arrangement consists of chains of coordination octahedra and tetrahedra running along the c axes with a similar configuration. Calcium ions in fairfieldite and sodium ions in kröhnkite exhibit the same role: they occupy the interstices left vacant by the chains connecting them to form a three-dimensional framework and are each surrounded by six oxygen atoms and one water molecule. From Fig. 2, where the structure of fairfieldite and a part of the atomic arrangement occurring in kröhnkite are schematically projected along the b^* axis, the resemblance of the chain motif is evident and explains the good agreement between the lattice constants in the two minerals. In fact the c translation vector represents the period in the chain and $a \sin \beta$ the distance between two parallel chains in the ac plane.

The most remarkable difference in the two structures occurs in the reciprocal array of chains in the bc planes: in kröhnkite two parallel chains are shifted one half period along c, as is clear if one considers the presence of the glide plane at $\frac{1}{4} b$. This fact may account for the approximate doubling of the b parameter.

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Crystal Structure of an Orthorhombic Modification of Methyl Stearate

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A new orthorhombic modification of methyl stearate has been found. The cell parameters are $a = 5·61$, $b = 7·35$, $c = 95·15$ Å and the space group is Pnab; the unit-cell contains 8 molecules. The carbon chains are arranged in the orthorhombic packing $O\perp$. The molecules form the same double sheets as have been found in the monoclinic modification. However, chains in neighbouring sheets are inclined with respect to each other.

Introduction

During melting and freezing of methyl stearate, phenomena such as pre-melting and 'after-melting' (Smit, 1946; Simonelli & Higuchi, 1962) occur, which make the interpretation of melting curves and dilatometric measurements difficult. In order to study these phenomena, crystals of methyl stearate (purity > 99·8%) were grown from a CS_2 solution at $-15°C$ to $-12°C$ and from a melt at 37–38°C. Two crystal forms were obtained from CS_2 solution:

(a) a monoclinic form M_1, described by Aleby & von Sydow (1960) with unit-cell parameters $a = 5·61$, $b = 7·33$, $c = 106·6$ Å, $\beta = 116°47'$, $d_{001} = 95·2$ Å;

(b) an orthorhombic form, which will be described in this paper.

The crystals obtained from the melt were of poor quality. A second monoclinic form M_2 was found with the a and b dimensions about the same as those of the monoclinic and orthorhombic modifications from CS_2, but the c dimension was 47·9 Å. Some crystals from the melt appeared to be intergrowths of the orthorhombic form from the CS_2 solution and a twin of the monoclinic form from the melt. The form M_2 was not studied further in this investigation.

Experimental

The unit-cell parameters and space group were determined by taking rotation and Weissenberg photographs calibrated with Al lines using Cu $K\alpha$ radiation:

Methyl stearate   : $C_{19}H_{38}O_2$
Molecular weight: 298·49
Unit cell   : orthorhombic
$a=$ 5·613 ± 0·005 Å
$b=$ 7·354 ± 0·005
$c=$ 95·147 ± 0·004
Eight molecules per unit cell.
Calculated density: 1·010 g.cm^{-3}
Absent reflexions : $hk0$ when k is odd
                    $h0l$ when h is odd
                    $0kl$ when $k+1$ is odd.
Space group: *Pnab*.

Three-dimensional intensity data were obtained from retigraph diagrams (Ni-filtered Cu-radiation, multiple-film technique). Two series were taken at room temperature, about [100] with levels $h=0, 1...5$, and about [010] with levels $k=0,1,2$. 737 independent reflexions were measured photometrically and corrected for the Lp factor. No absorption correction was applied.

