of tetradecanamide as compared to tetradecane ($\Delta T = 100°$ C.), where no hydrogen-bond system is possible, and to tetradecanoic acid ($\Delta T = 51°$ C.), where only a one-dimensional system is possible. The crystal growth of tetradecanamide is much larger in the a and b directions than in the c direction, where the only attraction between the sheets of dimers is the van der Waals interaction between the terminal methyl groups. The weak attraction between sheets also introduces the observed cleavage along the (001) plane. The crystals also show a cleavage along an ($h0l$) plane whose indices have not been determined owing to the thinness of the crystals, but which is probably a cleavage between the rows of dimers.

The arrangement of the paraffin chains in tetradecanamide is quite similar to the structure reported for form A of potassium caprate (Vand, Lomer & Lang, 1949). In both compounds the paraffin chains are tilted strongly in the b direction, with successive rows in the a direction oppositely inclined. However, there is a striking difference in the orientation of the planes of the chains. In the tetradecanamide the planes of the chains are nearly parallel to the a axis, while in potassium caprate they are reported to be more nearly normal to the a axis.

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On the Structure of the Crystal Form *B* of Stearic Acid

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Form B of stearic acid, $C_{17}H_{35}COOH$, is monoclinic with $a = 5\cdot591$, $b = 7\cdot404$, $c = 49\cdot38$ Å and $\beta = 117° 22'$. The cell contains four molecules. The space group is $C_{2h}^5-P2_1/a$. The packing of the hydrocarbon chains is of the common orthorhombic type. The hydrocarbon chains are deformed near the carboxylic groups.

Introduction

The crystalline *B*-form of normal fatty acids with an even number of carbon atoms was first investigated with X-rays by Müller (1927). He determined the unit-cell dimensions and the space group of the *B*-form of stearic acid and made a very promising start in calculating the crystal structure. As no continuation of his work appeared, the problem has been taken up in Uppsala as a part of an investigation of the crystal behaviour of normal fatty acids (see Stenhagen & von Sydow (1953), von Sydow (1954a, b), and Abrahamsson & von Sydow (1954)). Thibaud & Dupré La Tour (1932) redetermined the unit cell of form B with X-rays and Trillat & v. Hirsch (1932) the smallest axis-plane with electron diffraction. Verma (1955) has determined the unit-cell dimensions of the *B*-form of palmitic acid.

Preparation of crystals

The very pure stearic acid used was prepared by Prof. E. Stenhagen and his collaborators. It has a melting point of 69·7° C. Francis & Piper (1939) found for the same acid 69·6° C.

According to Müller (1927), the *B*-form of stearic acid crystallizes from carbon disulfide, and according to Stenhagen & von Sydow (1953) and others it crystallizes together with the *C*-form from petroleum (b.p. 40–60° C.). If large quantities are used, formation of the *B*-form is favoured, and in this way large crystals of this form were obtained.

The crystals grew in rhombic plates having an acute angle of 74°. Müller (1927) found the same value. Investigation in polarized light revealed that twinning was very common among the crystals. In one case X-ray photographs had to be taken before twinning

could be detected, as the angle between the twins was so small.

X-ray data

Rotation and Weissenberg photographs about the *a* and *b* axes were taken with Cu *K* radiation from a gas tube. The cell dimensions were calculated from a powder photograph obtained with a Guinier camera using Cu *Kα* radiation. The following data were obtained:

Molecular formula: $C_{18}H_{36}O_2$.
Molecular weight: 284·47.
Unit cell: monoclinic.
$a = 5·591 \pm 0·011$, $b = 7·404 \pm 0·008$, $c = 49·38 \pm 0·10$ Å;
   $\beta = 117° 22' \pm 7'$.
$d(001) = 43·85 \pm 0·05$ Å.
Four molecules per unit cell.
Number of electrons: 640.
Density calculated: $1·041 \pm 0·005$ g.cm.$^{-3}$.
Density measured: 1·036 g.cm.$^{-3}$.
Absent reflexions: $(h0l)$ when h odd, $(0k0)$ when k odd.
Space group: $C_{2h}^5 - P2_1/a$.

