The Crystal Structure of the B-Form of Fatty Acids

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The structure of the crystal form B of stearic acid has been rein-
vestigated in order to obtain detailed information of the relation
between this form and an unusual form (B₁) of fatty acids recently
found. There is a disorder of static type in the polar region of the struc-
ture and the dominating structure corresponds to dimerization of the
molecules by hydrogen bonds.

A new crystal form of normal fatty acids occurring in 11-bromoundecanoic acid [1] appeared to be closely related to the ordinary B-form. This form, termed B_1, seemed to differ from the B-form only in the carboxyl group region as their X-ray diffraction patterns are very similar but the OH-out-of-plane vibration in the infrared absorption spectra of the two forms are quite different. This is a most remarkable type of polymorphism in long-chain compounds.

The crystal structure of the B-form of stearic acid was earlier determined in one projection [2] only, and as a deeper insight into the relations between the two forms requires knowledge about their structures in three dimensions, we started a reinvestigation of the B-form.

Holland and Nielsen [3] have described a new form of stearic acid (termed E) and according to the infrared absorption data this form appears to be isotypic with the B_1-form.

X-RAY DATA

Crystals prepared by von Sydow [2] were used. Rotation and Weissenberg photographs were taken about the a and b axes using $CuK\alpha$ radiation. The unit cell given by von Sydow [2] was transformed to a cell with β as near 90° as possible (for convenience in the computer calculations). The dimensions are then

$$a = 5.591 \pm 0.011 \text{ Å} \quad b = 7.404 \pm 0.008 \text{ Å} \quad c = 43.99 \pm 0.10 \text{ Å}$$

$$\beta = 94.6 \pm 0.15°$$

The unit cell contains four molecules related by space group symmetry $P2_1/a$. It was noticed, however, that three diffuse reflexions appeared on Weissenberg photographs exposed for a very long time. The indices of these reflexions are (0,2.5,0), (0,3,0) and (0,5,0) corresponding to a disorder with an "ideal" lattice (following Wooster's nomenclature [4]) without 2_1-symmetry and doubled in the b-axis direction. Many crystals were examined all showing these diffuse reflexions with the same relative intensities. The disorder in the structure will be further discussed below.

The reflexion intensities were estimated visually using the multiplefilm technique. 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 ANALYSIS

Approximate (xz)-coordinates were obtained from a Patterson (010)-projection and the known coordinates of the (100)-projection.[2] The (xz)-projection was first refined by a few cycles of structure factor and electron density calculations. A difference synthesis showed pronounced anisotropic temperature movements in the hydrocarbon chain region of the structure. Full-matrix least-squares refinement was then started with anisotropic temperature factors for all atoms except for those in the carboxyl group (as indicated by the difference map). The hydrogen atoms were included in the structure factor calculations with positions according to known data from normal paraffins. The structure was refined to an R-value of 0.168 when the shifts were about one third of the standard deviations.

The final (xz)-coordinates from the present analysis and y-coordinates according to von Sydow[2] were used for a three-dimensional least-squares refinement. The refinement did not proceed normally: the agreement between observed and calculated structure factors improved very slowly and the vibration parameter values fluctuated strongly. This is probably an effect of the disorder which evidently seems to show up to a smaller extent in the (xz)-projection. The three-dimensional refinement was therefore not continued further. All the structural parameters given here are those derived from projectional data. The three-dimensional electron-density series (Fig. 1) was, however, calculated in order to see whether the disorder influences the appearance of the electron density noticeably, and it will be discussed below in connection with the disorder.
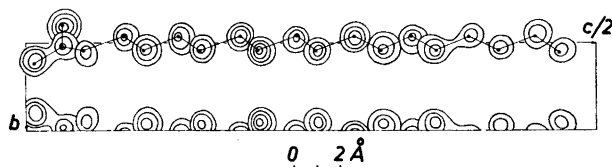

Fig. 1. A composite drawing of the three-dimensional electron density series. Contours are given at intervals of 1 e·Å⁻³ starting with 2 e·Å⁻³.

