a=5\cdot61\pm0\cdot02$, $b=7\cdot33\pm0\cdot02$, $c=106\cdot6\pm0\cdot6$ Å;
$\beta=116^\circ\ 47'\pm20'$.
$d(001)=95\cdot2\pm0\cdot3$ Å.

Eight molecules per unit cell.
Number of electrons: 1344.
Density calculated: $1\cdot013\pm0\cdot007$ g.cm.$^{-3}$.
Density measured: 1·007 g.cm.$^{-3}$.
Absent reflexions: hkl, when $k+l$ odd, $h0l$, when h or l odd, and $0k0$, when k odd.
Space group: C_s^4–Aa or C_{2h}^6-A2/a.

From structural considerations to be explained later, the space group $A2/a$ was chosen. This is consistent with the absence of piezoelectric effect. (Thanks are due to Mr T. Lundström for help with the measurements.) The statistical method of Howells, Philips &

Rogers (1950) applied to the $0kl$-zone also indicated this space group, but this evidence is not conclusive, since the distribution of atoms in this structure is probably not sufficiently random.

The intensities of the $h0l$ and $0kl$-reflexions ($\sin^2\theta < 0{\cdot}9$) were estimated visually by two observers using the multiple-film technique with scale. They were corrected for the polarization and Lorentz factors. No correction for absorption was applied. Two sets of relative observed structure amplitudes were computed and were later put on an absolute scale by comparison with calculated structure factors.

Structure determination

From the first the authors were struck by the similarity of this structure to the structure of the *B*-form of stearic acid (von Sydow, 1955*a*). The latter has the space group $P2_1/a$ with

$$a=5{\cdot}591,\ b=7{\cdot}404,\ c=49{\cdot}38\ \text{Å};\ \beta=117°\ 22'$$

and four molecules per unit cell. The only principal difference seems to be that the structure of methyl stearate is an *A*-centered version of the structure of the *B*-form of stearic acid and consequently the unit cell is about twice as long. This leads inevitably to the space group choice $A2/a$ instead of Aa.

Both these structures have an orthorhombic subcell with every second chain-plane approximately perpendicular to the others (Bunn, 1939; Vainshtein & Pinsker, 1950). They should both be classified as $0\perp(101)$ following a suggestion by Vand (1954) complemented by von Sydow (1958). The subcell dimensions derived for methyl stearate are

$$a_s=5{\cdot}07,\ b_s=7{\cdot}33,\ c_s=2{\cdot}53\ \text{Å};\ \beta_s=89°.$$

The structural information given by von Sydow (1955*a*) was applied to the space group of methyl stearate, and cycles of structure-factor and electron-density calculation were performed for the *yz*-projection. Atom scattering factors were taken from McWeeny (1951) and from Vand *et al.* (1957). In the later stages the structure factors were computed on the BESK-computer of the Swedish Board for Computing Machinery. The electron-density maps were prepared with Beevers–Lipson strips (3°) and a Fourier machine constructed by Hägg & Laurent (1946). There was some uncertainty whether the translation of one half in the *y*-direction, constituting the difference between the space groups $P2_1/a$ and $A2/a$,

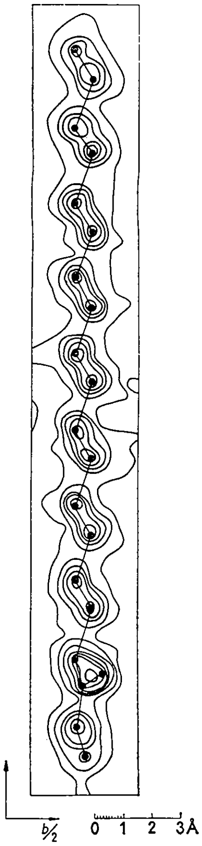

Fig. 1. Electron-density projection of methyl stearate along the *a*-axis. Contours given at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

