

The Crystal Structure of the D-Form of 11-Bromoundecanoic Acid

KÅRE LARSSON

Crystallography Group, Institute of Medical Biochemistry, University of Göteborg, Sweden

The D-form of 11-bromoundecanoic acid is monoclinic with $a = 5.63 \pm 0.03$ Å, $b = 5.33 \pm 0.03$ Å, $c = 44.05 \pm 0.25$ Å and $\beta = 92^\circ 10' \pm 40'$. The space group is $P2_1/c$ with four molecules per unit cell. The structure consists of double-layers of dimers like most fatty acids. The chains are parallel within these double-layers but the direction of the chain-tilt alternates in successive double-layers.

11-Bromoundecanoic acid is investigated in connection with a study of the crystallographic effect of an ω -bromine atom replacing a terminating methyl group in long-chain compounds. Five crystal forms of the bromo acid have been found. Their phase behaviour is reported separately¹, where also the principles of nomenclature are given. In the D-form the layer arrangement is of a new type. Although the D-form crystallizes only under very special circumstances it has been possible to determine the crystal structure completely.

PREPARATION OF CRYSTALS

The preparation of the available samples of 11-bromoundecanoic acid has been described earlier². The D-form has only been obtained in very small amounts together with the C-form, and the conditions for formation of these crystal forms from solution are described in Ref.² The crystals formed beautiful plates with edges along [100] and [010] and showed (001)-cleavage. At 42°C the D-form melts and solidifies immediately in a higher melting form (the E-form³).

X-RAY DATA

Rotation and Weissenberg photographs were taken about the a and b axes with a calibrated camera using $\text{CuK}\alpha$ radiation. The following X-ray data were obtained:

Unit cell: monoclinic

$a = 5.63 \pm 0.03$ Å; $b = 5.33 \pm 0.03$ Å; $c = 44.05 \pm 0.25$ Å; $\beta = 92^\circ 10' \pm 40'$

Four molecules per unit cell

Table 1. Atomic coordinates.

	x/a	y/b	z/c
C ₁	0.664	0.208	0.0230
C ₂	0.801	0.013	0.0384
C ₃	0.927	0.135	0.0644
C ₄	0.047	0.870	0.0807
C ₅	0.221	0.960	0.1043
C ₆	0.321	0.679	0.1165
C ₇	0.487	0.746	0.1452
C ₈	0.638	0.497	0.1505
C ₉	0.815	0.566	0.1798
C ₁₀	0.940	0.292	0.1884
C ₁₁	0.119	0.373	0.2147
Br	0.345	0.093	0.2272
O ₁	0.273	0.734	0.0025
O ₂	0.478	0.348	0.0346

Density calculated*: $1.22 \pm 0.02 \text{ g.cm}^{-3}$
 Long spacing $d(001)$: $44.02 \pm 0.15 \text{ \AA}$

The space group is $P2_1/c$ corresponding to absent reflexions ($h0l$) when l odd and ($0k0$) when k odd. The intensities of the ($0kl$) and ($h0l$) reflexions were estimated visually using the multiplefilm technique with a scale. Corrections were applied for the Lorentz and polarisation factors but not for absorption. Absolute values were later obtained by comparison with calculated structure factors.

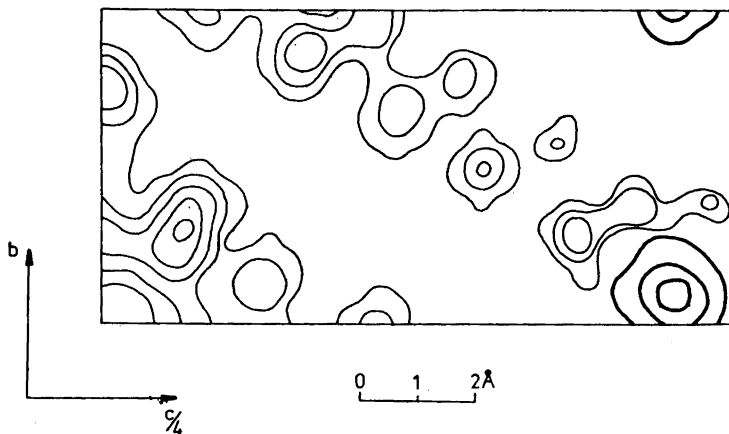


Fig. 1. Bromine-phased electron-density projection along the a -axis on an arbitrary scale. Only every tenth contour is drawn around the bromine atom.

