ACTA CHEMICA SCANDINAVICA 17 (1963) 221–226

Polymorphism of 11-Bromoundecanoic Acid

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Five crystal forms of 11-bromoundecanoic acid have been found. The structure of three of these, the C-, D- and E-forms, have been described earlier. The other two crystal forms, B and B_1, are closely related but only the former is strictly isomorphous with the B-form of normal fatty acids. The phase behaviour is discussed and the infrared spectra are related to the crystal structures.

The possibilities of isomorphous replacement of atoms or groups of atoms in long-chain compounds with heavy atoms are studied at this Institute. In this connection the phase behaviour of 11-bromoundecanoic acid has been investigated for a comparison with lauric acid.

Five crystal forms have been obtained, two of which are isomorphous with the B- and C-forms of normal fatty acids. The nomenclature of the crystal forms has been based on that of even fatty acids [1]. The crystal forms isomorphous with unsubstituted fatty acids have got corresponding names (B- and C-forms). A crystal form which is very similar to the B-form has been called B_1. The other crystal forms, which have no correspondence in normal fatty acids, have been called D and E in order of decreasing long spacing.

EXPERIMENTAL

The preparation of the available samples of 11-bromoundecanoic acid of different degrees of purity has been described earlier [2], and the effect of impurities will be discussed in this report. The phase transitions and the stability range of the crystal forms have been studied in an X-ray camera built for continuous recording of diffraction pattern *versus* temperature (DPT) diagrams [3]. These diagrams are excellent for detection of phase transitions. The rate of heating or cooling was 15° per hour. CuK radiation was used and the distance between the specimen and the film plane was 10 cm. The behaviour at the transition points has been observed in a Kofler heating stage microscope [11]. X-Ray powder photographs were taken in a Guinier camera using Cu$K\alpha$ radiation. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer equipped with a sodium chloride prism. The solid substances were ground with potassium bromide and pressed to pellets (3 mg of substance was used for 300 mg of potassium bromide). The temperature of the sample during the run was kept at about 25° with the aid of a fan.

FORM B

Crystallization of very pure samples of 11-bromoundecanoic acid has been performed from different solvents at −20 and + 20°C, and the B-form was obtained in all cases. The existence of this form is remarkable as neither lauric acid nor myristic acid crystallize in the B-form [1].

Beautiful single crystals for X-ray work were grown from light petroleum (b.p. 40—60°C). Rotation and Weissenberg photographs taken with Cu$K\alpha$ radiation gave the following X-ray data:

Unit cell: monoclinic.
$a = 5.73 \pm 0.02$ Å; $b = 7.54 \pm 0.03$ Å; $c = 34.8 \pm 0.3$ Å;
$\beta = 118.8° \pm 0.6°$; $d(001) = 30.5 \pm 0.2$ Å.
Four molecules per unit cell.
Density calculated: 1.23 ± 0.01 g.cm^{-3}.
Absent reflexions: ($h0l$) when h odd, ($0k0$) when k odd.
Space group: $P\ 2_1/a$.

von Sydow gives the following unit cell data for the B-form of stearic acid [4]: $a = 5.591 \pm 0.011$ Å; $b = 7.404 \pm 0.008$ Å; $\beta = 117°22' \pm 7'$. Both a and b as well as the monoclinic angle β are significantly smaller than in 11-bromoundecanoic acid. This is in accordance with similar decreases in these dimensions with increasing chain length of the C-form of fatty acids [5]. As the X-ray diffraction pattern of the B_1-form is very similar to that of the B-form, identification of these crystal forms must be based on infrared spectra. The establishment of one of these forms as the true B-form is discussed in the paragraph on the infrared results.

