in the lower half-crystal and again producing a twin fault. To generalize these results to planes of normal stacking pattern

$$\dots 1234 \dots n \dots ,$$

we may form a sessile either by inserting two extra half-planes or by removing $n-2$.

A complementary pair of half-dislocations, E and N, separated by a stacking fault of monolayer twin, are illustrated in Fig. 6. The dislocation E is constructed by inserting an extra half-plane and, in the usual way, allowing the atoms on its right-hand side to relax to the equilibrium configuration characteristic of the perfect crystal; on the left hand side, however, the atoms are allowed to relax only as far as the alternative equilibrium configuration characteristic of the twinned crystal, this being maintained over a certain distance, as shown. The passage of such a dislocation through the crystal leaves in its wake a monolayer twin, which could be formally produced by a homogeneous translation $\lambda\mathbf{b}$ of the upper half-crystal: $\mathbf{b}$ is the unit lattice vector in the twinning direction, and $\lambda/d_{(hkl)}$ the twinning shear. The dislocation N contains no extra half-plane, nor is it deficient in a half-plane, its function being to connect the monolayer twin on its right with the perfect crystal on its left. Its Burgers vector is evidently $(1-\lambda)\mathbf{b}$.

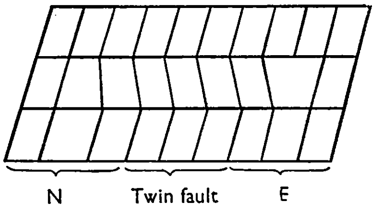

Fig. 6. Extended dislocation consisting of a complementary pair of half-dislocations, E and N, separated by a monolayer twin fault. E contains an extra half-plane, but not N.

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On the Structure of the Crystal Form C' of n-Hendecanoic Acid

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The crystalline C'-form of n-hendecanoic acid, $C_{10}H_{21}COOH$, is monoclinic with $a = 9{\cdot}622$, $b = 4{\cdot}915$, $c = 34{\cdot}18$ Å and $\beta = 131° 17'$. Space group C_{2h}^5–$P2_1/a$; four molecules in the unit cell. The investigation was carried out at 23° C., which is only 5° C. below the melting point of the acid. The chains are packed in the common orthorhombic way, but there are large distortions: the chains are probably bent and twisted helically.

Introduction

Normal fatty acids with an odd number of carbon atoms can occur in three polymorphic forms called A', B' and C'. The crystal structure of the first two have been described by von Sydow (1954*a*, *b*, 1955*b*).

According to Stenhagen & von Sydow (1953) the crystalline C'-form is only stable just below the melting point, and the temperature interval of stability decreases with increasing chain length. Thus a short acid would be more favourable from the X-ray technical point of view, having a relatively wide interval at a more suitable temperature. n-Hendecanoic acid was chosen, the C'-form of which, according to Garner & Randall (1924) and de Boer (1927), exists between the melting point and a temperature between 12·5° C. and 17° C.

Preparation of crystals

The n-hendecanoic acid was obtained from Prof. E. Stenhagen and his collaborators. Its m.p. was 28·0–28·4° C.

The C'-form is always obtained at temperatures between 17° C. and 28° C., but the macrocrystalline shape is strongly dependent on the mode of crystallization. Crystallization from the melt always gives conglomerates of crystals which often contain supercooled liquid acid. In order to get crystals suitable for X-ray work, different solvents were tried. Crystallization from carbon tetrachloride solution gave the best crystals, although not very good. They were always twinned, which mostly could be detected in polarized light, and they were often bent owing to their softness near the melting point. Like all the other crystal forms of fatty acids, these crystals are biaxial positive. As the acute bisectrix can be supposed to be parallel to the carbon chains it has been found useful to determine the approximate direction of this bisectrix in the crystals.