* The density of the crystals has not been measured as no sample of the pure D-form has been obtained.

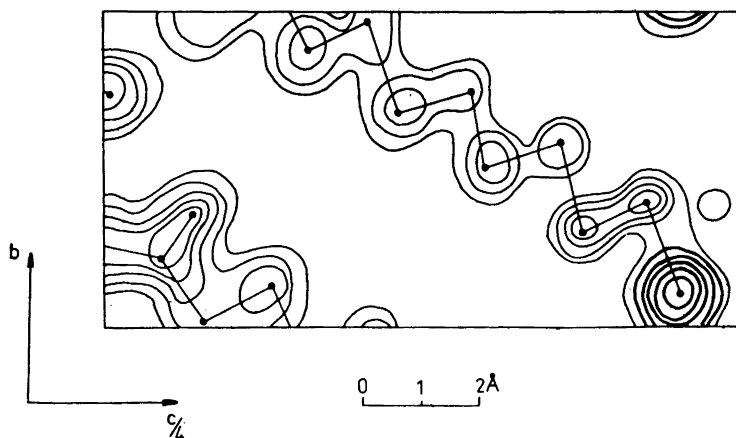


Fig. 2. Electron-density projection along the a -axis. Contours are given at intervals of 1 e. \AA^{-2} and at 5 e. \AA^{-2} around the bromine atom starting with 2 e. \AA^{-2} .

STRUCTURE DETERMINATION

The arrangement of the chains was evident directly from the space group requirements and the intensity distribution among the $(h0l)$ and $(0kl)$ -reflexions, as the intensity of reflexions corresponding to planes parallel to the chain axes dominate. From Patterson (100) - and (010) -projections the position of the bromine atom in the asymmetric unit was derived. Bromine-phased electron density projections along the short axes were then calculated and the (100) -projection is shown in Fig. 1. The whole structure was readily derived from these projections, and all atoms were included in the next cycle of structure-factor and electron density calculation.

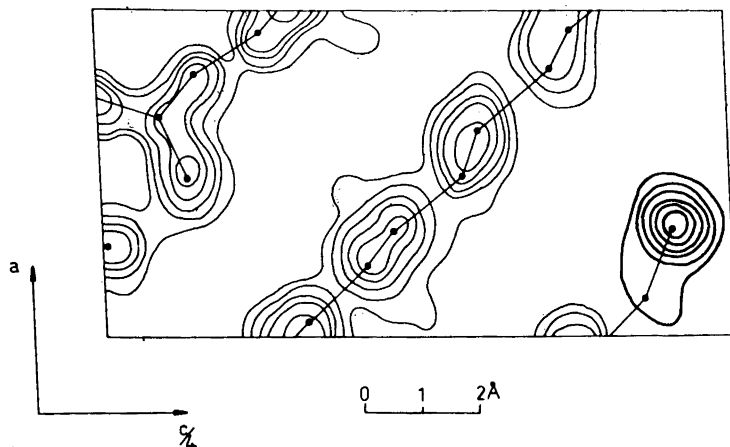


Fig. 3. Electron-density projection along the b -axis. Contours are given at intervals of 1 e. \AA^{-2} and at 5 e. \AA^{-2} around the bromine atom and carbon atom C_{11} starting with 2 e. \AA^{-2} .

Table 2. Observed and calculated structure factors ($0kl$).

