

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

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The structure of one crystal form of 11-bromoundecanoic acid has been shown to be isomorphous with the C-form of dodecanoic (lauric) acid and a comparison with that form is made. The bromine contact planes are somewhat closer than the corresponding methyl planes in lauric acid.

The crystal behaviour of 11-bromoundecanoic acid is being investigated. The aim is to study the effect of a bromine atom replacing the terminating methyl group in a simple compound, where the crystal forms of the unsubstituted compound (lauric acid) are known and a direct comparison can be made. The possibility of isomorphous replacement of methyl groups with bromine atoms is of course of great importance for the structure analysis of complicated long-chain compounds.

PREPARATION OF CRYSTALS

Several samples of 11-bromoundecanoic acid were available. Two of them had been prepared by different workers using the method described by Ashton & Smith¹. This acid is an intermediate in the production of the French polyamide "Rilsan" and an industrial sample of the acid from the Organico company (Paris) was purified and kindly supplied by Mr. K. Serck-Hanssen. The available samples have been purified in different ways and are used for a detailed investigation of the polymorphic behaviour of the bromo acid².

Crystallization from the melt gives the C-form, as even-numbered fatty acids do. The C-form has only been obtained from solution when somewhat impure samples have been used. It was found accidentally that beautiful single-crystals of the C-form were formed from a solution of a mixture of the acid and its triglyceride dissolved in light petroleum (b.p. 40–60°). These were used for the X-ray work. The C-form melts at 44.5–45.5°. The melt immediately solidifies in a higher melting modification.

X-RAY DATA

Rotation and Weissenberg photographs were taken with CuK radiation about the *a* and *b* axes using a calibrated camera. X-Ray data are listed in

Table 1 together with those of the C-form of lauric acid. The unit cell for lauric acid given by Vand *et al.*³ has been transformed to suit the choice of a unit cell where β is as near 90° as possible. The transformation matrix is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{bmatrix}$$

Absent reflexions are ($h0l$) when h is odd and ($0k0$) when k is odd corresponding to space group $P2_1/a$. The unit cell contains four molecules.

The intensities of the ($h0l$) reflexions were estimated visually using the multiple-film 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.

STRUCTURE DETERMINATION

From the X-ray data it was apparent that the structure was isomorphous with the C-form of lauric acid. The coordinates given by Vand *et al.*³ were not used as the first trial structure, however, as experiences in the use of the heavy-atom method were desirable for long-chain compounds with a regular distribution of light atoms.

A Patterson (010)-projection was calculated and the bromine position readily derived. A bromine-phased electron density projection showed the whole structure and no other peaks of appreciable height.

All atoms were included in the next cycle of structure-factor and electron density calculation. A difference synthesis was made and new coordinates and temperature factors were derived. The hydrogen atoms were included at this stage with coordinates taken from the data given by Vainshtein and Pinsker⁴. The reliability index R_1 was here 0.25. Anisotropic least-squares refinement for atoms except hydrogens was then applied. Due to the large number of parameters in comparison with the number of independent reflexions the shifts were correlated with difference syntheses. It was found that only the heavy atom showed marked anisotropic vibration whereas the vibrations of the light atoms could be fairly well accounted for by an isotropic temperature factor ($B = 4.5 \text{ \AA}^2$). All positional shifts from the third round of least-squares refinement were considerably less than the estimated standard deviations

Table 1. X-Ray data.

	11-Bromoundecanoic acid	Dodecanoic acid
a	$9.66 \pm 0.06 \text{ \AA}$	$9.524 \pm 0.02 \text{ \AA}$
b	$4.96 \pm 0.03 \text{ \AA}$	$4.965 \pm 0.01 \text{ \AA}$
c	$28.07 \pm 0.15 \text{ \AA}$	$27.62 \pm 0.05 \text{ \AA}$
β	$99^\circ 54' \pm 1'$	$96^\circ 55' \pm 7'$
$c \sin \beta$	$27.65 \pm 0.15 \text{ \AA}$	$27.42 \pm 0.06 \text{ \AA}$
density calc.	$1.22 \pm 0.02 \text{ g.cm}^{-3}$	1.034 g.cm^{-3}
density obs.	1.24 g.cm^{-3}	1.032 g.cm^{-3}

Table 2. Coordinates of the atoms.