X-ray data

Rotation and Weissenberg photographs were taken at 23° C. with Cu K radiation. The cell dimensions were calculated from a powder photograph obtained at the same temperature with a Guinier camera using Cu $K\alpha$ radiation. The following data were obtained:

Molecular formula: $C_{11}H_{22}O_2$.
Molecular weight: 186·29.
Unit cell: monoclinic.
$a=9{\cdot}622\pm0{\cdot}030$, $b=4{\cdot}915\pm0{\cdot}008$, $c=34{\cdot}18\pm0{\cdot}10$ Å;
$\beta = 131^\circ\,17'\pm15'$.
$d(001) = 25{\cdot}68\pm0{\cdot}05$ Å.
Four molecules per unit cell.
Number of electrons: 416.
Absent reflexions: $(h0l)$ when h odd, $(0k0)$ when k odd.
Space group: C_{2h}^5–$P2_1/a$.

Owing to the poor crystals available the reflexions obtained were rather ill-shaped. The intensities were estimated by eye, using the multiple-film technique. Two sets of films differing in exposure were used and the results were compared with the intensities estimated from a set of films obtained with another crystal. 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 brought to an absolute scale by comparison with calculated structure factors.

Patterson projection

In order to determine the chain direction in the cell and the carbon–carbon distance in the chain, a Patterson projection along the b axis was prepared. The function was modified in a way suggested by Lipson & Cochran (1953, p. 172):

$$M(S) = \left(\frac{1}{\hat{f}}\right)^2 \exp\left(-\frac{\pi^2}{p}S^2\right) \text{ with } p = 7{\cdot}25\,.$$

The projection obtained was, however, rather diffuse, indicating irregularities in the hydrocarbon chains. A row of flat peaks was taken as an indication of the chain direction.

Sub-cell

With the assumed chain direction one can easily see that the common orthorhombic packing of hydrocarbon chains fits rather well into the unit cell of the C'-form of n-hendecanoic acid. This packing, which is described by Bunn (1939) and by Vainshtein & Pinsker

Table 1. *Coordinates of the atoms*

Atom	x/a	z/c
O_1	0·914	0·0061
O_2	0·067	0·0591
C_1	0·979	0·0443
C_2	0·918	0·0749
C_3	0·016	0·1249
C_4	0·983	0·1592
C_5	0·067	0·2060
C_6	0·031	0·2411
C_7	0·108	0·2860
C_8	0·074	0·3204
C_9	0·140	0·3655
C_{10}	0·120	0·3995
C_{11}	0·175	0·4432

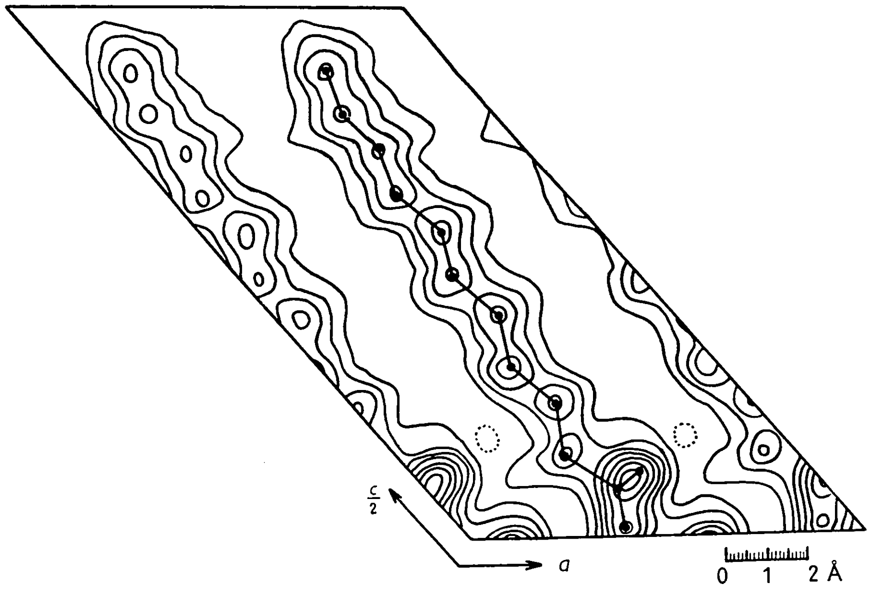

Fig. 1. The C'-form of n-hendecanoic acid: electron-density projection along the b axis.