Table 1. Observed and calculated structure factors (h0l).

h 0 l	100 F_o	100 $|F_c|$	h 0 l	100 F_o	100 $|F_c|$
0 0 12	3135	−3325	9	1327	−1611
14	3725	−3977	10	2732	−2831
16	4035	−3876	2 0 11	9981	−10615
18	7435	−6423	13	5123	−4209
20	8164	7622	15	3059	−2832
27	1069	1269	17	1965	−1277
28	1098	1257	19	1698	−1893
29	1234	1613	21	1586	−1502
30	1033	906	23	1585	1149
31	1181	1422	25	1731	1488
38	2782	2899	27	1856	1356
39	1331	1691	29	2447	2983
40	3126	−2831	30	1253	1433
41	1193	− 786	31	9785	−7482
42	1029	−1032	−4 0 36	1712	−2574
44	1422	−1689	35	1713	1441
−2 0 31	986	1104	34	1237	962
30	1373	1911	19	1012	−1127
29	3289	3823	16	1858	−1083
28	1952	−2414	15	986	310
27	6563	−5894	13	973	−1828
26	1165	− 772	5	1531	− 553
24	1695	1291	4	1527	1943
22	1751	1753	3	1734	1571
21	811	712	2	1413	1517
20	1675	1505	1	1729	1573
19	775	− 576	4 0 2	2477	−2105
18	1601	−1408	4	6791	5343
16	1190	−1483	7	1543	1760
15	914	− 233	9	1225	757
13	2481	−2435	22	3590	−3295
12	777	− 333	23	1694	1324
11	5591	−4820	24	2184	2995
10	3897	−3866	−6 0 5	1960	1895
9	13141	10159	3	1971	−1333
8	7150	−6854	0 0 4	946	892
7	7039	−7733	5	2075	3323
6	3672	−3782	7	1730	2359
4	2347	−1885	10	1619	−1955
3	983	− 984	19	1929	−1292
2	1531	981	22	1790	1831
1	1076	−1018	23	1649	− 942
2 0 1	1216	1031	24	1902	1824
2	1386	506	25	1907	1935
3	1227	−1211	26	1657	1464
4	1579	−1682	34	1399	1618
5	1421	1086	35	828	765
6	1850	−1978	36	1466	1992
7	1459	−1596	46	808	−1064
8	2464	−2494	2 0 0	1064	1194

The calculations were performed on the Datasaab D21 computer using programmes written by Abrahamsson *et al.*[5] The atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. III, p. 202.

DISCUSSION OF THE RESULTS

The final positional and vibrational parameters are given in Table 1. Observed and calculated structure factors are listed in Table 2. The average value for the carbon-carbon bond distance is 1.53 and the average bond angle in the hydrocarbon chain is 114.4° (using y-coordinates from Ref. 2).

The molecular arrangement viewed along the a-axis has been shown earlier [6] and a detailed view of the packing in the carboxyl group region is illustrated in Fig. 2 based on positions derived from the three-dimensional electron-density maps as the carboxyl group atoms are not resolved in the short-axes projections. The molecules are hydrogen bonded into dimers. A second short intermolecular oxygen-oxygen contact (3.52 Å) is shown in Fig. 2, and it is obvious that only a rather small displacement or twisting of the carboxyl group in the asymmetric unit is needed in order to change the hydrogen bonding into infinite chains parallel to the b-axis. Such infinite chains of helical hydrogen bonds have been found earlier in formic [6] and acetic [7] acid and also in 2D-methyloctadecanoic acid [8] and (—)-2-methyl-2-ethyl-eicosanoic acid.[9]

