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# On the Structure of the Crystal Form *B′* of *n*-Pentadecanoic Acid

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Form *B′* of *n*-pentadecanoic acid, $C_{14}H_{29}COOH$, is triclinic with

$$a = 5{\cdot}543 \text{ Å},\ b = 8{\cdot}061 \text{ Å},\ c = 42{\cdot}58 \text{ Å};\ \alpha = 114^\circ\ 18',\ \beta = 114^\circ\ 13',\ \gamma = 80^\circ\ 37'.$$

The cell contains four molecules. The crystals show no piezo-electric effect, indicating space-group $C_i^1$–$P\bar{1}$. Fourier projections along the shortest axis were prepared. The packing of the hydrocarbon chains is of the common orthorhombic type with the plane of every second chain almost perpendicular to the plane of the others. The chains are not quite parallel.

## Introduction

As is well known, normal fatty acids exhibit polymorphism. At least six different crystal forms are possible, three for acids with an even number of carbon atoms and at least three for acids with an odd number. The transitions between these different forms have been investigated by Stenhagen & von Sydow (1953).

Von Sydow (1954) has derived the crystal structure of form *A′* of odd acids. Its unit cell is triclinic and it has the triclinic packing of hydrocarbon chains described by Müller & Lonsdale (1948) and later found in silver soaps by Vand, Aitken & Campbell (1949) and in trilaurin by Vand & Bell (1951).

No other unit-cell determinations or crystal-structure studies of long-chain normal fatty acids with an odd number of carbon atoms have been made.

## Preparation of crystals

Prof. E. Stenhagen and his collaborators put the very pure specimen of *n*-pentadecanoic acid at my disposal. It was the same specimen as that used by von Sydow (1954) and had a melting point of 52·3° C., compared with 52·26° and 52·1° C. according to Meyer & Reid (1933) and Francis, Piper & Malkin (1930), respectively.

According to Stenhagen & von Sydow (1953), the form *B′* of *n*-pentadecanoic acid is formed when the acid is crystallized from the melt and (together with form *A′*) from glacial acetic acid. The crystals obtained in these ways are, however, much too small for single-crystal work. To get larger ones other solvents were tried: benzene, toluene, ethanol, carbon disulfide, ethyl ether, and benzyl alcohol (compare von Sydow (1954)).

Benzene gave the best crystals of form *B′*. They were not very large but larger than the crystals of form *A′* described by von Sydow (1954). It is very striking that acids with an odd number of carbon atoms give much smaller crystals than acids with an even number. This, together with their rarity in nature, may explain why very little X-ray work has been done on the odd acids.

## Optical studies

The crystals grow in lath-shaped thin plates and, where the short edge is seen, it forms an angle of 72° with the long side. Twinning was very common. In most cases it was easily seen when the crystals were observed under polarized light; no distinct extinction was then obtained. In some cases X-ray rotation photographs had to be taken to decide if twinning existed. At last a few rather uniform but small crystals of form *B′* were picked out.

The crystals were found to be biaxial positive with the acute bisectrix parallel to the chain direction. The cross-section of the crystals used was approximately 0·15×0·07 mm.

## X-ray data

Rotation photographs and zero- and *n*-layer Weissenberg photographs about the *a* axis and $[\bar{1}10]$ were taken using Cu *K* radiation and a calibrated camera. A method described by Vand (1948) was partly used when the cell dimensions were determined. The following data were obtained:

Molecular formula: $C_{15}H_{30}O_2$.
Molecular weight: 242·39.
Unit cell: triclinic.
$a = 5{\cdot}543 \pm 0{\cdot}010,\ b = 8{\cdot}061 \pm 0{\cdot}030,\ c = 42{\cdot}58 \pm 0{\cdot}14$ Å.
$\alpha = 114^\circ\ 18' \pm 11',\ \beta = 114^\circ\ 13' \pm 13',\ \gamma = 80^\circ\ 37' \pm 6'$.
$d(001) = 35{\cdot}88 \pm 0{\cdot}08$ Å.
Four molecules per unit cell.
Number of electrons: 544.
Density calculated: 1·018±0·013 g.cm.$^{-3}$.
Density measured: 1·02 g.cm.$^{-3}$.
Space group: $C_1^1$–$P1$ or $C_i^1$–$P\bar{1}$.