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
000	416	—	$2,0,\overline{11}$	26	−24	$4,0,\overline{18}$	3	− 2
001	49	49	$2,0,\overline{12}$	3	− 1	$4,0,\overline{19}$	3	2
002	12	12	$2,0,\overline{13}$	19	−22	$4,0,\overline{20}$	3	3
003	52	53	$2,0,\overline{14}$	10	−11	$4,0,\overline{21}$	4	5
004	3	1	$2,0,\overline{15}$	10	− 5	$4,0,\overline{22}$	3	5
005	28	26	$2,0,\overline{16}$	< 3	5	$4,0,\overline{23}$	4	3
006	12	− 9	$2,0,\overline{17}$	< 3	4	$4,0,\overline{24}$	4	5
007	5	4	$2,0,\overline{18}$	3	3	$4,0,\overline{25}$	< 4	0
008	15	−15	$2,0,\overline{19}$	5	6	$4,0,\overline{26}$	7	10
009	8	− 8	$2,0,\overline{20}$	3	2	$4,0,\overline{27}$	11	−11
0,0,10	9	−13	$2,0,\overline{21}$	5	4	$4,0,\overline{28}$	15	−14
0,0,11	13	−15	$2,0,\overline{22}$	< 4	− 1	$4,0,\overline{29}$	< 4	− 1
0,0,12	12	−13	$2,0,\overline{23}$	4	3	$4,0,\overline{30}$	5	− 5
0,0,13	24	27	$2,0,\overline{24}$	< 4	− 1	$4,0,\overline{31}$	< 4	− 2
0,0,14	15	17	$2,0,\overline{25}$	7	9			
0,0,15	10	10	$2,0,\overline{26}$	< 4	3	$60\overline{1}$	< 4	− 5
0,0,16	11	14	$2,0,\overline{27}$	8	− 9	$60\overline{2}$	8	4
0,0,17	9	6	$2,0,\overline{28}$	4	− 1	$60\overline{3}$	12	−15
0,0,18	9	8	$2,0,\overline{29}$	< 4	− 2	$60\overline{4}$	< 4	− 7
0,0,19	6	3						
0,0,20	4	4	400	4	−11	$6,0,\overline{11}$	< 4	− 8
0,0,21	< 4	0	401	3	2	$6,0,\overline{12}$	8	−13
			402	5	− 7	$6,0,\overline{13}$	10	−11
200	95	101	403	5	− 4	$6,0,\overline{14}$	19	−15
201	15	7	404	6	− 5	$6,0,\overline{15}$	28	−33
202	34	38	405	4	− 3	$6,0,\overline{16}$	< 3	− 1
203	3	3	406	4	− 1	$6,0,\overline{17}$	8	8
204	< 3	11	407	< 4	0	$6,0,\overline{18}$	< 3	− 1
205	7	− 3	408	< 4	2	$6,0,\overline{19}$	< 3	− 1
206	7	2	409	< 4	2	$6,0,\overline{20}$	4	1
207	4	− 1	4,0,10	< 4	− 6	$6,0,\overline{21}$	4	2
208	4	1	4,0,11	6	− 5	$6,0,\overline{22}$	4	3
209	3	1	4,0,12	< 4	5	$6,0,\overline{23}$	4	3
2,0,10	7	− 4				$6,0,\overline{24}$	5	4
2,0,11	12	−13	$40\overline{1}$	23	25	$6,0,\overline{25}$	4	2
2,0,12	4	4	$40\overline{2}$	4	− 1	$6,0,\overline{26}$	4	1
2,0,13	9	10	$40\overline{3}$	37	−40	$6,0,\overline{27}$	< 4	3
2,0,14	6	3	$40\overline{4}$	10	14	$6,0,\overline{28}$	12	−14
2,0,15	6	1	$40\overline{5}$	4	− 8	$6,0,\overline{29}$	4	− 5
2,0,16	< 4	3	$40\overline{6}$	10	10	$6,0,\overline{30}$	5	2
			$40\overline{7}$	8	− 4	$6,0,\overline{31}$	< 4	− 3
$20\overline{1}$	147	154	$40\overline{8}$	8	− 4			
$20\overline{2}$	64	−75	$40\overline{9}$	18	−11	$8,0,\overline{16}$	< 4	− 5
$20\overline{3}$	12	12	$4,0,\overline{10}$	27	−22	$8,0,\overline{17}$	7	10
$20\overline{4}$	< 3	0	$4,0,\overline{11}$	28	−23	$8,0,\overline{18}$	5	3
$20\overline{5}$	17	6	$4,0,\overline{12}$	25	−31	$8,0,\overline{19}$	< 4	− 1
$20\overline{6}$	10	12	$4,0,\overline{13}$	18	−18			
$20\overline{7}$	17	−13	$4,0,\overline{14}$	54	−68	$8,0,\overline{29}$	< 4	− 5
$20\overline{8}$	3	− 2	$4,0,\overline{15}$	30	−40	$8,0,\overline{30}$	5	4
$20\overline{9}$	25	−25	$4,0,\overline{16}$	< 3	2	$8,0,\overline{31}$	4	1
$2,0,\overline{10}$	9	− 7	$4,0,\overline{17}$	4	− 1	$8,0,\overline{32}$	< 4	0