Atom	11-Bromoundecanoic acid		Dodecanoic acid	
	x/a	z/c	x/a	z/c
O ₁	0.8725	0.0060	0.8799	0.0067
O ₂	0.9495	0.0520	0.9381	0.0538
C ₁	0.8703	0.0385	0.8655	0.0429
C ₂	0.7680	0.0741	0.7500	0.0750
C ₃	0.7570	0.1160	0.7483	0.1208
C ₄	0.6384	0.1517	0.6251	0.1483
C ₅	0.6296	0.1931	0.6251	0.1958
C ₆	0.5314	0.2258	0.4983	0.2242
C ₇	0.5150	0.2701	0.4955	0.2739
C ₈	0.4055	0.3020	0.3783	0.2992
C ₉	0.3948	0.3436	0.3724	0.3483
C ₁₀	0.2691	0.3791	0.2499	0.3742
C ₁₁	0.2552	0.4215	0.2393	0.4237
C ₁₂	—	—	0.1183	0.4492
Br	0.1116	0.4531	—	—

and the R_1 -value was 0.14. The final temperature factor used for the bromine atom was $\exp(-0.015 h^2 - 0.0013 l^2 - 0.0012 hl)$.

The final electron density projection is shown in Fig. 1. The coordinates of the atoms are given in Table 2 together with those of the C-form of lauric acid transformed to the same unit cell. Observed and calculated structure factors are listed in Table 3. Structure factor calculations, Fourier summations and least-squares refinement were performed on a Mercury computer using programs described by Mills and Rollett⁵. The atomic scattering factors for bromine were taken from Thomas and Umeda⁶ and for carbon and oxygen from Berghuis *et al.*⁷

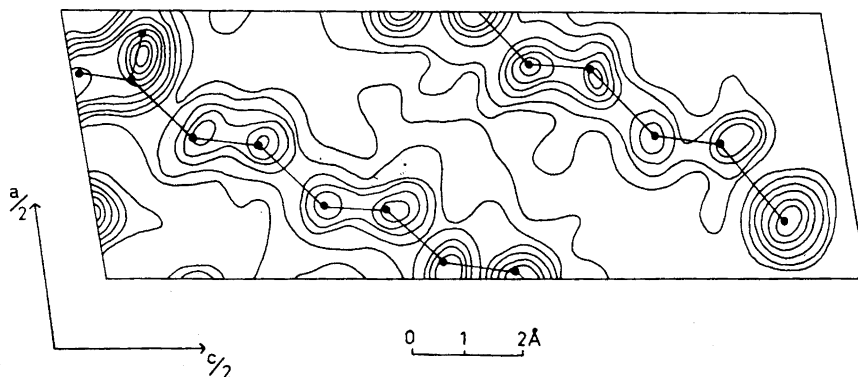


Fig. 1. Electron-density projection along the b axis. Contours are given at intervals of $1 \text{ e}\text{\AA}^{-3}$ for carbon and oxygen and $5 \text{ e}\text{\AA}^{-3}$ for bromine starting with $1 \text{ e}\text{\AA}^{-3}$.

Table 3. Observed and calculated structure factors.

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
0 0 0	—	138	2 0 $\overline{26}$	8.5	10.1
3	5.5	— 5.0	$\overline{27}$	1.7	— 5.4
4	12.8	10.7	4 0 0	22.4	—20.7
5	5.9	4.7	1	12.5	10.2
6	9.8	— 6.8	2	12.7	—12.4
7	16.9	14.4	5	9.8	— 9.9
8	25.2	—22.5	6	6.4	— 9.4
9	27.0	20.4	7	8.7	— 8.6
10	28.8	—24.4	8	17.1	18.4
11	24.1	20.5	9	12.8	—18.0
12	29.2	—23.7	10	11.0	12.7
13	13.5	14.2	11	11.9	—14.6
14	6.2	— 4.0	13	4.6	— 8.3
15	7.5	7.7	$\overline{1}$	15.4	14.0
18	8.5	11.5	$\overline{2}$	29.1	—22.7
20	9.7	12.4	$\overline{3}$	12.2	12.3
21	5.0	— 7.9	$\overline{4}$	27.0	—26.6
22	8.4	10.5	$\overline{6}$	27.8	—27.4
2 0 1	8.9	9.7	$\overline{7}$	19.7	—18.0
2	6.9	5.7	$\overline{8}$	11.0	10.2
3	6.1	7.0	$\overline{9}$	17.1	—17.4
4	72.5	—70.7	$\overline{10}$	17.6	16.3
5	22.0	20.5	$\overline{11}$	18.1	—19.3
6	32.7	—31.5	$\overline{12}$	18.7	18.4
7	9.6	14.0	$\overline{13}$	17.6	—16.8
8	10.1	—12.2	$\overline{14}$	19.0	17.1
9	7.9	5.8	$\overline{15}$	12.5	— 8.5
12	9.5	11.5	$\overline{16}$	11.7	9.9
13	7.9	—11.2	$\overline{19}$	12.9	12.4
14	10.8	13.9	$\overline{20}$	22.8	—19.5
15	9.8	—13.1	$\overline{22}$	9.9	—11.8
16	15.5	17.8	$\overline{24}$	8.8	—10.5
17	8.0	—10.5	6 0 0	8.2	11.5
$\overline{1}$	5.2	— 4.8	1	7.9	—11.0
$\overline{2}$	14.0	15.0	2	8.3	10.1
$\overline{3}$	14.0	—12.9	3	9.3	—13.4
$\overline{4}$	26.5	27.7	4	7.1	8.2
$\overline{5}$	18.2	—16.8	5	8.0	— 9.3
$\overline{6}$	29.1	28.3	2	7.0	5.3
7	18.4	—15.6	$\overline{3}$	12.3	12.9
8	25.6	26.9	$\overline{4}$	13.4	—16.0
9	8.5	— 9.4	$\overline{5}$	7.4	8.3
$\overline{10}$	16.2	21.9	6	11.8	—14.7
$\overline{13}$	9.9	11.8	7	10.9	13.0
$\overline{14}$	11.9	—14.4	8	13.2	—14.8
$\overline{15}$	11.8	14.8	9	8.4	9.8
$\overline{16}$	17.1	—16.4	$\overline{10}$	12.4	—12.5
$\overline{17}$	13.5	15.1	$\overline{15}$	13.5	—13.4
$\overline{18}$	15.5	—15.5	$\overline{16}$	15.8	14.0
$\overline{19}$	9.7	10.5	$\overline{19}$	9.1	—11.3
$\overline{20}$	9.1	—10.4	$\overline{20}$	8.4	7.6
$\overline{21}$	5.0	4.2	$\overline{21}$	7.6	— 4.6
$\overline{22}$	5.1	— 5.9	8 0 0	9.9	12.2
$\overline{24}$	10.6	12.6			