Determination of the structure

The $0kl$ photographs of the orthorhombic form and monoclinic form M_1 showed a striking resemblance,

Table 1. *Final atomic parameters and estimated standard deviations*

(a) Positional parameters ($\times 10^4$)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
C(Me)	261	41	2585	42	111	1
O(1)	8189	25	2198	25	207	1
O(2)	−9674	23	3320	24	383	1
C(1)	8510	31	2557	31	346	1
C(2)	6410	30	2018	36	435	1
C(3)	6687	30	2851	31	583	1
C(4)	4495	32	2093	30	672	1
C(5)	4548	32	2859	30	822	1
C(6)	2594	29	2119	32	915	1
C(7)	2474	30	2889	33	1061	1
C(8)	496	32	2116	28	1155	1
C(9)	586	31	2900	29	1298	1
C(10)	8459	30	2129	30	1391	1
C(11)	8352	31	2902	32	1544	1
C(12)	6444	27	2085	31	1628	1
C(13)	6416	36	2864	33	1782	1
C(14)	4311	30	2088	33	1865	1
C(15)	4356	32	2933	30	2021	1
C(16)	2389	32	2139	29	2103	1
C(17)	2333	35	2904	31	2261	1
C(18)	318	36	2103	37	2345	1
H(1)	4765		2499		386	
H(2)	6327		552		445	
H(3)	6466		4340		575	
H(4)	8345		2468		628	
H(5)	2855		2383		623	
H(6)	4728		609		681	
H(7)	4304		4349		813	
H(8)	6285		2668		868	
H(9)	901		2205		864	
H(10)	2909		633		927	
H(11)	2145		4384		1050	
H(12)	4181		2819		1112	
H(13)	−1215		2290		1108	
H(14)	817		646		1166	
H(15)	1765		4382		1290	
H(16)	−510		2163		1372	
H(17)	9561		2932		1325	
H(18)	8876		658		1403	
H(19)	7950		4398		1535	
H(20)	35		2822		1598	
H(21)	4717		2256		1579	
H(22)	6810		610		1638	
H(23)	6081		4365		1772	
H(24)	8046		2651		1833	
H(25)	2657		2357		1815	
H(26)	4611		609		1873	
H(27)	4066		4373		2013	
H(28)	6029		2638		2070	
H(29)	723		2366		2052	
H(30)	2645		646		2106	
H(31)	2206		4363		2258	
H(32)	3983		2595		2314	

Table 1 (cont.)

(b) Thermal parameters ($\times 10^4$). Temperature factor:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*2U_{12}+klb^*c^*2U_{23}+hla^*c^*2U_{13})\right].$$