The absence of piezo-electric effect (I am indebted to Mr J. Baecklund for help with the measurements) is consistent with the space-group $C_i^1$–$P\bar{1}$, which has a centre of symmetry.

### 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: $a_0$ = 5·07, $b_0$ = 7·35 Å, $\gamma_0$ = 90° 23′. These dimensions are very like those of an orthorhombic packing of hydrocarbon chains described by Bunn (1939) ($a_0$ = 7·40, $b_0$ = 4·93 Å, $\gamma_0$ = 90°) and by Vainshtein & Pinsker (1950) ($a_0$ = 4·96, $b_0$ = 7·41 Å, $\gamma$ = 90°). In this packing the plane of every second chain is almost perpendicular to the plane of the others. From these data it seems probable that the crystal form *B′* of acids with an odd number of carbon atoms has this orthorhombic packing of its hydrocarbon chains.

### Structure factors and electron-density projection

As the available crystals were so small, only rather few reflexions were recorded: thus only 63 (0*kl*) reflexions were obtained with an exposure of 82 hr.

Table 1. *Co-ordinates of the atoms*

| Atom | *y/b* | *z/c* | Atom | *y/b* | *z/c* |
|---|---|---|---|---|---|
| $O_1H_1$ | 0·428 | 0·013 | $H_3$ | 0·612 | 0·076 |
| $O_2$ | 0·314 | 0·040 | $H_5$ | 0·220 | 0·091 |
| $C_1$ | 0·424 | 0·041 | $H_7$ | 0·627 | 0·134 |
| $C_2+H_2$ | 0·452 | 0·066 | $H_9$ | 0·252 | 0·152 |
| $C_3+H_4$ | 0·380 | 0·1008 | $H_{11}$ | 0·659 | 0·195 |
| $C_4+H_6$ | 0·467 | 0·1242 | $H_{13}$ | 0·284 | 0·213 |
| $C_5+H_8$ | 0·412 | 0·1619 | $H_{15}$ | 0·691 | 0·256 |
| $C_6+H_{10}$ | 0·500 | 0·1853 | $H_{17}$ | 0·316 | 0·274 |
| $C_7+H_{12}$ | 0·444 | 0·2230 | $H_{19}$ | 0·723 | 0·317 |
| $C_8+H_{14}$ | 0·532 | 0·2464 | $H_{21}$ | 0·348 | 0·335 |
| $C_9+H_{16}$ | 0·477 | 0·2841 | $H_{23}$ | 0·755 | 0·378 |
| $C_{10}+H_{18}$ | 0·564 | 0·3075 | $H_{25}$ | 0·380 | 0·396 |
| $C_{11}+H_{20}$ | 0·509 | 0·3452 | $H_{27}$ | 0·787 | 0·439 |
| $C_{12}+H_{22}$ | 0·597 | 0·3686 | $H_{29}$ | 0·412 | 0·457 |
| $C_{13}+H_{24}$ | 0·541 | 0·4063 | $H_{30}$ | 0·642 | 0·486 |
| $C_{14}+H_{26}$ | 0·629 | 0·4297 | | | |
| $C_{15}+H_{28}$ | 0·574 | 0·4674 | | | |
| $O_1^1H_1^1$ | 0·920 | 0·004 | $H_3^1$ | 0·108 | 0·086 |
| $O_2^1$ | 0·814 | 0·031 | $H_5^1$ | 0·696 | 0·079 |
| $C_1^1$ | 0·915 | 0·032 | $H_7^1$ | 0·121 | 0·145 |
| $C_2^1+H_2^1$ | 0·948 | 0·076 | $H_9^1$ | 0·730 | 0.140 |
| $C_3^1+H_4^1$ | 0·856 | 0.0890 | $H_{11}^1$ | 0.155 | 0·206 |
| $C_4^1+H_6^1$ | 0·961 | 0·1345 | $H_{13}^1$ | 0·764 | 0·201 |
| $C_5^1+H_8^1$ | 0.890 | 0·1504 | $H_{15}^1$ | 0·189 | 0.267 |
| $C_6^1+H_{10}^1$ | 0·995 | 0·1960 | $H_{17}^1$ | 0·798 | 0·262 |
| $C_7^1+H_{12}^1$ | 0·924 | 0·2119 | $H_{19}^1$ | 0·223 | 0·329 |
| $C_8^1+H_{14}^1$ | 0·029 | 0·2574 | $H_{21}^1$ | 0·832 | 0.324 |
| $C_9^1+H_{16}^1$ | 0·959 | 0·2733 | $H_{23}^1$ | 0·257 | 0·390 |
| $C_{10}^1+H_{18}^1$ | 0·063 | 0·3189 | $H_{25}^1$ | 0.866 | 0·385 |
| $C_{11}^1+H_{20}^1$ | 0·993 | 0·3348 | $H_{27}^1$ | 0·291 | 0.452 |
| $C_{12}^1+H_{22}^1$ | 0·098 | 0·3803 | $H_{29}^1$ | 0·900 | 0.447 |
| $C_{13}^1+H_{24}^1$ | 0·027 | 0·3962 | $H_{30}^1$ | 0·142 | 0·492 |
| $C_{14}^1+H_{26}^1$ | 0·132 | 0·4418 | | | |
| $C_{15}^1+H_{28}^1$ | 0·061 | 0·4577 | | | |