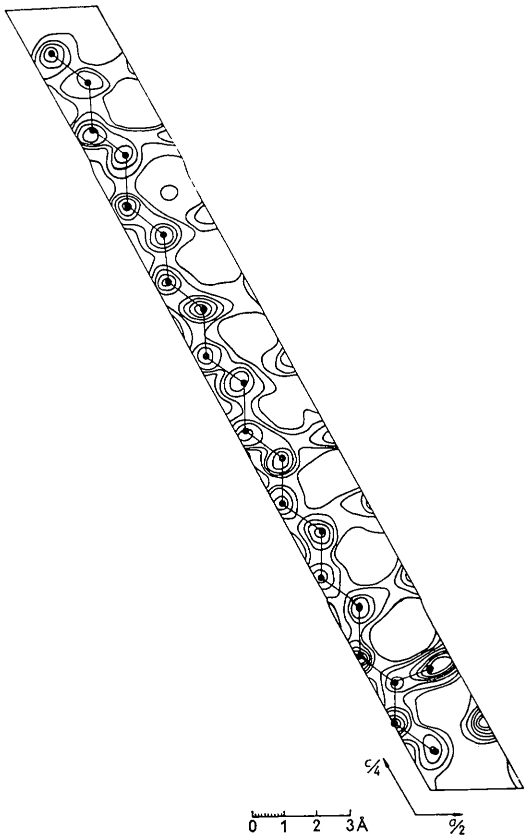

Fig. 2. Electron-density projection of methyl stearate along the *b*-axis. Contours given at intervals of 1 e.Å^{-2} starting with 2 e.Å^{-2}.

Table 1. *Coordinates of the atoms in methyl stearate*

	x/a	y/b	z/c
C_{18}	0·121	0·207	0·2355
C_{17}	0·229	0·298	0·2258
C_{16}	0·106	0·201	0·2110
C_{15}	0·209	0·297	0·2019
C_{14}	0·096	0·201	0·1869
C_{13}	0·197	0·295	0·1778
C_{12}	0·082	0·207	0·1629
C_{11}	0·188	0·291	0·1538
C_{10}	0·066	0·209	0·1391
C_9	0·188	0·288	0·1302
C_8	0·057	0·211	0·1150
C_7	0·172	0·290	0·1062
C_6	0·042	0·211	0·0913
C_5	0·170	0·291	0·0821
C_4	0·031	0·209	0·0674
C_3	0·156	0·290	0·0584
C_2	0·019	0·207	0·0433
C_1	0·133	0·247	0·0342
C_{me}	0·141	0·258	0·0119
O_1	0·001	0·221	0·0213
O_2	0·357	0·338	0·0383

appeared in the ester-group planes or in the end-group planes of the hydrocarbon chains, but the authors felt that the first alternative was preferable since the chemical differences between stearic acid and methyl stearate appear there; this was found to be correct and will also be discussed later.

The x-coordinates for the xz-synthesis were originally found by studying the reflexions $20\bar{2}$, 200, 202. Then followed several cycles of structure-factor calculations and electron-density maps for the xz-projection. The x-, y- and z-coordinates have been refined by several difference syntheses along the a- and b-axes. In the xz-projection, a temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$ with $B=5{\cdot}8$, was applied. The final value of the reliability index R was 0·18, omitting non-observed reflexions. In the yz-projection an R-value of 0·20 was obtained with the same B-value. An anisotropic temperature factor was then tried,

$$\exp\left[-(B+C\sin^2(\varphi-\psi)\sin^2\theta/\lambda^2)\right],$$

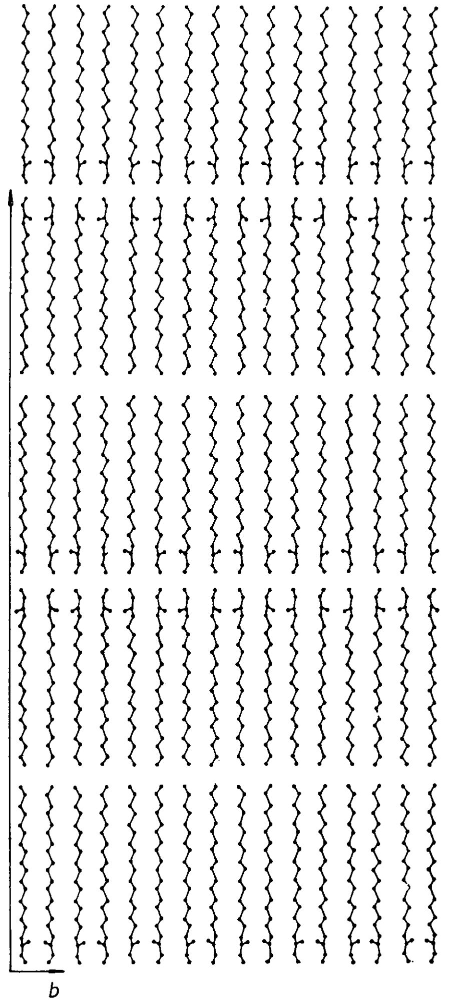

Fig. 3. Schematic view of methyl stearate seen along the a-axis.

