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On the Structure of the Crystal Form E of 11-Bromoundecanoic Acid

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The molecules in the E-form of 11-bromoundecanoic acid form layers where the lateral arrangement of the chains is head-to-tail. The chains tilt 40° towards the end group planes. The triclinic cell contains two molecules related by a centre of symmetry, and the dimensions are: $a = 4.80 \pm 0.04$ Å; $b = 11.72 \pm 0.10$ Å; $c = 12.41 \pm 0.10$ Å; $\alpha = 107°11' \pm 1°$; $\beta = 92°34' \pm 1°$; $\gamma = 81°26' \pm 1°$.

Four crystal forms of 11-bromoundecanoic acid have been obtained, all of which transform into a fifth form, the E-form, at their melting point. The phase behaviour and the nomenclature of the different crystal forms are reported separately [1]. The most remarkable feature concerning the E-form is the lateral head-to-tail arrangement of the chains, as the other four forms, from which it is obtained, have the usual head-to-head chain arrangement.

PREPARATION OF CRYSTALS

The preparation of the available samples of 11-bromoundecanoic acid has been described earlier [2]. The E-form is easily obtained by heating any of the other crystal forms to their transition point between 40 and 45°C when the E-form is formed irreversibly. The E-form can also crystallize from the melt and from solution under special conditions described in the report of the phase behaviour [1]. The crystals for the X-ray work were grown in light petroleum (b.p. 40 – 60°C) and their melting point was 50.1 – 50.4°C. They were badly shaped thin needles along [100] and twin formation along the needle axis was very common. Many crystals were examined but only one gave reflexions of quality good enough for intensity estimation.

X-RAY DATA

Rotation and Weissenberg photographs were taken with Cu$K\alpha$ radiation about the a axis using a calibrated camera. The following X-ray data were obtained:

Unit cell: triclinic
$a = 4.80 \pm 0.04$ Å; $b = 11.72 \pm 0.10$ Å; $c = 12.41 \pm 0.10$ Å; $\alpha = 107°11' \pm 1°$; $\beta = 92°34' \pm 1°$; $\gamma = 81°26' \pm 1°$.
Long spacing $d(001)$: 11.87 ± 0.10 Å
Two molecules per unit cell
Density calculated: 1.23 ± 0.03 g.cm.$^{-3}$
Density observed: 1.22 g.cm.$^{-3}$

Space group $P\bar{1}$ was chosen. The intensities of the $(h0l)$ reflexions were estimated visually using the multiplefilm technique with scale. They were corrected for the polarization and Lorentz factors but not for absorption. Absolute values were later obtained by comparison with calculated structure factors.

SUBCELL

In the reciprocal lattice the periodic hydrocarbon chains should give rise to small groups of strong reflexions forming a sublattice. This sublattice is not so pronounced in 11-bromoundecanoic acid as in, *e.g.*, normal fatty acids due to the large contribution from the bromine atoms to the total scattering. Using mean values for the dimensions of the triclinic subcell given by Abrahamsson [3], a model of the reciprocal triclinic sublattice was made. This could be fitted into the reciprocal lattice with the sublattice points coinciding with groups of strong reflexions. The final structure also established this chain packing. The $(a_S c_S)$-plane of the triclinic subcell is parallel to the (bc)-plane in the unit cell, and the c_S subcell axis forms an angle of 66° towards the c axis.

STRUCTURE DETERMINATION

A Patterson (100)-projection was calculated from which the bromine position could readily be derived. A bromine-phased electron density projection then showed the whole structure. It is seen in Fig. 1 and a comparison with

Table 1. Atomic coordinates.

	y/b	*z/c*
C_1	0.165	0.088
C_2	0.277	0.155
C_3	0.361	0.288
C_4	0.477	0.293
C_5	0.580	0.377
C_6	0.688	0.445
C_7	0.206	0.462
C_8	0.105	0.392
C_9	0.990	0.256
C_{10}	0.881	0.256
C_{11}	0.782	0.165
Br	0.651	0.101
O_1	0.099	0.015
O_2	0.109	0.119

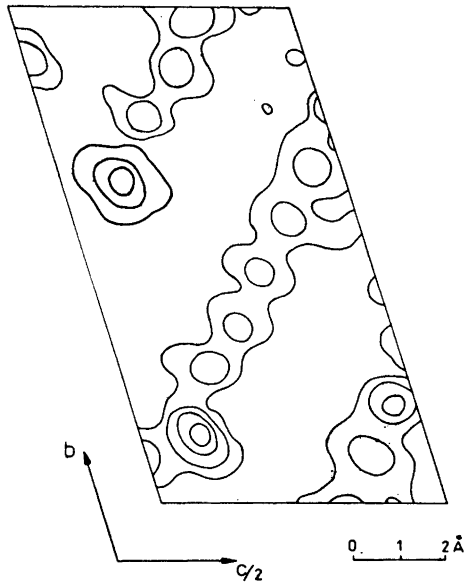

Fig. 1. Bromine-phased electron-density projection along the *a*-axis on an arbitary scale. Only every fifth contour is drawn around the bromine atom.