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
0,0, 0	—	468	0,2, 1	57	— 68
4	95	116	2	48	— 53
6	30	— 30	3	63	66
8	40	45	5	36	— 40
12	36	— 28	6	36	— 45
14	41	35	7	40	41
16	76	— 73	8	14	— 11
18	72	62	9	22	— 27
20	77	— 70	10	24	— 22
22	68	74	11	19	14
24	65	— 66	12	13	— 12
26	71	72	13	19	18
30	17	13	15	14	— 13
			16	35	— 39
0,1, 1	25	29	17	33	28
2	17	— 4	18	28	24
3	21	14	19	62	— 68
4	29	25	21	34	31
5	18	8	23	47	— 51
6	128	—141	25	32	35
7	107	—111	27	24	— 24
8	33	33	29	23	22
9	75	90			
10	81	— 76			
11	81	— 76	0,3, 2	19	— 13
12	38	36	4	25	24
13	75	74	6	41	— 37
14	46	— 38	8	42	38
15	62	— 63	10	57	— 60
16	34	36	12	63	64
17	45	43	13	27	— 36
18	19	— 18	14	28	— 35
19	28	— 23	16	28	23
20	20	18	18	00	— 10
25	20	17			
26	24	28			
27	20	18			
29	22	— 23	0,4, 0	29	— 15
30	37	34	1	29	— 22
31	31	35	2	29	21
32	20	— 23	3	29	25
33	39	— 40	4	30	— 18
35	23	21	6	30	29

The atomic coordinates were refined by cycles of structure factor calculation and difference syntheses. From the appearance of the difference syntheses it seemed reasonable to apply an anisotropic temperature factor on the bromine atom and an isotropic over-all temperature factor on the other atoms. The final values for these are: $\exp(-0.075 h^2 - 0.00055 l^2 + 0.0019 hl)$ and $\exp(-0.059 k^2 - 0.00104 l^2 - 0.0011 kl)$ for the bromine atom and $B = 5.9 \text{ \AA}^2$ and 6.5 \AA^2 for the other atoms in the xz - and yz -projection, respectively. No hydrogen atoms were included. The R -values are 0.17 for ($h0l$) and 0.12 for ($0kl$).

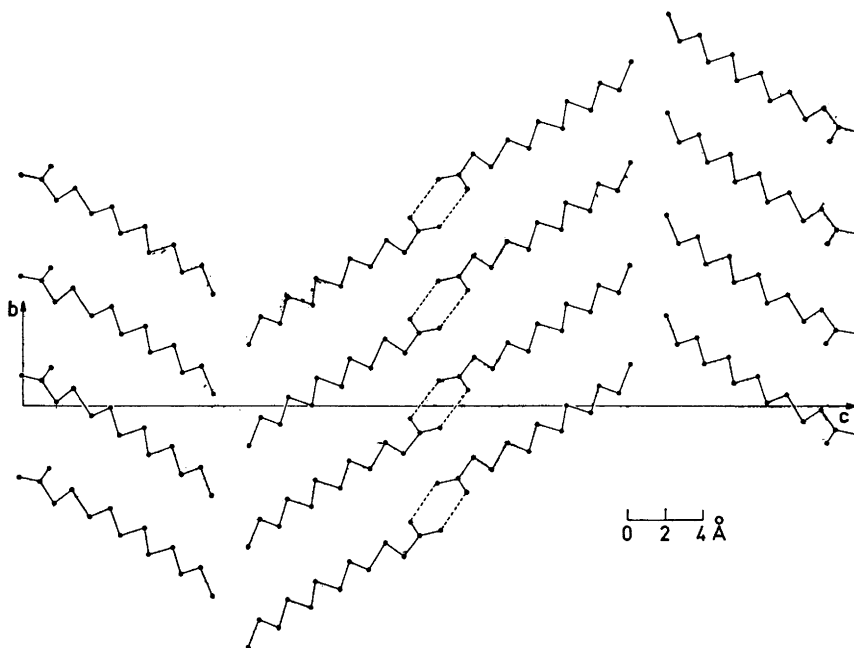
Table 3. Observed and calculated structure factors ($h0l$).