(1950), has the plane of every second chain almost perpendicular to the plane of the others. In the reciprocal lattice the orthorhombic packing should show up as strong reflexions distributed orthorhombically in the monoclinic lattice of the acid. This was easily confirmed and it was concluded that the crystalline C'-form has this packing of its hydrocarbon chains.

Structure factors and electron-density projection

With the assumptions mentioned above, structure factors were calculated. The periodicity in the hydrocarbon chains was used in the calculations 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'. A temperature factor $\exp -B(\sin\theta/\lambda)^2$, with B finally taken equal to 9·7 Å^2, was applied.

Successive electron-density projections along the shortest axis were prepared, alternating with structure factor calculations.

The projections soon revealed that the carbon atoms were not distributed in the regular way of the orthorhombic sub-cell; therefore all the atoms had to be treated separately in the structure-factor calculation. The hydrogen atoms were later included and given approximate coordinates which were calculated from the data given by Vainshtein & Pinsker (1950). As the hydrogen atoms do not lie periodically they contribute very little to the structure factors.

Several difference syntheses were carried out in order to correct the coordinates of the heavier atoms.

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 0·19 when the non-observed reflexions are omitted. For the much better formed $(00l)$ reflexions R_1 is equal to 0·10.

Discussion of the results

As with all the other crystal forms of normal fatty acids with the orthorhombic packing of the chains, twinning is very common for the C'-form of *n*-hendecanoic acid. The twins always have their (001) planes parallel, which is the case for the other crystal forms as well.

The crystal structure of the C'-form is very like that of the C-form of acids with an even number of carbon atoms. The structure of the latter has been described by Vand, Morley & Lomer (1951). Both forms have the same space group, the same chain packing, and the carboxylic groups situated in the same sub-cell plane. According to Vand's (1954) suggestion, both these structures can be described by $O(021)$, where O denotes the orthorhombic packing and (021) are approximately the indices in the sub-cell of the ab plane of the main cell, if the shortest axis is a.

The increment of long spacing for the C'-form is 2·15 Å according to Stenhagen & von Sydow (1953). If the distance between alternate carbon atoms is between 2·52 Å, as in the C-form of lauric acid (Vand *et al.*, 1951), and 2·54 Å, found by Vainshtein & Pinsker (1950) in a paraffin, the angle of tilt will be approximately 58°.

The projection in Fig. 1 reveals that the hydrocarbon chains are neither straight nor planar. They have their centre lines bent and the chain planes are probably helically twisted round their centre lines. These distortions from the orthorhombic packing are caused by at least two factors: the proximity of the experimental temperature to the melting point of the acid and the presence of carboxylic groups. Near the melting point the thermal motion of the atoms is very large. This allows the molecules to become easily deformed. The carboxylic groups which couple the molecules to dimers cannot fit into the ideal orthorhombic packing of the chains but must deform the packing at least near the groups. In the case of the C'-form, which is stable only just below the melting point, the deformation will involve more atoms in the chain than in the case of the B'-form of *n*-pentadecanoic acid and the B-form of stearic acid (von Sydow, 1954*b*, 1955*a*), for which the deformation includes only the first carbon atom in the hydrocarbon chain.

In the C'-form the chain planes of two coupled molecules are parallel.

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