Two observers estimated the intensities by eye from two different sets of films, using the multiple-film technique of de Lange, Robertson & Woodward (1939) The strongest reflexion was 2000 times stronger than the weakest one observed. 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 on an absolute scale by comparison with calculated structure factors.

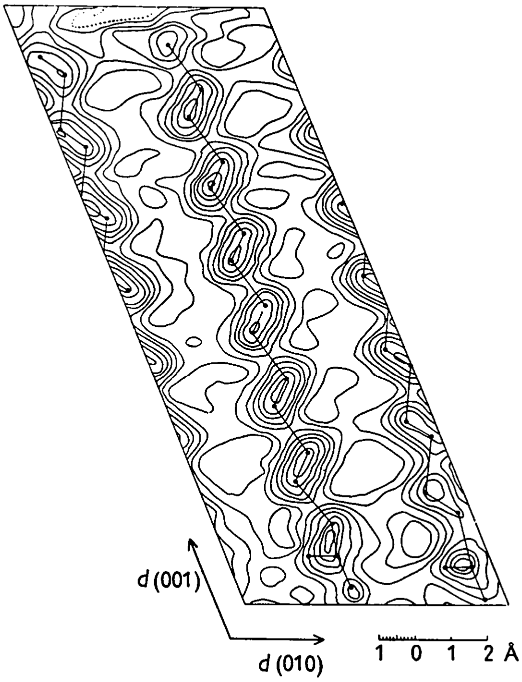

Fig. 1. Electron-density projection along the *a* axis.

When the structure factors were calculated for the first time atomic coordinates were taken from the orthorhombic subcell determined by Vainshtein & Pinsker (1950). The subcell theory for long-chain compounds, first suggested by Müller (1927) and later developed by Vand (1951), was used. At the beginning the $CH_2$ groups were treated as single atoms having $f = f_C + 2f_H$. The carboxylic groups were placed in the most probable way.

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'.

The Fourier summations were carried out with Robertson strips, Beevers–Lipson strips and a machine designed by Hägg & Laurent (1946).

