The Crystal Structure of the B-form of Stearic Acid

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The crystal structure of the B-form of stearic acid has been studied by X-ray diffraction. The structural parameters were refined by the block-diagonal least-squares method, and the final R value was 0.084. In this structure, the bond between the second and third carbon atoms was found to be the *gauche* conformation, although the other bonds were in the *trans* conformation usually seen in normal fatty acids.

The crystal structure of the B-form of stearic acid has been studied only by two-dimensional Fourier methods. von Sydow[1] determined the crystal structure in the a-axis projection, and subsequently Larsson and von Sydow[2] determined it in the b-axis projection. Larsson and von Sydow[2] mentioned, however, that an attempted three-dimensional refinement was not successful because of the disorder in the crystal.

The present authors could obtain fairly good single crystals of the B-form of stearic acid, and reinvestigated its crystal structure.

Experimental

Stearic acid was purified by recrystallization from a methanol solution. The B-form crystal was obtained by crystallization in a 2,2,4-trimethylpentane solution, kept for two weeks at room temperature.

The infrared absorption spectrum showed that the crystal was in the B-form, not in the E-form discovered by Holland and Nielsen.[3] Twinning was not observed for the crystal used.

The diffraction intensities were measured by means of a Rigaku-Denki four-circle diffractometer by using graphite monochromated Cu $K\alpha$ radiation.† The crystal data and experimental conditions are given in Table 1, compared with the corresponding data of other workers.[1,2]

Structure Determination

The $|F_c(hkl)|$ values calculated from (x,z) coordinates by Larsson *et al.*[2] and the (y,z) coordinates calculated by von Sydow,[1],†† did not agree with the $|F_o(hkl)|$ values obtained in this experiment; the disagreement of $(11l)$ reflections was especially

Table 1. Crystal data, experimental conditions, and methods of analysis

	Present work (1977)	von Sydow[1] (1955)	Larsson and von Sydow[2],[a] (1966)
Crystal system	Monoclinic	Monoclinic	Monoclinic
a	5.587(10) Å	5.591(11) Å	5.591(11) Å
b	7.386(6)	7.404(8)	7.404(8)
c	49.33(8)	49.38(10)	43.99(10)
β	117.24°(9)	117.22°(7)	94.60°(15)
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$
Total number of reflections	640($2\theta \leqq 120$)	158($\theta \leqq 60$)	100
Measurement of intensity	Four-circle diffractrometer with a scintillation counter	Weisenberg photograph by eye	Weisenberg photogradh by eye
$\frac{\sum\|k\|F_o^p\| - \|F_o^A\|\|}{\sum\|F_o^A\|}$ [b]	—	0.19(k=1.45)	0.21(k=1.00)
Analysis	Three-dimensional Least-squares method	$0kl$ projection Fourier and difference Fourier method	$h0l$ projection Full matrix least-squares method (Three-dimensional least-squares refinement was not successful.)
R	0.084	0.18	0.168

a) A transformed unit cell given by von Sydow (1955) was chosen for convenience of calculation. However, the c and β values given by Larsson *et al.* might be somewhat erroneously determined; more reasonable values would be c=43.84 Å and β=89.56°. If these corrective values are used, the unit cell given by Larsson *et al.* can be transformed by the following matrix to that of Sydow or the present authors.

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 4 & 0 & 1 \end{vmatrix}$$

b) $|F_o^p| : |F_o|$ of the present work. $|F_o^A| : |F_o|$ by other authors.[1,2]

† The table of the observed and calculated structure factors has been deposited with the Office of the Chemical Society of Japan (Document No. 7828).

†† The z coordinates prepared by Larsson *et al.*[2] are almost identical with those prepared by von Sydow.[1]

noticeable. The least-squares method did not lead to further refinement at the R-value of 37% when their coordinates were used.

The present authors, therefore, reinvestigated the structure, determining the positions of carbon atoms from the Patterson map and the packing of the molecules.