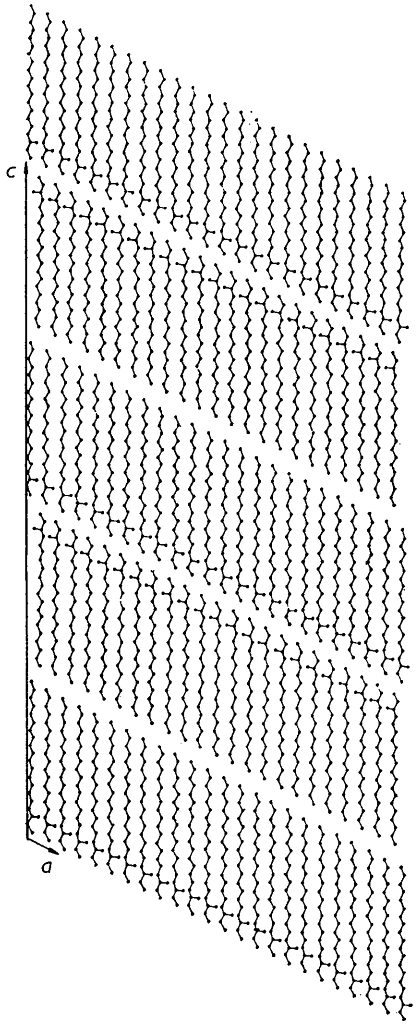

Fig. 4. Schematic view of methyl stearate seen along the b-axis.

where φ is the angle between the reciprocal vector ($0kl$) and the c^*-axis and ψ the angle between the direction of the maximum scattering factor and the c^*-axis, which, in this projection, is 0 (Cochran, 1951). With $B=4\cdot75$ and $C=2\cdot4$ an R-value of 0·18 was obtained. In the last stages of refinement, the hydrogen atoms were included in the structure factor calculations. They were given coordinates derived from the data by Vainshtein & Pinsker (1950) but with a slightly shorter C–H distance (1·05 Å) which is in better agreement with the difference maps. The coordinates are given in Table 1 and observed and calculated structure factors in Tables 2 and 3. The electron-density maps are shown in Figs. 1 and 2.

The mean value of the carbon–carbon bond lengths is 1·54 Å and of the angles between these bonds is 111°.

Discussion

All hydrocarbon chains have their planes in {110}. This affects the macrocrystalline shape and the crystals are always bounded by {110} planes and, of course, by (001) giving rhombic plates. The acute angle calculated from the cell dimensions is 74° 45′ as compared with the observed 74° for methyl stearate and for the *B*-form of stearic acid.

In Figs. 3 and 4 many unit cells of the methyl stearate are shown projected along the shortest axes.

Table 2. *Observed and calculated structure factors* ($0kl$)