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
0,0, 0	—	468	1,0,44	17	— 17
6	32	— 30			
8	47	46	2,0, $\overline{22}$	16	— 22
12	36	— 29	$\overline{20}$	10	32
14	37	37	$\overline{18}$	84	—103
16	78	— 77	$\overline{16}$	78	68
18	69	68	$\overline{14}$	48	— 18
20	75	— 77	$\overline{12}$	39	40
22	86	82	$\overline{10}$	83	— 86
24	76	— 75	$\overline{8}$	24	1
26	91	82	$\overline{6}$	51	— 63
30	24	17	$\overline{4}$	17	— 2
36	14	17	0	43	— 37
38	16	— 21	2	47	45
40	19	24	4	87	— 72
42	20	— 25	6	66	68
			8	128	—107
			10	39	23
			12	34	— 61
1,0, $\overline{34}$	30	— 41	14	31	31
$\overline{32}$	28	44	16	53	— 68
$\overline{30}$	31	— 41	20	11	— 15
$\overline{28}$	44	50	24	23	24
$\overline{26}$	45	— 51	26	28	— 40
$\overline{24}$	51	53	28	32	41
$\overline{22}$	36	— 33	30	32	— 42
$\overline{20}$	35	37	32	36	44
$\overline{18}$	11	3	34	19	— 24
$\overline{16}$	29	9	36	34	31
$\overline{14}$	60	57	38	18	— 13
$\overline{12}$	27	— 43			
$\overline{10}$	167	167			
$\overline{8}$	258	—257			
$\overline{6}$	11	8	3,0, $\overline{26}$	18	25
$\overline{4}$	96	— 91	$\overline{24}$	27	— 24
$\overline{2}$	52	57	$\overline{20}$	27	— 44
0	67	— 63	$\overline{18}$	23	26
2	7	6	$\overline{16}$	18	— 11
4	21	— 11	$\overline{14}$	29	46
6	40	— 33	$\overline{10}$	14	26
8	65	61	$\overline{8}$	19	25
10	79	— 61	$\overline{6}$	16	— 13
12	124	108	$\overline{4}$	39	30
14	83	— 80	$\overline{2}$	43	— 44
16	147	129	0	59	44
18	67	— 57	2	39	— 37
22	30	— 33	4	41	40
24	11	18	6	44	— 53
26	15	— 20	8	39	40
28	18	— 23	10	17	— 12
30	12	14	14	13	18
32	30	— 38	16	11	— 8
34	28	30	18	34	42
36	29	— 37	20	28	— 25
38	21	32	22	44	45
40	20	— 34	24	33	— 38

Table 3. Cont.

hkl	$ F_o $	F_c	hkl	$ F_o $	F_c
3,0,26	29	30	4,0, 0	19	- 10
28	35	- 38	2	21	28
30	15	7	10	14	- 11
			12	26	22
4,0, $\overline{12}$	14	- 8	14	29	- 27
$\overline{10}$	16	18	16	30	30
$\overline{8}$	28	- 21	18	35	- 26
$\overline{6}$	27	23	20	42	26
$\overline{4}$	28	- 23	22	15	2
$\overline{2}$	30	36	24	16	10

The final electron density projections are shown in Fig. 2 and Fig. 3. The extra peak in the yz -projection also seen in the bromine-phased projection (Fig. 1) is a series termination effect, as it is not present in the difference syntheses. The coordinates of the atoms are given in Table 1. Observed and calculated structure factors are listed in Tables 2 and 3. The atomic scattering factors for bromine were taken from Thomas and Umeda² and for carbon and oxygen from Berghuis *et al.*³ Structure factor calculations and Fourier summations were performed on a Mercury computer using programs described by Mills and Rollett⁴.