The positions of oxygen atoms were obtained by means of difference synthesis. The hydrogen-atom positions, with the exception of that of the carboxyl hydrogen atom, were calculated by assuming C–H distances of 1.10 Å and a tetrahedral arrangement. The structure was refined by the block-diagonal least-squares method using the HBLS program (Ashida).[4] The R-value was reduced to 0.084. The final atomic parameters obtained are listed in Table 2.

The y and z coordinates obtained by the present authors do not significantly differ from those of von Sydow,[1] but the x coordinates of atoms, especially those near the carboxyl group, were not in agreement with those prepared by Larsson *et al.*[2]

Figure 1 illustrates the difference in the two structures by the projection along the b-axis. The two structures are different, especially near the carboxyl group. The atomic positions prepared by Larsson *et al.*[2] were too erroneous to be refined by the least-

Table 2(a). Fractional atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$) for C and O atoms

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	−1338(41)	278(29)	333(5)	391(103)	110(66)	8(2)	190(68)	60(11)	21(9)
C2	1564(30)	442(33)	578(5)	−189(74)	316(69)	8(2)	−136(69)	−16(8)	29(10)
C3	2181(31)	−458(30)	876(4)	170(85)	148(53)	3(1)	80(63)	−9(8)	8(7)
C4	910(38)	391(29)	1056(5)	356(105)	138(53)	8(2)	254(72)	57(11)	−16(9)
C5	2053(43)	−452(34)	1368(5)	710(151)	219(68)	5(2)	−205(89)	20(12)	13(9)
C6	803(41)	391(34)	1562(4)	535(124)	236(64)	2(1)	−132(83)	−7(10)	13(8)
C7	2045(32)	−328(31)	1881(5)	53(83)	177(59)	10(2)	−18(61)	46(10)	−17(9)
C8	753(35)	382(34)	2074(4)	210(98)	273(66)	5(2)	100(74)	5(9)	36(9)
C9	1945(46)	−367(32)	2399(5)	780(165)	134(55)	7(2)	4(82)	75(14)	−24(8)
C10	779(40)	413(32)	2595(5)	450(118)	152(54)	6(2)	23(80)	25(11)	−14(8)
C11	2004(37)	−356(30)	2920(5)	232(104)	126(51)	10(2)	104(70)	59(11)	−7(9)
C12	715(36)	373(33)	3106(5)	307(113)	206(65)	8(2)	225(74)	56(11)	6(9)
C13	2006(43)	−395(34)	3433(5)	748(157)	188(63)	5(2)	−51(89)	60(13)	−3(8)
C14	831(41)	388(34)	3629(5)	577(135)	229(70)	5(2)	−181(85)	44(11)	−3(9)
C15	2097(43)	−385(35)	3957(6)	546(141)	242(70)	11(2)	56(87)	101(14)	−33(10)
C16	876(37)	363(33)	4151(5)	261(108)	245(69)	7(2)	148(74)	27(10)	16(9)
C17	2224(54)	−419(39)	4476(6)	1104(200)	308(84)	7(2)	70(115)	97(16)	5(11)
C18	1155(49)	326(43)	4689(6)	445(139)	513(116)	13(3)	−235(113)	58(15)	−38(14)
O1	−2062(28)	1301(21)	94(3)	414(79)	216(39)	8(1)	102(49)	50(8)	35(7)
O1	−3041(25)	−764(21)	361(3)	356(75)	257(44)	7(1)	−101(57)	29(7)	12(6)

Table 2(b). Atom coordinates ($\times 10^3$) and isotropic temperature factors for H atoms (Å)