$0kl$	F_o	F_c
000	1344	1294
002	—	35
004	—	−54
006	—	11
008	63	−81
0,0,10	24	−22
0,0,12	101	−105
0,0,14	37	−36
0,0,16	83	−102
0,0,18	14	−20
0,0,20	53	−48
0,0,22	21	15
0,0,24	23	−35
0,0,26	34	36
0,0,28	21	−18
0,0,30	26	38
0,0,32	46	−43
0,0,34	6	−20
0,0,36	74	−74
0,0,38	8	33
0,0,40	162	−174
0,0,42	127	−123
0,0,44	100	93
0,0,46	33	21
0,0,48	51	30
0,0,50	40	32
0,0,52	37	34
0,0,54	27	27
0,0,56	12	11
0,0,58	7	1
0,0,60	11	−12
0,0,62	16	−17
0,0,64	22	−23
0,0,66	19	−22
0,0,68	17	−18
0,0,70	< 8	−12
0,0,80	< 9	−11
0,0,82	51	−52
0,0,84	34	37
0,0,86	48	48
0,0,88	< 9	4
0,0,90	15	15
0,0,92	< 9	0
011	9	−14
013	6	−11
015	< 3	2
017	3	7
019	10	17
0,1,11	12	16
0,1,13	17	21
0,1,15	9	10
0,1,17	10	9
0,1,19	8	−12
0,1,21	5	−9
0,1,23	23	29
0,1,25	11	−16
0,1,27	26	−30
0,1,29	< 5	−3
0,1,31	18	−17
0,1,33	12	17
0,1,35	21	−19
0,1,37	18	25
0,1,39	53	−48
0,1,41	25	29
0,1,43	107	106
0,1,45	14	−18
0,1,47	< 6	7
0,1,49	16	−20
0,1,51	< 7	−7
0,1,53	13	−15
0,1,55	< 7	−3
0,1,81	< 9	4
0,1,83	18	−21
0,1,85	9	−4
0,1,87	9	9
0,1,89	< 9	4
020	—	−639
022	—	−55
024	—	3
026	16	−22
028	36	20
0,2,10	11	7
0,2,12	49	48
0,2,14	23	22
0,2,16	47	55
0,2,18	15	20
0,2,20	35	43
0,2,22	< 5	5
0,2,24	20	29
0,2,26	15	−7
0,2,28	16	21
0,2,30	16	11
0,2,32	23	29
0,2,34	12	−8
0,2,36	40	38
0,2,38	10	−9
0,2,40	95	93
0,2,42	79	68
0,2,44	67	−54
0,2,46	19	−13
0,2,48	28	−19
0,2,50	23	−19
0,2,52	21	−16
0,2,54	16	−12
0,2,56	8	4
0,2,58	< 8	0
0,2,62	< 8	6
0,2,64	13	10
0,2,66	10	11
0,2,68	10	9
0,2,70	< 9	8
0,2,80	< 9	−5
0,2,82	36	35
0,2,84	21	−25
0,2,86	35	−36
0,2,88	< 9	−7
0,2,90	11	−14
0,2,92	< 9	−3
035	6	−5
037	11	−9
039	13	−15
0,3,11	19	−14
0,3,13	19	−17
0,3,15	13	−7
0,3,17	7	−5
0,3,19	7	14
0,3,21	12	12
0,3,23	32	27
0,3,25	20	21
0,3,27	34	29
0,3,29	8	8
0,3,31	22	21
0,3,33	11	−13
0,3,35	19	22
0,3,37	18	−28
0,3,39	60	46
0,3,41	31	−11
0,3,43	120	125
0,3,45	15	13
0,3,47	< 8	−14
0,3,49	18	20
0,3,51	< 8	7
0,3,53	14	17
0,3,55	< 8	4
0,3,81	< 9	−8
0,3,83	31	33
0,3,85	13	7
0,3,87	17	16
0,3,89	< 9	−6
0,3,91	9	13
0,3,93	< 8	−6
040	143	147
042	< 7	18
044	21	−6
046	< 7	11
048	14	10
0,4,10	< 7	12
0,4,18	< 7	−5
0,4,20	10	−17
0,4,22	< 7	−16
0,4,24	10	−23
0,4,26	8	−15
0,4,28	8	17
0,4,30	< 8	−5
0,4,32	< 8	−11
0,4,34	13	6
0,4,36	< 8	−3
0,4,38	9	11
0,4,40	31	−22
0,4,42	27	−18
0,4,44	20	17
0,4,46	< 8	2
0,4,80	< 9	−2
0,4,82	15	−12
0,4,84	< 9	10
0,4,86	14	17
0,4,88	< 8	8
0,5,33	< 9	7
0,5,35	15	15
0,5,37	< 9	8
0,5,39	46	−36
0,5,41	15	12
0,5,43	70	71
0,5,45	13	−8
0,5,47	< 9	12
0,5,79	< 8	−4
0,5,81	9	8
0,5,83	22	−22
0,5,85	8	−6
0,5,87	12	10
0,5,89	< 7	4
060	25	−12
062	< 9	−11
0,7,37	< 8	2
0,7,39	24	18
0,7,41	< 8	−4
0,7,43	35	−27
0,7,45	< 8	4

Table 3. *Observed and calculated structure factors* (*h*0*l*)