Successive electron-density projections along the shortest axis were prepared alternating with structure-factor calculations. Rather soon the carbon and hydrogen atoms were separated. The coordinates of the two hydrogen atoms relative to the corresponding

Table 2. *Observed and calculated structure factors*

| *hkl* | $\lvert F_o \rvert$ | $F_c$ |
|---|---|---|
| 000 | 544 | — |
| 001 | 58 | +56 |
| 002 | 9 | +10 |
| 003 | 56 | +48 |
| 004 | < 4 | + 4 |
| 005 | 37 | +38 |
| 006 | 5 | − 6 |
| 007 | 17 | +25 |
| 008 | 17 | −16 |
| 009 | 4 | +14 |
| 0,0,10 | 21 | −22 |
| 0,0,11 | < 5 | + 8 |
| 0,0,12 | 22 | −23 |
| 0,0,13 | 18 | +10 |
| 0,0,14 | 24 | −19 |
| 0,0,15 | 32 | +29 |
| 0,0,16 | 26 | −13 |
| 0,0,17 | 44 | −42 |
| 0,0,18 | < 6 | − 4 |
| 010 | < 4 | − 4 |
| 011 | < 4 | + 4 |
| 012 | < 4 | − 1 |
| 013 | < 5 | − 9 |
| 014 | < 5 | − 4 |
| 015 | < 5 | − 3 |
| 016 | < 6 | − 2 |
| 017 | < 6 | + 1 |
| 018 | < 6 | − 1 |
| 019 | < 7 | + 3 |
| 0,1,10 | < 7 | − 2 |
| 0,1,11 | < 7 | 0 |
| 0,1,12 | < 8 | − 9 |
| 0,1,13 | < 8 | + 3 |
| 0,1,14 | < 8 | −11 |
| 0,1,15 | 44 | +44 |
| 0,1,16 | < 9 | − 3 |
| 0,1,17 | 52 | −53 |
| 0,1,18 | < 9 | − 4 |
| $01\bar{1}$ | < 4 | + 4 |
| $01\bar{2}$ | < 4 | − 3 |
| $01\bar{3}$ | < 4 | 0 |
| $01\bar{4}$ | < 4 | − 2 |
| $01\bar{5}$ | < 5 | + 3 |
| $01\bar{6}$ | < 5 | − 4 |
| $01\bar{7}$ | < 5 | + 4 |
| $01\bar{8}$ | 5 | − 4 |
| $01\bar{9}$ | 6 | + 6 |
| $0,1,\overline{10}$ | 7 | − 7 |
| $0,1,\overline{11}$ | 6 | + 5 |
| $0,1,\overline{12}$ | 7 | − 8 |
| $0,1,\overline{13}$ | 7 | + 7 |
| $0,1,\overline{14}$ | 11 | −11 |
| $0,1,\overline{15}$ | 7 | +15 |
| $0,1,\overline{16}$ | < 7 | − 4 |
| $0,1,\overline{17}$ | 131 | −131 |
| $0,1,\overline{18}$ | 32 | + 8 |
| $0,1,\overline{19}$ | < 8 | + 6 |
| $0,1,\overline{20}$ | 16 | + 9 |
| $0,1,\overline{21}$ | < 9 | +13 |
| 020 | 205 | +184 |
| 021 | 22 | +17 |
| 022 | 70 | +73 |
| 023 | 17 | +10 |
| 024 | 25 | +31 |
| 025 | < 6 | − 5 |
| 026 | < 7 | +13 |
| 027 | < 7 | − 8 |
| 028 | < 7 | + 4 |
| 029 | < 7 | − 2 |
| 0,2,10 | < 8 | + 4 |
| 0,2,11 | < 8 | − 1 |
| 0,2,12 | < 8 | − 2 |
| 0,2,13 | < 8 | + 2 |
| 0,2,14 | < 9 | −11 |
| 0,2,15 | 72 | +74 |
| 0,2,16 | < 9 | 0 |
| 0,2,17 | 31 | −24 |
| 0,2,18 | < 10 | − 6 |
| $02\bar{1}$ | 23 | −20 |
| $02\bar{2}$ | 175 | −161 |
| $02\bar{3}$ | 21 | +18 |
| $02\bar{4}$ | 45 | −41 |
| $02\bar{5}$ | 8 | + 8 |