FORM B_1

This crystal form was discovered by K. Serck-Hanssen at this Institute. The industrial sample (described in Ref.[2]) was purified by extraction and recrystallized from light petroleum (b.p. 40—60°C). Large well-shaped crystals were obtained in this way, and the infrared spectrum indicated that this was a new crystal form. The X-ray powder photograph, however, seemed to be identical with that of the B-form. An X-ray single-crystal study was therefore started. Within the experimental errors the unit cell was the same as for the B-form. The intensity distributions, however, show small dissimilarities in the two forms, particularly for ($h0l$)-reflexions. The small structural differences are probably located at the carboxyl groups, and a further discussion on this is found in the paragraph on the infrared absorption.

The crystals of the samples of the B- and the B_1-form investigated have somewhat different morphology. The B-form grows in rhombic plates like the B-form of stearic acid [4]. The edges [100] and [120] form an angle of 62° and the crystals are elongated in the [100]-direction. The B_1-form also crystallizes in (001)-plates elongated parallel to the [100]-edge but edges along [010], [110], and [120] do often appear on the same crystal.

Fig. 1. DPT diagram for the B-form

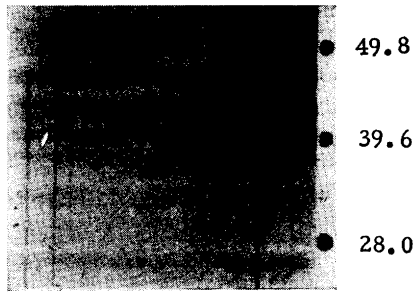


Fig. 2. DPT diagram for the C-form.

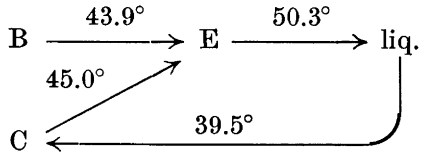
FORMS C, D AND E

The C-form is the only one isomorphous with a crystal form of lauric acid. A detailed comparison of these C-forms is given in Ref.[2]

The D- and E-forms are described in Refs.[6,7], respectively. Their formation and the effect of impurities is discussed further in the following paragraph.

PHASE TRANSITIONS

Heating of form B is illustrated by the DPT diagram in Fig. 1. A transition B → E takes place at 43.7—44.1°C and the E-form melts at 50.1—50.4°C. The B_1-form behaves in the same way. The melt solidifies to the C-form at 39.7—39.3°C. The DPT-diagram for heating of the C-form is reproduced in Fig. 2. The C-form undergoes a transition C → E at 44.8—45.2°C. Cooling and heating of the E-form have also been performed, showing that the transitions into the E-form are irreversible. The following scheme illustrates the behaviour of the polymorphous forms (the middle of the temperature intervals are given).



The D-form has only been found in very small amounts together with the C-form. From a solution in light petroleum (b.p. 40—60°C) of 11-bromoundecanoic acid and a small amount of its triglyceride these crystal forms were obtained. Otherwise they have only been found together in samples crystallized from the melt by very rapid cooling. A few single crystals were identified by their morphology and examined under the Kofler microscope. A phase transition occurred at 42°C, certainly D → E indicated by the formation of long needles, only shown by the E-form, and the melting point (50.3°C).

The transitions into the E-form are remarkable as the chains are completely rearranged. This transformation of the lateral packing of the molecules from