	X	Y	Z	B		X	Y	Z	B
H(C2)	167(88)	164(81)	63(9)	29(19)	H(C11)	427(40)	−19(32)	304(5)	10(7)
H(C2)	317(72)	−20(64)	48(8)	25(15)	H(C11)	175(40)	−175(35)	291(5)	10(7)
H(C3)	434(26)	−46(22)	103(3)	4(4)	H(C12)	−134(39)	17(34)	299(5)	10(7)
H(C3)	149(42)	−187(35)	86(5)	11(7)	H(C12)	78(38)	185(34)	311(4)	10(6)
H(C4)	−112(42)	8(33)	93(5)	11(7)	H(C13)	401(50)	−5(43)	355(6)	14(9)
H(C4)	126(44)	189(37)	109(5)	13(8)	H(C13)	180(42)	−191(36)	341(5)	11(8)
H(C5)	404(36)	−21(28)	148(4)	8(6)	H(C14)	−136(34)	10(28)	351(4)	7(5)
H(C5)	173(33)	−199(28)	134(4)	7(6)	H(C14)	112(34)	184(30)	365(4)	8(6)
H(C6)	−149(37)	5(28)	145(4)	8(6)	H(C15)	419(52)	−23(42)	404(6)	15(10)
H(C6)	114(34)	182(30)	158(4)	7(6)	H(C15)	177(39)	−182(32)	394(4)	9(6)
H(C7)	424(44)	−19(36)	199(5)	12(8)	H(C16)	−121(41)	22(33)	405(5)	10(7)
H(C7)	180(41)	−175(38)	188(5)	12(7)	H(C16)	111(33)	189(28)	415(4)	7(5)
H(C8)	−136(39)	16(32)	196(5)	10(7)	H(C17)	417(48)	−24(43)	458(6)	15(9)
H(C8)	80(40)	189(36)	209(5)	10(7)	H(C17)	193(31)	−182(26)	445(4)	6(5)
H(C9)	406(45)	−11(38)	251(6)	13(9)	H(C18)	−104(31)	6(25)	459(4)	5(5)
H(C9)	178(30)	−180(26)	238(3)	5(5)	H(C18)	234(51)	−25(30)	494(5)	10(6)
H(C10)	−142(33)	13(28)	247(4)	8(6)	H(C18)	134(47)	178(36)	470(5)	12(8)
H(C10)	97(36)	183(31)	261(4)	9(6)					

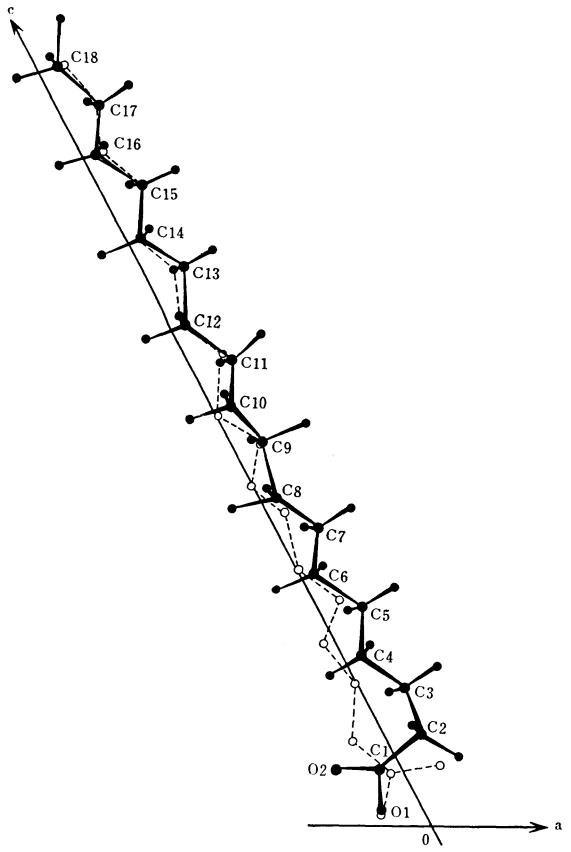

Fig. 1. The molecular structure projected along the b-axis. The structure obtained by Larsson *et al.* is shown by dotted lines (transformed into author's unit cell).

squares calculations.