Fig. 4. Molecular arrangement projected along the a -axis.

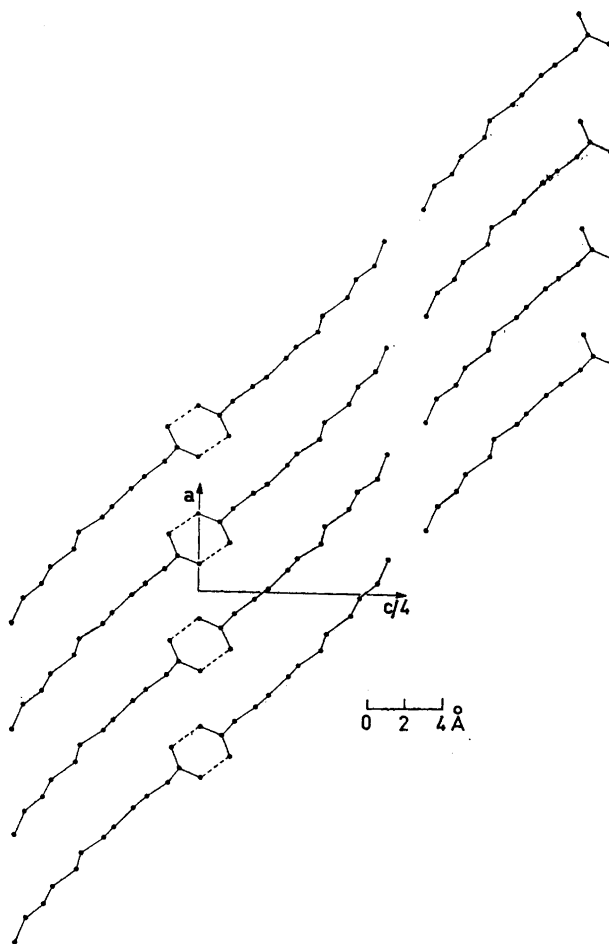


Fig. 5. Molecular arrangement projected along the *b*-axis.

DISCUSSION

The arrangement of the molecules is shown in Figs. 4 and 5. The most striking feature of the structure is the chain arrangement obvious in the *a*-axis projection. The chains are parallel in double-layers and tilted at the same angle towards the end-group planes, but the direction of the chain-tilt alternates in successive double-layers. Such arrangement of the layers has only been found in monoglycerides⁷. Change of chain direction within a molecule is however more common and has been found in methyl branched fatty acids⁸, cyclopropane fatty acids⁹ and oleic acid¹⁰.

Table 4. Bond lengths and angles in the molecule.

O ₁ -C ₁	1.23 Å	O ₁ -C ₁ -O ₂	116°
O ₂ -C ₁	1.40 Å	O ₁ -C ₁ -C ₂	116°
C ₁ -C ₂	1.45 Å	O ₂ -C ₁ -C ₂	127°
C ₂ -C ₃	1.48 Å	C ₁ -C ₂ -C ₃	106°
C ₃ -C ₄	1.71 Å	C ₂ -C ₃ -C ₄	98°
C ₄ -C ₅	1.48 Å	C ₃ -C ₄ -C ₅	106°
C ₅ -C ₆	1.68 Å	C ₄ -C ₅ -C ₆	98°
C ₆ -C ₇	1.59 Å	C ₅ -C ₆ -C ₇	104°
C ₇ -C ₈	1.59 Å	C ₆ -C ₇ -C ₈	103°
C ₈ -C ₉	1.64 Å	C ₇ -C ₈ -C ₉	104°
C ₉ -C ₁₀	1.66 Å	C ₈ -C ₉ -C ₁₀	103°
C ₁₀ -C ₁₁	1.57 Å	C ₉ -C ₁₀ -C ₁₁	100°
C ₁₁ -Br	2.02 Å	C ₁₀ -C ₁₁ -Br	112°