Table 2. Atomic coordinates with standard deviations given within brackets and vibration parameters of the (xz)-projection. The anisotropic temperature factor is defined by

$$\exp-2\pi^2(h^2a^*\cdot U_{11}^2 + l^2e^{*2}\cdot U_{33} + 2hla^*c^*\cdot U_{31})$$

|	x	$\sigma(x)$	z	$\sigma(z)$	U_{11}	U_{33}	I_{13}	B
O1	0.220	(0.032)	0.0069	(0.0030)	—	—	—	1.4
O2	−0.007	(0.025)	0.0331	(0.0028)	—	—	—	1.3
C1	0.246	(0.035)	0.0326	(0.0043)	—	—	—	1.2
C2	0.439	(0.031)	0.0512	(0.0037)	0.0001	0.0070	−0.0226	—
C3	0.411	(0.039)	0.0871	(0.0038)	0.0721	0.0001	0.0145	—
C4	0.609	(0.029)	0.1049	(0.0037)	0.0083	0.0041	−0.0260	—
C5	0.553	(0.043)	0.1347	(0.0051)	0.0842	0.0437	0.0140	—
C6	0.752	(0.047)	0.1523	(0.0041)	0.0985	0.0127	−0.0010	—
C7	0.817	(0.031)	0.1894	(0.0041)	0.0001	0.0223	−0.0020	—
C8	1.009	(0.042)	0.2042	(0.0053)	0.0816	0.0506	−0.0323	—
C9	0.979	(0.033)	0.2392	(0.0046)	0.0186	0.0391	−0.0374	—
C10	1.207	(0.030)	0.2554	(0.0049)	0.0001	0.0984	0.0549	—
C11	1.266	(0.023)	0.2882	(0.0034)	0.0001	0.0107	0.0035	—
C12	1.427	(0.032)	0.3108	(0.0040)	0.0317	0.0624	0.0422	—
C13	1.494	(0.035)	0.3390	(0.0041)	0.0453	0.0220	−0.0148	—
C14	1.650	(0.028)	0.3593	(0.0037)	0.0063	0.0271	−0.0242	—
C15	1.730	(0.043)	0.3884	(0.0069)	0.0775	0.2010	−0.0599	—
C16	1.923	(0.037)	0.4132	(0.0046)	0.0835	0.0610	−0.0361	—
C17	1.915	(0.028)	0.4464	(0.0042)	0.0001	0.0772	−0.0799	—
C18	2.129	(0.041)	0.4672	(0.0043)	0.1001	0.0498	−0.0060	—
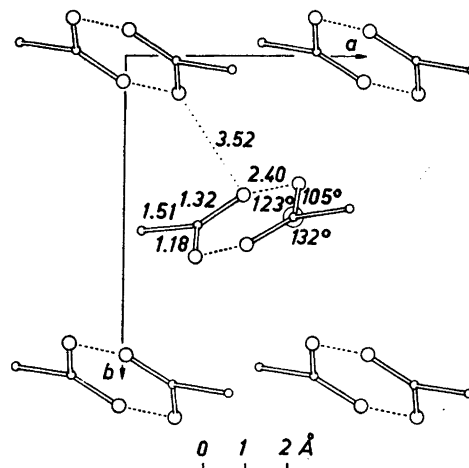
Fig. 2. Detail of the carboxyl group region
projected along the c-axis,

Disorder in the hydrocarbon chain region in this structure is very improbable as this chain packing $(O\perp)$ as well as this type of layer stacking occurs frequently in long-chain compounds. A disorder in the carboxyl group region corresponding to the two alternative hydrogen bond systems, however, would give just the same diffuse diffraction effects as we have observed with an "ideal" lattice with doubled b-axis and lacking the 2_1-symmetry of the "distribution" lattice.[4] The three-dimensional electron-density series (Fig. 1) indicates that one alternative (with dimers) dominates very strongly as no spurious peaks of considerable height appear. It must, however, be emphasized that the calculation of phase angles is based only on one alternative, which of course favours this structure on the maps.

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