*h*0*l*	F_o	F_c
000	1344	1312
002	—	50
004	—	−42
006	—	10
008	—	−90
0,0,10	—	−36
0,0,12	—	−118
0,0,14	37	−46
0,0,16	97	−107
0,0,18	14	−20
0,0,20	52	−53
0,0,22	22	23
0,0,24	22	−25
0,0,26	36	48
0,0,28	20	−16
0,0,30	24	37
0,0,32	42	−43
0,0,34	6	6
0,0,36	75	−76
0,0,38	6	6
0,0,40	156	−166
0,0,42	120	−115
0,0,44	98	86
0,0,46	28	22
0,0,48	45	40
0,0,50	39	32
0,0,52	35	32
0,0,54	24	25
0,0,56	9	9
0,0,58	< 7	0
0,0,60	10	−12
0,0,62	14	−16
0,0,64	20	−21
0,0,66	16	−20
0,0,68	6	−16
0,0,70	8	−12
0,0,72	< 8	− 2
0,0,80	< 9	11
0,0,82	45	−44
0,0,84	27	30
0,0,86	41	38
0,0,88	< 9	4
0,0,90	13	12
0,0,92	< 9	0
200	20	17
202	103	−108
204	39	44
206	< 6	−21
208	32	37
2,0,10	9	−17
2,0,12	6	8
2,0,14	29	−43
2,0,16	18	−22
2,0,18	39	−59
2,0,20	24	−33
2,0,22	37	−59
2,0,24	13	−21
2,0,26	20	−34
2,0,28	< 6	2
2,0,30	9	−16
2,0,32	9	14
2,0,34	13	−11
2,0,36	< 8	2
2,0,38	39	−32
2,0,40	57	−72
2,0,42	84	92
2,0,44	34	30
2,0,46	< 9	9
2,0,48	11	8
2,0,50	< 9	6
2,0,52	9	9
2,0,54	< 9	8
2,0,56	9	13
2,0,58	< 9	10
$\bar{2}00$	20	17
$\bar{2}02$	286	292
$\bar{2}04$	17	−41
$\bar{2}06$	28	23
$\bar{2}08$	27	−29
$\bar{2}$,0,10	< 6	− 6
$\bar{2}$,0,12	9	− 5
$\bar{2}$,0,14	17	11
$\bar{2}$,0,16	18	17
$\bar{2}$,0,18	32	26
$\bar{2}$,0,20	27	32
$\bar{2}$,0,22	26	16
$\bar{2}$,0,24	11	− 4
$\bar{2}$,0,26	< 6	−20
$\bar{2}$,0,28	18	−28
$\bar{2}$,0,30	26	−32
$\bar{2}$,0,32	35	−44
$\bar{2}$,0,34	26	−23
$\bar{2}$,0,36	32	−24
$\bar{2}$,0,38	< 6	13
$\bar{2}$,0,40	41	7
$\bar{2}$,0,42	187	159
$\bar{2}$,0,44	135	127
$\bar{2}$,0,46	< 6	−10
$\bar{2}$,0,48	52	42
$\bar{2}$,0,50	18	−10
$\bar{2}$,0,52	11	8
$\bar{2}$,0,54	39	−38
$\bar{2}$,0,56	16	−14
$\bar{2}$,0,58	46	−50
$\bar{2}$,0,60	23	−28
$\bar{2}$,0,62	42	−44
$\bar{2}$,0,64	14	−11
$\bar{2}$,0,66	26	−20
$\bar{2}$,0,68	< 6	5
$\bar{2}$,0,70	9	− 5
$\bar{2}$,0,72	9	11
$\bar{2}$,0,74	9	− 6
$\bar{2}$,0,76	11	5
$\bar{2}$,0,78	13	−14
$\bar{2}$,0,80	9	−10
$\bar{2}$,0,82	30	−29
$\bar{2}$,0,84	143	−127
$\bar{2}$,0,86	44	42
$\bar{2}$,0,88	32	32
$\bar{2}$,0,90	21	18
$\bar{2}$,0,92	29	23
$\bar{2}$,0,94	20	17
$\bar{2}$,0,96	25	20
$\bar{2}$,0,98	13	12
$\bar{2}$,0,100	17	13
400	24	−19
402	< 9	3
4,0,36	< 9	2
4,0,38	13	−20
4,0,40	37	43
4,0,42	17	25
4,0,44	11	2
4,0,46	< 6	8
$\bar{4}00$	24	−19
$\bar{4}02$	< 9	− 3
$\bar{4}04$	11	12
$\bar{4}06$	< 9	− 6
$\bar{4}08$	11	6
$\bar{4}$,0,10	< 9	9
$\bar{4}$,0,22	< 9	−17
$\bar{4}$,0,24	14	−26
$\bar{4}$,0,26	14	−22
$\bar{4}$,0,28	17	−19
$\bar{4}$,0,30	< 9	− 6
$\bar{4}$,0,36	< 9	11
$\bar{4}$,0,38	9	10
$\bar{4}$,0,40	13	− 2
$\bar{4}$,0,42	22	−32
$\bar{4}$,0,44	118	122
$\bar{4}$,0,46	35	43
$\bar{4}$,0,48	13	11
$\bar{4}$,0,50	9	8
$\bar{4}$,0,52	9	− 8
$\bar{4}$,0,54	< 9	2
$\bar{4}$,0,56	13	−10
$\bar{4}$,0,58	< 9	9
$\bar{4}$,0,60	9	− 4
$\bar{4}$,0,62	9	12
$\bar{4}$,0,64	< 9	− 3
$\bar{4}$,0,66	9	6
$\bar{4}$,0,68	< 9	−10
$\bar{4}$,0,70	< 9	0
$\bar{4}$,0,72	14	−13
$\bar{4}$,0,74	< 9	− 4
$\bar{4}$,0,76	19	−18
$\bar{4}$,0,78	< 9	1
$\bar{4}$,0,80	20	−18
$\bar{4}$,0,82	27	18
$\bar{4}$,0,84	23	−18
$\bar{4}$,0,86	51	−51
$\bar{4}$,0,88	17	25
$\bar{4}$,0,90	< 9	7
$\bar{4}$,0,92	17	12
$\bar{4}$,0,94	11	7
$\bar{4}$,0,96	9	5
$\bar{4}$,0,98	< 9	1
$\bar{6}00$	< 6	6
$\bar{6}02$	26	20
$\bar{6}04$	< 6	2
$\bar{6}$,0,44	< 9	−22
$\bar{6}$,0,46	42	33
$\bar{6}$,0,48	< 9	4