DISCUSSION

The structure is completely isomorphous with the C-form of lauric acid having the common orthorhombic chain packing ($O \perp$) and the carboxyl groups in the (021)-plane of the subcell. In the C-form of lauric acid the chains are clearly bent in the a -axis projection. It is not uncommon that, even in normal long-chain compounds, the molecular packing requires small deviations from the planar zig-zag conformation. As expected, irregularities in the carbon chains become larger when the packing arrangement is more complex such as in branched fatty acids^{8,9}. The carbon atoms in the bromine substituted acid do not strictly follow the orthorhombic subcell according to the b -axis projection, as the normal to the chain axis through a carbon atom in one chain does not pass through carbon atoms of neighbouring chains. As this also applies to the same projection of lauric acid it seems likely that the chains are bent also in the bromo acid.

Differences in the dimensions and the coordinates are small as can be seen from Tables 1 and 2. The largest differences are found in the distances between alternate carbon atoms which can be calculated if one neglects that the chains are bent. The mean value is 2.65 Å for the bromo acid as compared with 2.51 Å for lauric acid. The standard deviations in the positions estimated from the least-squares treatment are 0.01 Å for the bromine atom, 0.05 Å for the oxygen atoms, and 0.08 Å for the carbon atoms. The angle of tilt of the carbon chains towards the (a, b)-plane is 54.3°, nearly the same as in lauric acid where it is 54.8°.

The effect of the bromine atom replacing a methyl group can best be studied by a comparison of the packing distances over the bromine and the methyl contact planes, respectively. The fact that lauric acid and 11-bromoundecanoic acid crystallize in isomorphous forms is in itself remarkable and indicates that an ω -bromine atom behaves very similar to a methyl group.

Assuming a bromine-carbon distance of 1.91 Å and that the y -coordinate of the carbon atoms are the same as in lauric acid, it is possible to calculate the packing distances over the bromine gap. All distances less than 5.5 Å from one methyl group to carbon atoms on the other side of the methyl gap for the C-form of lauric acid are given by von Sydow¹⁰ as a basis for estimation of the van der Waals interaction. These distances are given in Table 4

Table 4. Distances between the bromine atom and its nearest neighbours on the other side of the bromine gap and corresponding distances for lauric acid.

Number of distances	Atom on the other side of the gap	Distance (Å)	Corresponding distance (Å) for lauric acid
1	Br	3.77	3.85
2	Br	4.15	4.28
1	C ₁₁	3.95	4.01
1	C ₁₁	4.77	4.72
1	C ₁₁	5.40	5.18
1	C ₁₀	5.19	5.45
1	C ₁₀	5.37	5.45

together with the corresponding distances for 11-bromoundecanoic acid. The bromine-bromine distances are about 0.1 Å shorter than the methyl-methyl distances. The other distances for the bromo acid are smaller or larger than the corresponding ones in lauric acid, due to the effects of a shorter gap but longer chain-terminating bond distance. The end group contact planes are evidently closer in 11-bromoundecanoic acid than in lauric acid corresponding to a van der Waals radius for the bromine atom about 0.05 Å less than that of the methyl group, in accordance with the literature values (*cf.* Ref.¹¹).

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