|	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{33}	$\sigma(U_{33})$	$2U_{12}$	$\sigma(2U_{12})$	$2U_{23}$	$\sigma(2U_{23})$	$2U_{31}$	$\sigma(2U_{31})$
C(me)	752	153	1986	383	485	119	−218	452	148	348	375	229
O(1)	777	89	1656	198	329	64	−400	261	−202	210	68	136
O(2)	640	83	1148	140	520	72	−214	231	−216	187	38	151
C(1)	473	102	998	262	273	90	2	265	−55	226	−130	164
C(2)	389	105	1201	223	430	101	−308	321	−197	281	188	175
C(3)	479	103	725	166	290	86	181	280	138	230	224	173
C(4)	577	115	554	155	507	104	47	300	−202	245	38	208
C(5)	469	108	487	151	646	118	13	283	−222	252	171	202
C(6)	388	100	693	174	472	104	51	281	76	255	492	173
C(7)	417	111	757	196	541	109	97	313	17	263	−161	188
C(8)	551	108	493	133	418	92	41	304	−346	234	−164	196
C(9)	489	107	525	138	386	96	−196	297	176	218	−78	176
C(10)	439	100	633	154	329	86	−90	285	238	226	228	168
C(11)	545	111	738	176	433	97	2	309	−211	261	350	195
C(12)	312	91	728	167	337	91	53	278	106	232	−24	159
C(13)	830	137	709	183	352	94	−88	337	−354	239	17	209
C(14)	425	109	891	180	318	88	−65	296	−360	239	−85	165
C(15)	631	120	600	156	280	83	8	305	−283	226	260	188
C(16)	619	115	439	136	338	96	−54	287	−291	210	147	173
C(17)	651	122	960	207	152	81	−58	336	−344	246	177	156
C(18)	576	126	1608	280	352	96	−297	405	−56	311	488	181
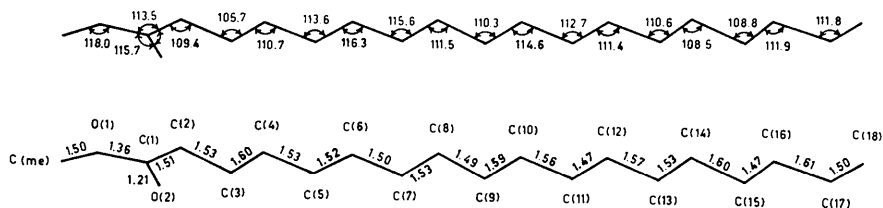
Fig. 1. Intramolecular distances and angles of orthorhombic methyl stearate.
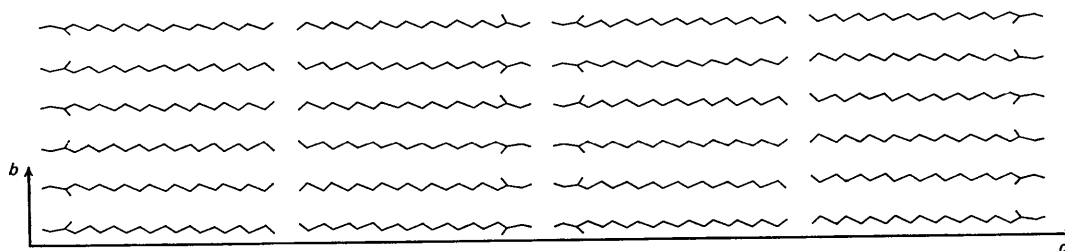
Fig. 2. Projection of a number of methyl stearate molecules along the a axis.
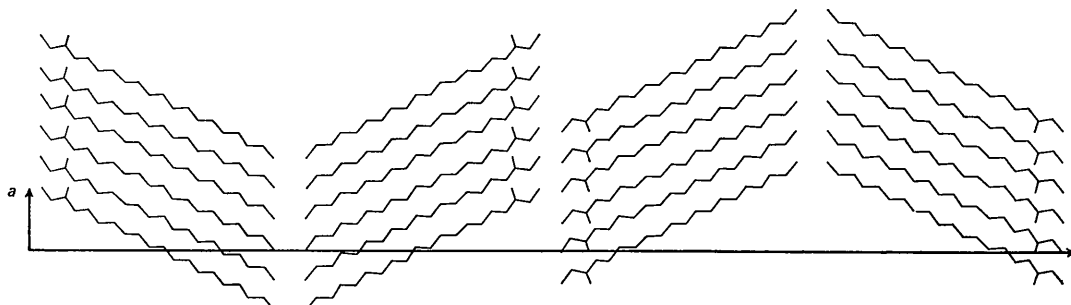
Fig. 3. Projection of a number of methyl stearate molecules along the b axis.
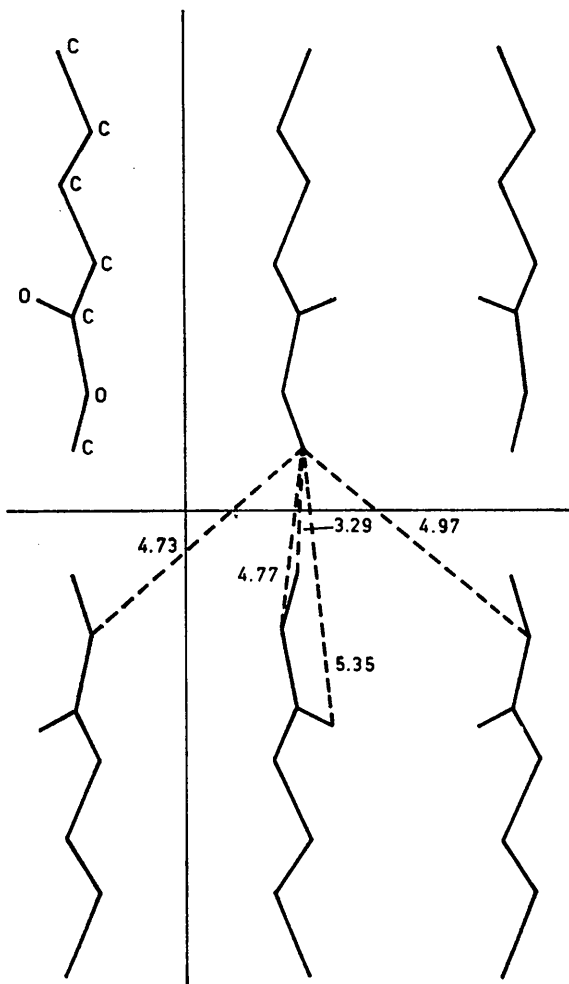
Fig. 4. Intermolecular contacts in the ester group region of orthorhombic methyl stearate.