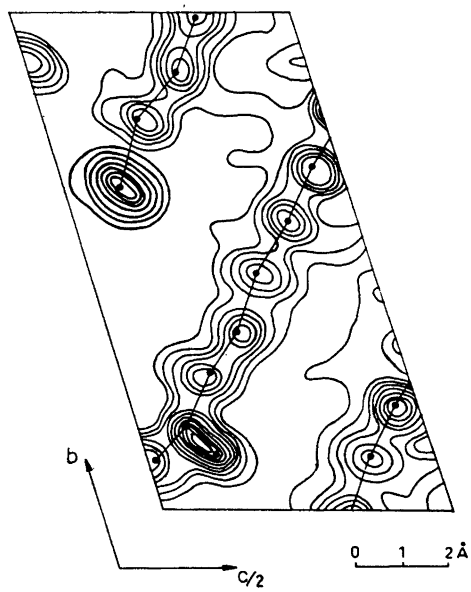

Fig. 2. Electron-density projection along the *a*-axis. Contours are given at intervals of 1 e. $Å^{-2}$ and at 5 e. $Å^{-2}$ around the bromine atom starting with 1 e. $Å^{-2}$.

Table 2. Observed and calculated structure factors.

hkl	$\|F_o\|$	F_c	*hkl*	$\|F_o\|$	F_c
0,0,0	—	11.7	0,4,$\bar{2}$	20.2	−18.5
2	8.5	7.3	$\bar{1}$	28.4	−28.3
3	24.2	−10.6	0	29.1	−29.1
4	30.0	−25.1	1	21.7	−17.3
5	27.8	−22.8	3	18.6	16.4
6	18.8	−15.3	4	24.8	21.4
8	5.2	8.7	5	20.1	18.0
9	8.2	12.0	8	15.9	−21.8
0,1,$\bar{7}$	13.2	16.3	0,5,$\bar{8}$	6.9	−10.3
$\bar{6}$	14.8	−19.1	$\bar{7}$	15.2	−15.8
$\bar{5}$	11.9	11.9	$\bar{6}$	9.9	− 9.4
$\bar{2}$	11.3	−10.3	$\bar{4}$	7.0	7.0
$\bar{1}$	12.9	−12.9	$\bar{3}$	11.9	11.8
1	10.3	5.3	$\bar{2}$	10.9	12.5
2	20.2	16.1	0	9.5	− 8.9
3	27.3	22.2	1	18.2	−16.5
4	23.5	19.5	2	23.6	−20.1
5	12.1	10.5	3	20.6	−17.6
6	4.4	2.5	4	9.7	−11.3
			6	13.0	14.5
0,2,$\bar{9}$	5.0	− 7.4			
$\bar{8}$	12.5	−11.4	0,6,$\bar{9}$	10.4	11.0
$\bar{7}$	15.3	−15.1	$\bar{6}$	10.7	− 5.8
$\bar{6}$	8.9	− 6.5	$\bar{4}$	15.3	−14.2
$\bar{4}$	24.0	22.4	$\bar{3}$	16.3	−17.4
$\bar{3}$	86.2	80.8	$\bar{2}$	14.4	−14.6
$\bar{2}$	5.1	12.9	0	13.6	12.4
0	15.6	−12.9	1	18.7	18.3
1	31.8	−28.5	2	16.6	16.3
2	36.4	−33.0	3	8.1	7.8
3	29.1	−27.0	5	26.3	−24.8
5	11.2	6.6	6	12.9	−16.8
6	19.0	17.1	7	9.6	−11.1
7	17.7	17.8			
8	12.1	14.1	0,7,$\bar{6}$	7.6	7.3
			$\bar{5}$	7.6	9.8
0,3,$\bar{6}$	6.6	− 6.6	$\bar{2}$	7.2	−10.1
$\bar{5}$	14.4	−12.9	$\bar{1}$	9.1	−15.8
$\bar{4}$	20.6	−18.1	0	7.9	−13.9
$\bar{2}$	13.8	− 9.1	3	17.1	15.8
$\bar{1}$	12.4	13.0			
0	18.5	17.7	0,8,$\bar{3}$	9.1	9.1
1	21.2	16.3	$\bar{2}$	10.3	11.8
2	10.4	5.4	$\bar{1}$	8.2	10.1
4	12.7	−13.7	2	21.2	−20.0
5	13.1	−16.4	3	8.6	−10.2
6	13.3	−15.4	4	7.8	− 7.7
7	6.7	−10.3			
9	8.4	11.2	0,9,$\bar{3}$	7.0	− 7.7
			0	10.8	12.6
0,4,$\bar{7}$	8.1	9.4	2	8.4	11.2
$\bar{6}$	32.4	33.2			
$\bar{3}$	7.8	−10.1	0,10,$\bar{1}$	11.1	−12.7