Discussion

The bond lengths, bond angles, and internal rotation angles are shown in Table 3. An ORTEP[6] drawing is shown in Fig. 2.

It is evident from Fig. 1 or Fig. 2 that the molecules of the B-form of stearic acid do not form an all-*trans* zigzag chain, such as is usually found in fatty acids. The bond between the second and the third carbon atoms is in the gauche conformation. The internal rotation angle of this bond is calculated to be 68°, as is indicated in Table 3(c). von Sydow[1] suggested that the hydrocarbon chain was deformed near the carboxylic group, but he gave no details. Larsson *et al.*[2] did not mention this deformation; their structure was seen to be, rather, an all-*trans* zigzag chain.

The planarity of the chain is shown in Table 4. The dihedral angle between the plane of the carbon main chain and the plane containing the carboxyl group is 70°.

The subcell is orthorhombic, with dimentions of a_s=4.96 Å, b_s=7.39 Å, and c_s=2.50 Å. This is nearly the same as the C-form of lauric acid.[5]

The arrangement of the end group is shown in Fig. 3. As is commonly found in fatty acids, the molecules are bound together to form dimers through hydrogen bonds between the carboxyl groups. The hydrogen bond length is 2.65 Å, and the closest intermolecular

Table 3(a). Bond lengths (l/Å) and their estimated standard deviations

C1-O1	1.30(3)	C8-C9	1.53(3)
C1-O2	1.28(3)	C10-C11	1.54(4)
C1-C2	1.52(2)	C11-C12	1.50(4)
O2-O3	1.50(3)	C12-C13	1.54(3)
C3-C4	1.50(3)	C13-C14	1.51(4)
C4-C5	1.50(3)	C14-C15	1.55(3)
C5-C6	1.55(4)	C15-C16	1.51(4)
C6-C7	1.50(3)	C16-C17	1.54(3)
C7-C8	1.53(4)	C17-C18	1.53(5)

Table 3(b). Bond angles (φ/°) and their estimated standard deviations

C2-C1-O1	117(2)	C10-C9-C8	115(2)
C2-C1-O2	112(2)	C11-C10-C9	114(2)
C1-C1-O2	121(2)	C12-C11-C10	113(2)
C3-C2-C1	115(2)	C13-C12-C11	113(2)
C4-C3-C2	116(2)	C14-C13-C12	113(2)
C5-C4-C3	110(2)	C15-C14-C13	114(2)
C6-C5-C4	111(2)	C16-C15-C14	114(2)
C7-C6-C5	113(2)	C17-C16-C15	112(2)
C8-C7-C6	114(2)	C18-C17-C16	115(2)
C9-C8-C7	115(2)		

Table 3(c). Internal rotation angles (φ/°)

C3-C2-C1-O1	168	C11-C10-C9-C8	−180
C3-C2-C1-O2	−10	C12-C11-C10-C9	−177
C4-C3-C2-C1	−68	C13-C12-C11-C10	−179
C5-C4-C3-C2	−171	C14-C13-C12-C11	177
C6-C5-C4-C3	180	C15-C14-C13-C12	−180
C7-C6-C5-C4	−176	C16-C15-C14-C13	−179
C8-C7-C6-C5	−176	C17-C16-C15-C14	−179
C9-C8-C7-C6	178	C18-C17-C16-C15	178
C10-C9-C8-C7	176		