Conclusions from the unit cell

If the unit cell is cut with a plane perpendicular to the *c* axis the cross-section will have the following dimensions: $a_0 = 4·96$ Å, $b_0 = b = 7·40$ Å, $\gamma_0 = \gamma = 90°$. These dimensions are very like those of an orthorhombic packing of hydrocarbon chains described by Bunn (1939) ($a_0 = 7·40$ Å, $b_0 = 4·93$ Å, $\gamma_0 = 90°$) and Vainshtein & Pinsker (1950) ($a_0 = 4·96$ Å, $b_0 = 7·41$ Å, $\gamma_0 = 90°$). In this packing the plane of every second hydrocarbon chain is almost perpendicular to the plane of the others. From these data one can rather definitely conclude that the crystalline *B*-form has this orthorhombic packing of its hydrocarbon chains.

Structure factors and electron-density projection

$(0kl)$ reflexions up to $\theta = 60°$ were recorded. Two observers estimated the intensities by eye from two different sets of multiple films obtained with one smaller and one larger single crystal, respectively. The intensities were corrected with the normal polarization and Lorentz factors. No absorption corrections were applied. A set of relative, observed structure factors was calculated and was later reduced to an absolute scale by comparison with calculated structure factors.

As $I(020)$ and $I(040)$ are very strong, and $I(02l)$ and $I(04l)$ with small l-values are weak, the two molecules in one half of the cell were placed parallel with the *c* axis and equally spaced, according to the assumed orthorhombic packing. Structure factors were calculated using atomic coordinates from the orthorhombic sub-cell described by Vainshtein & Pinsker (1950). At the beginning the CH_2 groups were treated as single atoms having $f = f_C + 2f_H$. The periodicity in the hydrocarbon chains has been used in the calculations of structure factors in a way suggested by Müller (1927) and developed by Vand (1951).

Atomic scattering factors were taken from McWeeny (1951), using for oxygen $f = \frac{1}{3}(f^\perp + 2f^{\parallel})$ and for carbon the values for 'valence states'.

Successive electron-density projections along the shortest axis were prepared, alternating with structure-factor calculations. The carbon and hydrogen atoms were soon separated and the hydrogen atoms were given coordinates which were calculated from the data given by Vainshtein & Pinsker (1950).

Every second C–C distance is too short to be resolved in this projection with the available reflexions. In order to refine the coordinates of the carbon atoms in the chains several $(F_o - F_c)$ syntheses were carried out. The difference maps were of course also used in

Table 1. *Coordinates of the atoms*

Atom	y/b	z/c	Atom	y/b	z/c	Atom	y/b	z/c
O_1H_1	0·113	0·0087	—	—	—	—	—	—
O_2	0·898	0·0379	—	—	—	—	—	—
C_1	0·020	0·0320	—	—	—	—	—	—
C_2	0·040	0·0507	H_2	0·040	0·039	H_3	0·197	0·051
C_3	0·960	0·0866	H_4	0·960	0·099	H_5	0·803	0·087
C_4	0·040	0·1026	H_6	0·040	0·091	H_7	0·197	0·103
C_5	0·960	0·1385	H_8	0·960	0·151	H_9	0·803	0·139
C_6	0·040	0·1545	H_{10}	0·040	0·143	H_{11}	0·197	0·155
C_7	0·960	0·1904	H_{12}	0·960	0·202	H_{13}	0·803	0·190
C_8	0·040	0·2064	H_{14}	0·040	0·194	H_{15}	0·197	0·206
C_9	0·960	0·2423	H_{16}	0·960	0·254	H_{17}	0·803	0·242
C_{10}	0·040	0·2583	H_{18}	0·040	0·246	H_{19}	0·197	0·258
C_{11}	0·960	0·2942	H_{20}	0·960	0·306	H_{21}	0·803	0·294
C_{12}	0·040	0·3102	H_{22}	0·040	0·298	H_{23}	0·197	0·310
C_{13}	0·960	0·3461	H_{24}	0·960	0·358	H_{25}	0·803	0·346
C_{14}	0·040	0·3621	H_{26}	0·040	0·350	H_{27}	0·197	0·362
C_{15}	0·960	0·3980	H_{28}	0·960	0·410	H_{29}	0·803	0·398
C_{16}	0·040	0·4140	H_{30}	0·040	0·402	H_{31}	0·197	0·414
C_{17}	0·960	0·4499	H_{32}	0·960	0·462	H_{33}	0·803	0·450
C_{18}	0·040	0·4659	H_{34}	0·040	0·454	H_{35}	0·197	0·466
H_{36}	0·979	0·493	—	—	—	—	—	—

The *y* and *z* coordinates of the atoms of the other molecule in the half unit cell are related to the coordinates, listed above, by the mirror plane $y = \frac{1}{4}$.