| $02\bar{6}$ | 23 | −20 |
| $02\bar{7}$ | < 7 | 0 |
| $02\bar{8}$ | 23 | −19 |
| $02\bar{9}$ | 10 | −11 |
| $0,2,\overline{10}$ | 24 | −22 |
| $0,2,\overline{11}$ | 25 | −21 |
| $0,2,\overline{12}$ | 26 | −20 |
| $0,2,\overline{13}$ | 31 | −19 |
| $0,2,\overline{14}$ | 20 | −13 |
| $0,2,\overline{15}$ | 39 | +12 |
| $0,2,\overline{16}$ | 11 | +15 |
| $0,2,\overline{17}$ | 87 | +81 |
| $0,2,\overline{18}$ | 9 | +11 |
| $0,2,\overline{19}$ | 14 | −22 |
| $0,2,\overline{20}$ | < 8 | + 7 |
| $0,2,\overline{21}$ | < 9 | − 8 |
| $0,2,\overline{22}$ | < 9 | +11 |
| $0,2,\overline{23}$ | < 9 | − 1 |
| $0,2,\overline{24}$ | < 10 | +10 |
| $0,2,\overline{25}$ | < 10 | − 6 |
| $0,2,\overline{26}$ | < 10 | + 5 |
| $0,2,\overline{27}$ | < 10 | − 7 |
| $0,2,\overline{28}$ | < 11 | + 3 |
| $0,2,\overline{29}$ | < 11 | − 9 |
| $0,2,\overline{30}$ | < 11 | + 3 |
| $0,2,\overline{31}$ | < 11 | − 8 |
| $0,2,\overline{32}$ | < 11 | + 4 |
| $0,2,\overline{33}$ | < 12 | − 7 |
| $0,2,\overline{34}$ | 30 | −30 |
| $0,2,\overline{35}$ | < 12 | + 7 |
| $0,3,\overline{16}$ | < 8 | + 7 |
| $0,3,\overline{17}$ | 34 | −47 |
| $0,3,\overline{18}$ | < 9 | + 9 |
| $0,3,\overline{19}$ | 54 | +54 |
| $0,3,\overline{20}$ | < 9 | + 2 |
| 040 | < 8 | + 8 |
| 041 | < 9 | − 3 |
| 042 | < 9 | + 6 |
| 043 | < 9 | − 8 |
| 044 | < 9 | + 6 |
| 045 | < 9 | − 9 |
| 046 | < 9 | + 7 |
| 047 | < 10 | − 8 |
| 048 | < 10 | + 8 |
| 049 | < 10 | −12 |
| 0,4,10 | < 10 | + 9 |
| 0,4,11 | < 10 | −11 |
| 0,4,12 | < 11 | +19 |
| 0,4,13 | < 11 | −15 |
| 0,4,14 | < 11 | +15 |
| 0,4,15 | 24 | +32 |
| 0,4,16 | < 12 | +13 |
| $04\bar{1}$ | < 8 | − 8 |
| $04\bar{2}$ | 87 | −100 |
| $04\bar{3}$ | < 8 | +13 |
| $04\bar{4}$ | < 8 | + 7 |
| $04\bar{5}$ | < 8 | − 4 |
| $04\bar{6}$ | < 8 | + 3 |
| $04\bar{7}$ | < 8 | − 2 |
| $04\bar{8}$ | < 8 | + 1 |
| $04\bar{9}$ | < 8 | − 1 |
| $0,4,\overline{10}$ | < 8 | + 2 |
| $0,4,\overline{11}$ | < 8 | + 6 |
| $0,4,\overline{12}$ | < 8 | + 2 |
| $0,4,\overline{13}$ | < 8 | + 8 |
| $0,4,\overline{14}$ | < 9 | − 1 |
| $0,4,\overline{15}$ | 16 | +15 |
| $0,4,\overline{16}$ | < 9 | 0 |
| $0,4,\overline{17}$ | 32 | +38 |
| $0,4,\overline{18}$ | < 9 | − 8 |
| $0,4,\overline{19}$ | 72 | −76 |
| $0,4,\overline{20}$ | < 9 | + 7 |
| $0,6,\overline{18}$ | < 11 | +18 |
| $0,6,\overline{19}$ | 41 | −81 |
| $0,6,\overline{20}$ | 13 | +29 |
| $0,6,\overline{21}$ | < 11 | −11 |