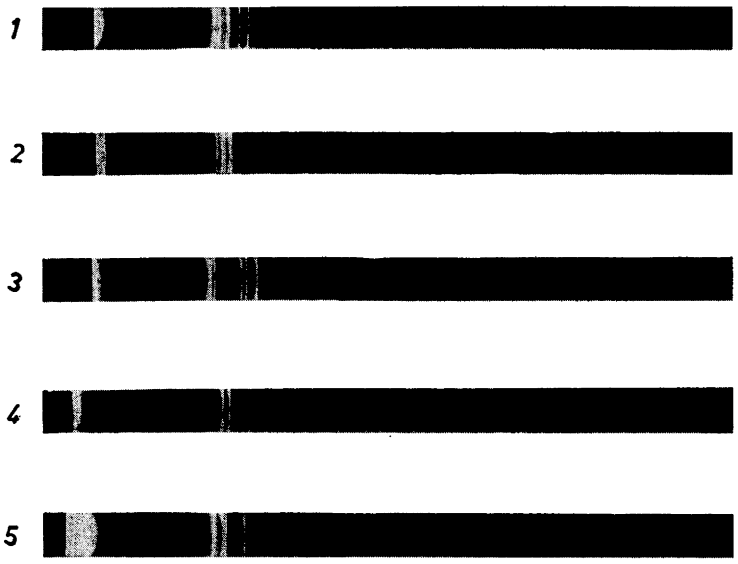


Fig. 3. X-Ray powder photographs of the B-form (1), the C-form (2), and the E-form (3). The B-form of stearic acid (4) and the C-form of lauric acid (5) are included for comparison.

head-to-head into head-to-tail is probably achieved by displacements of the molecules, which can be parallel during the transition. In that case the melt behaves like a nematic liquid crystal. The possibility that polar interaction between the bromine atoms and the carboxyl group hydrogens is responsible for this is briefly discussed in Ref.[7] These transitions do not take place in the solid state. Observation in the Kofler microscope showed that both forms are in equilibrium with liquid substance at the transition point. A considerable supercooling of the melt is necessary before the C-form crystallizes, as can be seen in the scheme above. If the melt is heated only a few degrees above the melting point, the E-form crystallizes from the melt on cooling. This indicates that some order persists after melting.

The importance of impurities is clearly demonstrated by the crystal forms obtained from solution. The industrial sample in a purified form gives the E-form from light petroleum, while recrystallization of this E-form has always given the E-form. The crystallization of mixtures of 11-bromoundecanoic acid with the triglyceride of this acid has also been studied. The C-form has been obtained from solutions containing less acid than triglyceride. When smaller amounts of triglyceride are present the B-form crystallizes, and with still less triglyceride the C- and D-form crystallize together.

The X-ray powder films of the different crystal forms are shown in Fig. 3. The patterns from the C-form of lauric acid and the B-form of stearic acid are given for comparison. They show that the isomorphism is not clearly evident from the powder patterns only, due to the large contribution from the bromine atoms to the total X-ray scattering.

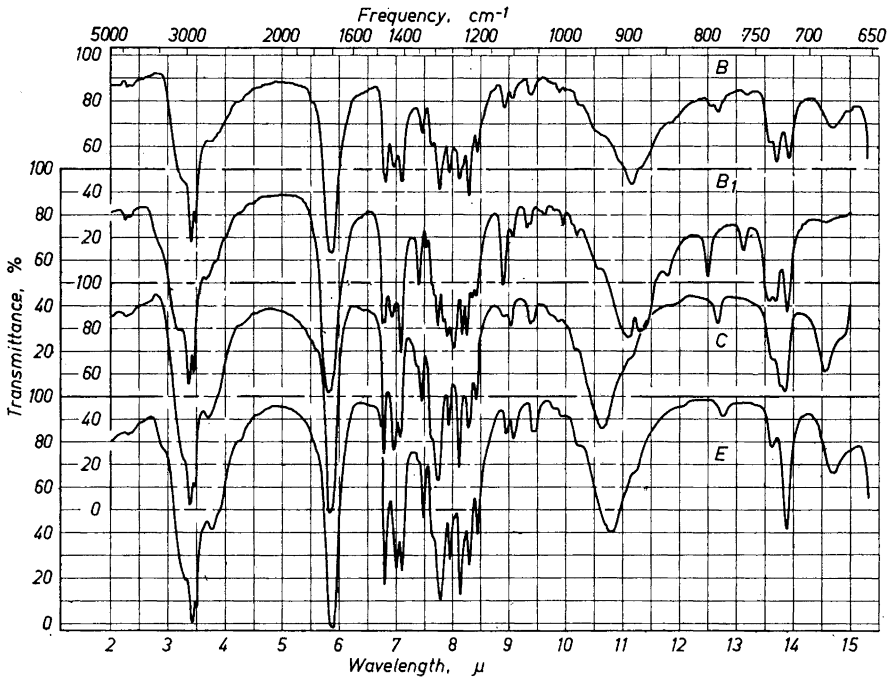


Fig. 4. Infrared absorption spectra of the crystal forms B, B_1, C, and E.