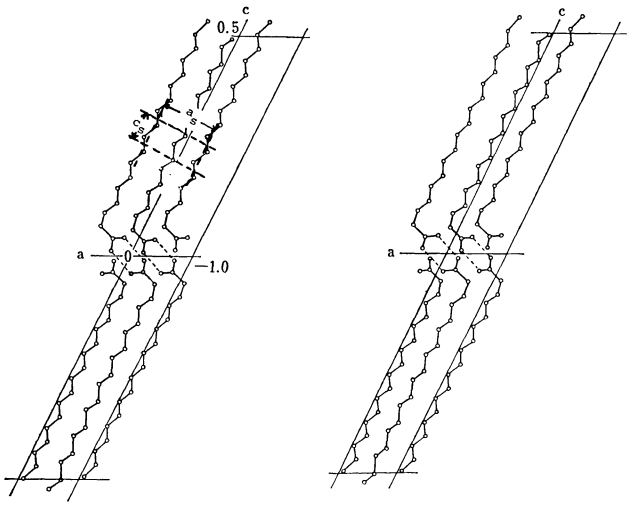

Fig. 2. A perspective view along the b direction drawn by ORTEP The a_sc_s plane of a subcell is shown by dotted lines.

Table 4. Least-squares planes and displacements of atoms from the planes

Carbon chain	Carboxyl group
$LX+MY+NZ=D$	$LX+MY+NZ=D$
$L=0.681$	$L=-0.256$
$M=0.732$	$M=0.731$
$N=-0.002$	$N=0.633$
$D=3.851$	$D=-1.302$

The equation expressed in the orthogonal Cartesian systm:
$Z//\mathbf{c}$ $X//\mathbf{a}^*$ $Y//\mathbf{c}\times\mathbf{a}^*$ in Å unit

Atom	Deviation	Atom	Deviation
C3	0.02	C1	−0.01
C4	0.05	C2	0.00
C5	−0.03	O1	0.00
C6	0.03	O2	0.00
C7	0.03		
C8	−0.02		
C9	−0.03		
C10	0.03		
C11	−0.01		
C12	−0.05		
C13	−0.03		
C14	−0.01		
C15	0.00		
C16	−0.01		
C17	0.02		
C18	0.06		
C1[a)]	−0.77		
C2[a)]	0.30		
O1[a)]	−0.46		
O2[a)]	−1.91		

a) These atoms are not included in the least-squares calculation.
The dihedral angle between the two planes=70°

distance of the end group (except the hydrogen bond) is 3.1 Å. This distance is nearly equal to that of the A-super form of lauric acid[7] and is shorter than that of the C-form of lauric acid,[5] in which the closest distance is 3.4 Å. This is because the C-form, the highest temperature form, is likely to have a looser structure than the B- and A- forms.

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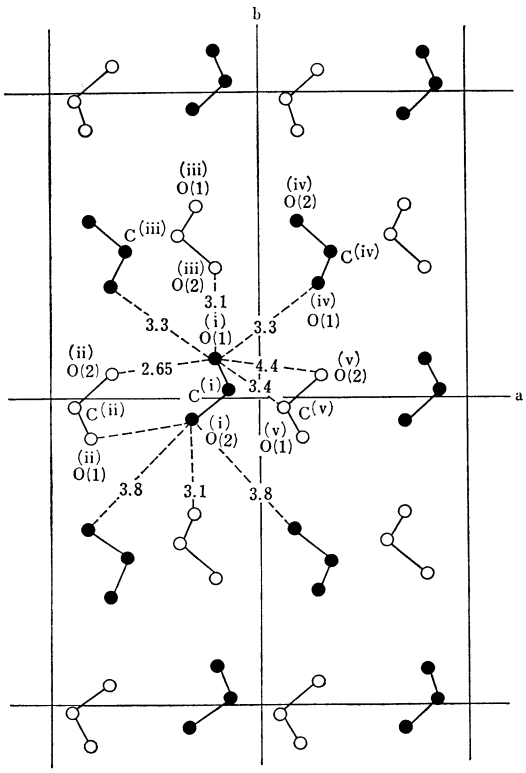

Fig. 3. Projection along the c axis.
Upper layer atoms ●,
lower layer atoms ○.
Symmetry operation code (i) x, y, z,
(ii) $-x, -y, -z$,
(iii) $1/2-x, 1/2+y, -z$,
(iv) $1/2+x, 1/2-y, z$,
(v) $1-x, 1-y, -z$.

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