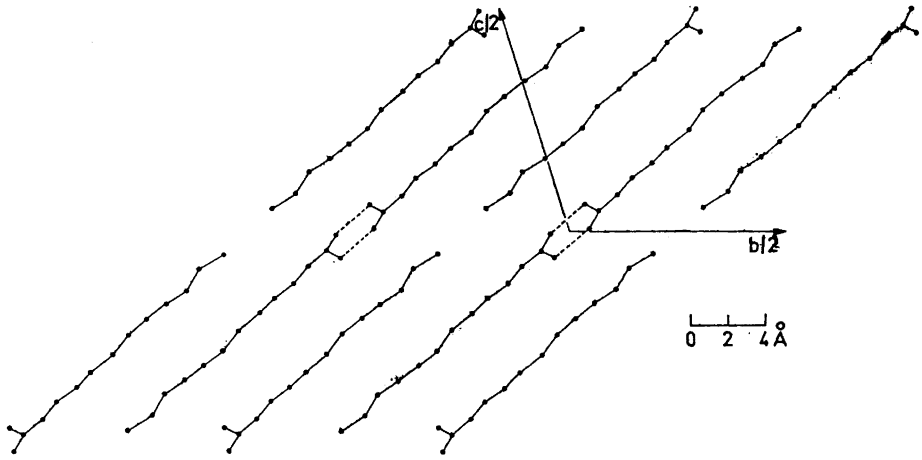

Fig. 3. Molecular arrangement projected along the *a*-axis.

the final electron density projection in Fig. 2 shows only small differences. All atoms were included in the next cycle of structure-factor and electron density calculation. A difference synthesis was made based on the new coordinates which showed anisotropic vibration for the bromine atom. Anisotropic vibration parameters were therefore introduced for the bromine atom, while an over-all isotropic temperature factor was used for the other atoms. The structure was refined by successive difference syntheses. The final temperature factors used were $\exp(-0.075\ k^2-0.101\ l^2-0.052\ kl)$ for the bromine atom and B = 3.1 Å^2 for the other atoms. No hydrogen atoms were included. The reliability index R is 0.15.

The coordinates of the atoms are given in Table 1, and observed and calculated structure factors are listed in Table 2. The final electron density projection is shown in Fig. 2. Structure factor calculations and Fourier summations were performed on a Mercury computer using programs described by Mills and Rollett [4]. The atomic scattering factors for bromine were taken from Thomas and Umeda [5] and for carbon and oxygen from Berghuis *et al.*[6]

DISCUSSION

The structure seen along the short axis is shown in Fig. 3. The result is limited to one projection only as no other projection with acceptable resolution could be obtained and the quality of the crystals was too bad for a collection of three-dimensional intensity data.

As the subcell c_S axis is parallel to the (*bc*)-plane the distance between alternate carbon atoms in the chain can be calculated from these projection data. The mean value is 2.55 Å.

The angle of tilt of the chains towards the end group planes is 40° which is a remarkably small value. As pointed out in connection with the structure description of the D-form of 11-bromoundecanoic acid [7] there seems to be a tendency for a smaller angle of tilt in the ω-bromine substituted acids than in the unsubstituted fatty acids. Here, however, the lateral head-to-tail arrangement of the chains is of course also connected with the actual tilt. No polar interaction seems to exist between the carboxyl group hydrogen and the bromine atom, as this distance is too long. Such an attraction may however influence the orientation of the molecules at the transition point, so that a head-to-tail arrangement is achieved when the E-form crystallizes.

The hydrogen bond is of the usual type holding the molecules together in dimers. Assuming ordinary dimension in the carboxyl group approximate x-coordinates for these atoms were calculated. There is one short contact between non-equivalent oxygens in adjacent cells in the a-direction, and there is probably a polar attraction between the hydrogen atom bonded to one of these oxygens and the other oxygen atom. Such an interaction along the a-axis may explain the morphology as it is parallel to the needle-direction.

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