carbon atom were determined from the data of Vainshtein & Pinsker (1950). One of the two hydrogen atoms was found to coincide roughly with the carbon atom and has been given the same coordinates.

In the projection along the shortest axis every second C–C distance is too short to be resolved with the available reflexions. In order to refine the coordinates of the carbon atoms several difference maps using $(F_o - F_c)$ as Fourier coefficients were prepared. It was then found that the two hydrocarbon chains in one half of the unit cell are not quite parallel. Thus the single subcell region first used had to be divided into two different ones. The difference maps were of course also used to refine the coordinates of the atoms outside the subcell regions. 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 0·17.

## Discussion of the results

Twinning is very common among crystals of form *B′* of *n*-pentadecanoic acid and has also been observed for other crystal forms of normal fatty acids. One exception is form *A′* of odd-numbered acids (von Sydow, 1954). Many other long-chain compounds exhibit twinning (see for instance Müller (1927) and Stenhagen, Vand & Sim (1952)), and it is obvious that it is very common in compounds with long hydrocarbon chains.

The orthorhombic packing of the hydrocarbon chains which appears in this crystal form is the most common one in long-chain compounds and therefore probably the most stable one. This is in agreement with the observations of Stenhagen & von Sydow (1953) and others, who have found that crystal form *C* of even-numbered acids and form *B′* of odd-numbered acids are stable at room temperature. The crystal structure of form *C* was determined by Vand, Morley & Lomer (1951). From their data it can be concluded that the packing of the hydrocarbon chains is of the orthorhombic type, and thus both crystal forms have this packing. The difference in the dimensions of the cross-section of this unit cell and the orthorhombic cell of Vainshtein & Pinsker (1950) is partly due to the chain length and partly to the nature of the end group (cf. Abrahamsson & von Sydow, 1954).

The hydrocarbon chains in this crystal form are probably straight except near the carboxylic groups, where a small deformation is noticed. The orthorhombic packing is very tight with half of the chains having their planes almost perpendicular to the planes of the other half, and it probably does not allow bending as easily as the triclinic packing found in crystal form *A′* (von Sydow, 1954), where all planes of the chains are parallel. Vand, Morley & Lomer (1951) suggest, however, that form *C* of lauric acid has its chains bent.

As has been pointed out, the two chains in one half of the unit cell are not quite parallel. This effect is probably caused by the carboxylic groups.

The two molecules held together by hydrogen bonds have their chain planes perpendicular in the same way as in form *C* of lauric acid (Vand, Morley & Lomer, 1951).

The increment of long spacing for this crystal form, according to Stenhagen & von Sydow (1953), is 2·20 Å. Thus the angle of tilt is between 61° and 57°, probably close to the first value if the distance between alternate carbon atoms is between 2·521 Å (found in lauric acid by Vand, Morley & Lomer (1951)) and 2·610 Å (found in strontium laurate by Morley & Vand (1949)).

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