The chains are tilted 41° to the end group planes, which is a remarkably small value. According to Kitaigorodskii¹¹ the displacement of adjacent chains in *n*-paraffin hydrocarbons does not exceed one subcell period *c_s* as contacts between end groups and CH₂-groups will arise thus reducing the density of packing. This is also illustrated in normal fatty acids but in branched fatty acids the mutual displacement exceeds one subcell period due to space requirements of the branches⁸. In dicarboxylic acids¹²⁻¹⁴ the angles of tilt for both even and odd are about the same as for this D-form, which may indicate that the best accommodation of the carboxylic groups in the chain packing is achieved at this tilt. The difference in the shape between an *ω*-bromine atom and a methyl group and between the terminating bond lengths seem to favour a larger tilt of the chains in the bromo acids than in the unsubstituted fatty acids.

The molecules are hydrogen bonded into dimers. The length of the hydrogen bond is 2.73 Å and the angle C-OH...O is 109°. There are three more oxygen

contacts shorter than 4.0 Å. The C₂-C^{O₁} group is planar and the interplanar distance between the two hydrogen bonded groups is 1.17 Å.

Table 5. Distances between the bromine atom and its nearest neighbours on the other side of the gap for the C- and the D-form of 11-bromoundecanoic acid.

Number of distances	<i>C-form</i>		Number of distances	<i>D-form</i>	
	Atoms on the other side of the gap	Distance, <i>R</i> (Å)		Atoms on the other side of the gap	Distance (Å)
2	Br	3.73	1	Br	3.77
2	Br	5.18	2	Br	4.15
1	C ₁₁	4.06	1	C ₁₁	3.95
1	C ₁₁	3.90	1	C ₁₁	4.77
1	C ₁₀	4.41	1	C ₁₁	5.40
			1	C ₁₀	5.19
			1	C ₁₀	5.37

The bond lengths and angles are given in Table 3. The standard deviations in the atomic positions estimated from Cruickshank's formula¹⁷ are:

$$\begin{array}{l} \text{Br: } \sigma(x) = \sigma(y) = \sigma(z) = 0.01 \text{ \AA} \quad \text{O: } \sigma(x) = \sigma(y) = \sigma(z) = 0.05 \text{ \AA} \\ \text{C: } \sigma(x) = \sigma(y) = \sigma(z) = 0.08 \text{ \AA}. \end{array}$$

The packing of the hydrocarbon chains is triclinic (first described by Vand and Bell¹⁶ and later by von Sydow¹⁵ and Abrahamsson⁸). The subcell dimensions calculated from the final packing distances are: $a_s = 4.40 \text{ \AA}$; $b_s = 5.53 \text{ \AA}$; $c_s = 2.48 \text{ \AA}$; $\alpha_s = 67^\circ$; $\beta_s = 105^\circ$; $\gamma_s = 113^\circ$; the volume per CH_2 -group is 25.1 \AA^3 . In the b -axis projection of the structure the carbon chains look irregular and bent. The best least-squares plane through the carbon atoms in the chain has been calculated and the carbon atoms are situated up to 0.26 \AA from this plane. The distortion in the chain packing is thus significant. The carboxyl group plane is twisted 65° from this chain plane, and the bromine atom lies 0.30 \AA away from the latter plane.

The packing of the bromine and group planes can be expressed in terms of distances between a bromine atom and its neighbours on the other side of the gap. All such distances less than 5.5 \AA are collected in Table 5 together with those of the crystal form C².

$\Sigma n \cdot R^{-6}$, where R is an interatomic distance and n the number of equivalent distances, was used by von Sydow¹⁵ as a rough estimation of the van der Waals interaction. A calculation of the interaction over the gap according to this formula based only on the bromine atoms indicates a stronger interaction between the bromine planes in the C- than in the D-form.

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