Table 2. *Observed and calculated structure factors*

hkl	|Fo|	Fc	hkl	|Fo|	Fc	hkl	|Fo|	Fc
001	62	+63	0,1,19	26	−22	0,3,37	<10	− 8
002	22	+22	0,1,20	86	−72	0,3,38	49	+55
003	53	+55	0,1,21	16	−18	0,3,39	<10	−16
004	20	+12	0,1,22	24	−28	0,3,40	31	−37
005	50	+42	0,1,23	11	−14	0,3,41	<10	−12
006	< 3	+ 4	0,1,24	13	−14			
007	29	+27	0,1,25 .	8	−10			
008	13	−19	0,1,26	10	−12			
009	18	+12	0,1,27	< 8	− 6	040	104	+93
0,0,10	28	−33				041	27	−27
0,0,11	13	+ 1				042	29	−34
0,0,12	37	−43	0,1,37	<10	− 4	043	25	−24
0,0,13	< 5	− 5	0,1,38	13	+26	044	21	−30
0,0,14	42	−51	0,1,39	<10	− 9	045	17	−19
0,0,15	< 5	− 6	0,1,40	12	−19	046	18	−24
0,0,16	49	−59	0,1,41	<10	− 8	047	12	−13
0,0,17	< 6	− 2				048	17	−18
0,0,18	106	−105	020	349	+342	049	7	− 7
0,0,19	9	+ 9	021	16	+13	0,4,10	15	−13
0,0,20	143	+139	022	8	− 7	0,4,11	< 8	− 2
0,0,21	< 7	+ 9	023	6	+11	0,4,12	15	−11
0,0,22	29	+37	024	11	−10	0,4,13	< 8	− 1
0,0,23	< 7	+13	025	< 5	+ 8	0,4,14	15	−12
0,0,24	15	+24	026	14	−14	0,4,15	< 8	− 1
0,0,25	12	+15	027	< 5	+ 5	0,4,16	17	−17
0,0,26	12	+19	028	18	−18	0,4,17	< 8	− 4
0,0,27	12	+14	029	< 5	+ 1	0,4,18	39	−37
0,0,28	11	+14	0,2,10	24	−22	0,4,19	< 9	− 6
0,0,29	13	+10	0,2,11	10	− 2	0,4,20	26	+32
0,0,30	12	+ 8	0,2,12	27	−26	0.4,21	< 9	−10
0,0,31	12	+ 5	0,2,13	12	− 4			
0,0,32	9	+ 2	0,2,14	35	−30	0,4,37	< 9	+12
0,0,33	< 8	0	0,2,15	10	− 5	0,4,38	19	+22
0,0,34	9	− 1	0,2,16	40	−37	0,4,39	< 9	+11
0,0,35	< 8	− 5	0,2,17	< 7	− 4			
0,0,36	14	− 3	0,2,18	72	−71	0,5,15	< 9	+ 4
0,0,37	10	− 8	0,2,19	< 7	+ 1	0,5,16	19	+26
0,0,38	45	+27	0,2,20	79	+81	0,5,17	< 9	+ 9
0,0,39	17	−14	0,2,21	< 7	− 2	0,5,18	48	+62
0,0,40	49	−30				0,5,19	<10	+ 9
0,0,41	18	−11	0,2,37	<10	+ 2	0,5,20	69	−69
0,0,42	26	−20	0,2,38	34	+29	0,5,21	<10	+16
0,0,43	9	−10	0,2,39	<10	− 3			
0,0,44	14	−19	0,2,40	23	−15	0,5,37	< 9	− 3
0,0,45	< 9	− 8	0,2,41	<10	− 1	0,5,38	47	+81
0,0,46	12	−17	0,2,42	13	− 8	0,5,39	< 9	−13
0,0,47	< 9	− 6	0,2,43	<10	− 1	0,5,40	36	−39
						0,5,41	< 9	− 5
			0,3,16	< 8	− 1			
0,1,10	< 5	+ 2	0,3,17	14	−19	060	15	+ 6
0,1,11	9	− 7	0,3,18	34	+26			
0,1,12	< 5	− 2	0,3,19	18	−22	0,7,17	< 9	+15
0,1,13	13	−13	0,3,20	90	−88	0,7,18	35	+67
0,1,14	< 5	− 5	0,3,21	15	−15	0,7,19	< 9	+18
0,1,15	17	−17	0,3,22	24	−31	0,7,20	50	−51
0,1,16	< 6	− 4	0,3,23	< 9	−11	0,7,21	< 9	+24
0,1,17	25	−20	0,3,24	11	−18			
0,1,18	15	+15	0,3,25	< 9	− 7	080	18	−39

the refinement of the coordinates of the atoms in the carboxylic groups.