INFRARED ABSORPTION

The infrared spectra are given in Fig. 4. That of the D-form is not included, as only a few single-crystals could be identified from the mixture with the C-form. The identity of the crystal forms have been checked after the recording of their spectra. The B- and B_1-forms will be discussed first.

The carboxyl band in both forms shows a single peak with inflexions. The "mean value" for this band, defined by von Sydow [8] as the wave number that cuts the whole peak area in two equal parts, is 1705 cm^{-1} and 1720 cm^{-1} for the B- and B_1-forms, respectively. The corresponding value is 1711 cm^{-1} for the B-form of stearic acid [8]. The OH-out-of-plane band consists of one large peak at 895 cm^{-1} with shoulders for the bromo acid B-form. The B-form of stearic acid has a similar peak shape with the maximum absorption at 887 cm^{-1}. In the B_1-form, however, this band consists of two peaks about equal in intensity (at 902 and 883 cm^{-1}).

These similarities of the carboxyl group vibration between the B-form of 11-bromoundecanoic acid and the B-form of steric acid are considered to be sufficient to establish their isomorphism, while the use of their X-ray data were insufficient as mentioned before. There is probably a different hydrogen bond system in the B_1-form. Using the projection data of the B-form of steric acid [4] it is possible to calculate approximate three-dimensional carboxyl

group coordinates when a hydrogen bond length of 2.60 Å and a planar carboxyl group with carbon-oxygen distances 1.25 Å and 1.35 Å are assumed. These atomic positions indicate that two hydrogen bond systems are sterically possible, one of which is present in the B-form and the other in the B_1-form.

The OH-stretching vibration bands appear at 2910—2980 cm-1 for the B_1-form, at 2880—2950 cm^{-1} for the C-form, at 2870—2940 cm^{-1} for the B-form and at 2860—2930 cm^{-1} for the E-form. This indicates that the hydrogen bond strength increases in that order. The carbonyl band and the OH-out-of-plane band have the same positions in the C- and in the E-form. The "mean values" of these bands are: 1710 and 940 cm^{-1} for the C-form, and 1704 and 928 cm^{-1} for the E-form. The corresponding values are 1701 and 939 cm^{-1} for the C-form of palmitic acid [8].

The band progression corresponding to CH_2 twisting and wagging vibrations (1180—1330 cm^{-1}) is very similar for all forms. According to Chapman [9] the CH_2-rocking vibration in the 720 cm^{-1} region can be used for determination of the chain packing. This has been commented upon by Abrahamsson and Fischmeister [10]. Two peaks of the same intensity in this region indicate a chain packing where the plane of every second chain is perpendicular to the others, while one peak indicates parallel chains. The triclinic chain packing of the E-form and the orthorhombic packing ($O_{\perp}$) in the B-form are in accordance with the indications from their infrared absorption in this region. For the B_1- and C-forms, however, both with the orthorhombic chain packing ($O_{\perp}$), the corresponding peak shape is somewhat more complex and conclusions with regard to the chain packing based only on the infrared absorption would be uncertain.

I wish to thank Prof. E. Stenhagen, Dr. S. Abrahamsson and K. Serck-Hanssen for their interest and valuable discussions. Thanks are due to Mrs. M. Innes for technical assistance, Mrs. K. Nilsson for help with the infrared work, and Mr. L. Ahlquist for preparation of samples. I am also indebted to Dr. C. Lagercrantz for providing laboratory space in the Institute of Medical Physics. Grants in support of the Crystallography group have been obtained from *The National Institute of Arthritis and Metabolic Diseases, U.S.Public Health Service* (A-4006) and from *The Swedish Natural Science Research Council, The Swedish Medical Research Council* and *The Swedish Technical Research Council.*

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Received July 16, 1962.