Fig. 5. Packing of the end methyl groups of methyl stearate seen along the b axis of the (a) monoclinic modification, (b) orthorhombic modification.

indicating that both structures, as seen along the a axes, are the same. The coordinates of the molecule were transformed from the monoclinic cell to the orthorhombic cell. This affects only the x coordinates.

The 131 $0kl$ structure factors were calculated with these coordinates, giving an $R = \sum ||F_o| - |F_c||/\sum|F_c|$ of 0·34. From the Fourier projection calculated with the most reliable reflexions it appeared that the position of the molecule was about right and a three-dimensional refinement with all 737 observed reflexions was started.

After some cycles of least-squares refinement of co-ordinates and individual isotropic temperature factors the R index decreased to 0·21. A difference Fourier synthesis showed anisotropic temperature movement of the C and O atoms. Two more cycles refining co-ordinates and anisotropic temperature factors lowered the R index to 0·18. At this point the H atoms were included at calculated positions. A distance of 1·07 Å and angle of 109·5° was used, and $B_H = 3·0$ Å². R became 0·13 after two final cycles of refining only the positions and the temperature factors of the heavy atoms. The final atomic parameters and their e.s.d.'s
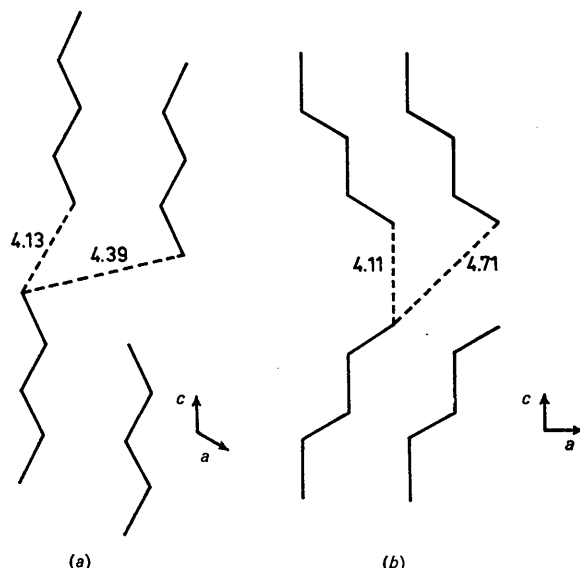
are given in Table 1. For the numbering of the atoms see Fig. 1.

Discussion

The intramolecular distances and angles are shown in Fig. 1. The mean value of the carbon–carbon bond lengths is 1·54 Å and that of the angles between these bonds, 111°. The C–O distances appear to be normal. Projections of a number of unit-cells along the a and b axes are shown in Figs. 2 and 3. The methyl stearate molecules form the same double sheets as have been found in the monoclinic modification. The hydrocarbon chains are arranged in the orthorhombic packing O, with the subcell dimensions $a_s = 5·02$, $b_s = 7·35$, $c_s = 2·54$, $\beta_s = 89·4°$. The intermolecular contacts in the ester group region shown in Fig. 4 are again the same as found by Aleby & von Sydow (1960). Chains in neighbouring sheets, however, are inclined with respect to each other. The packing of the end methyl groups of both modifications can be seen in Fig. 5.

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