The last electron-density projection is shown in Fig. 1, the atomic coordinates in Table 1, and observed and calculated structure factors in Table 2. The reliability index R_1 is 0·18.

Discussion of the results

All hydrocarbon chains have their centrelines in (110) and (1$\bar{1}$0). Half of the chains have their planes almost in (110) and the other half have their planes almost in (1$\bar{1}$0). This affects the macrocrystalline shape, and the faces of the crystals are always (110) and (1$\bar{1}$0) and of course (001), giving rhombic plates. The acute angle determined from the cell dimensions is 74° 6′, which agrees very well with the observed value 74°.

As in most long-chain compounds, twinning is very common among crystals of the B-form. In all observed cases the twins always had their (001) planes parallel,

and this is consistent with the weak van der Waals bonds between the methyl groups which lie in these planes.

The increment of long spacing for this crystal form is 2·32 Å, according to Stenhagen & von Sydow (1953). Thus the angle of tilt is between 67° and 66° if the distance between alternate carbon atoms is between 2·521 Å (found in form *C* of lauric acid by Vand, Morley & Lomer (1951)) and 2·54 Å (found in a paraffin by Vainshtein & Pinsker (1950)), respectively.
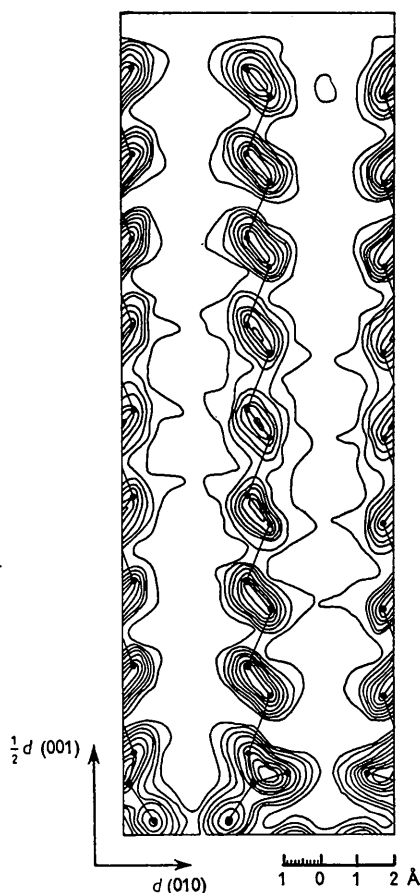

$\frac{1}{2}d\,(001)$

$d\,(010)$ 1   0   1   2 Å

Fig. 1. Electron-density projection along the *a* axis.

The packing of the hydrocarbon chains is of the common orthorhombic type. Vand (1954) has suggested a way of classifying long-chain compounds. The chain packing is described with a capital letter, e.g. *O*, for the orthorhombic packing, and this should be followed by (*hkl*), which are the indices in the sub-cell of the *a–b* plane of the main cell. In this way the *B*-form of stearic acid can be described as *O*(101), the *B'*-form of acids with an odd number of carbon atoms (von Sydow, 1954*b*) as *O*(111) and the *C*-form of acids with an even number of carbon atoms (Vand, Morley

& Lomer, 1951) as *O*(021) (if the shortest axis is *a*). The *A'*-form of acids with an odd number of carbon atoms (von Sydow, 1954*a*), which has a triclinic packing of the hydrocarbon chains, cannot be described with small indices. This is of course due to the fact that there is only one molecule per half unit cell.

From Fig. 1 it can be seen that the hydrocarbon chains are deformed near the carboxylic groups in the same way that was found by von Sydow (1954*b*) in the crystalline *B'*-form of *n*-pentadecanoic acid. The carboxylic groups are twisted out of the chain planes around the bond between the second and the third carbon atoms to allow hydrogen bonding between two carboxylic groups. The chain planes of two coupled molecules are almost perpendicular, as in the *B'*- and *C*-forms.

The low peaks projecting from most of the carbon atoms in Fig. 1 are probably caused by the hydrogen atoms, which in the projection are situated about 1·15 Å outside the carbon atoms in a direction perpendicular to the chain direction. The second of the two peaks projecting from the last carbon atom is probably caused by the third hydrogen atom in the methyl group. All the other hydrogen atoms are more or less masked by the carbon and oxygen atoms.

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