As can be seen, it is a typical sheet structure reminiscent of many other long chain structures, i.e. most crystal forms of the normal fatty acids (von Sydow, 1956*b*). Although there is no possibility of hydrogen bonding in methyl stearate as in normal fatty acids the molecules form double sheets (dimerization) like the acids, but unlike the ethyl esters and higher esters which form single sheets (Malkin, 1931).

A detail of the ester group region is shown in Fig. 5(*a*). The closest distance between the ester carbon atoms is 3·3 Å, which is unusually short, but considering the polar forces between oxygen and carbon atoms, is quite conceivable. These forces are probably the cause of the dimerization.

The *A*-centering of the structure has given possibilities for better molecular interaction compared with a non-centered structure as shown in Fig. 5(*b*). The non-centered structure similar to the *B*-structure of stearic acid would either have too short a carbon–carbon distance (2·3 Å) or have a larger total volume with a normal carbon–carbon distance, i.e. a lower density, and be less stable.

X-ray powder photographs of the crystalline solids obtained from different solvents and melt (see above) were found to be identical, except for the cases with rapid crystallization from melt and chloroform, where they were found to be similar to the others but with a simpler diagram. The melting point of this crystal form was found to be 38·6–39·0 °C. (the β-form according to Francis & Piper, 1939) as compared with 39·1–39·4 °C. found for the crystals used in the structure determination (the γ-form according to Francis & Piper, 1939). The two crystal forms obviously have very similar molecular arrangements.

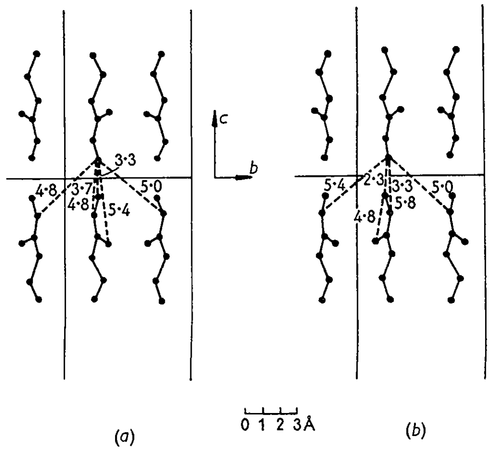

Fig. 5. The ester group regions of (*a*) the actual centered structure and (*b*) the corresponding non-centered structure.

This can be correlated with the centered and non-centered structures discussed above, i.e. the low melting form (β according to Francis & Piper, 1939) can be assumed to be similar to the *B*-form of normal fatty acids, which owing to the strong hydrogen bonds, can only have one of the two mentioned kinds of structure—the non-centered one.

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