The Crystal Structure of the B′-Form of Heptadecanoic Acid

Midori GOTO* and Eiichi ASADA†
National Chemical Laboratory for Industry, 1-1, Higashi, Yatabe, Ibaraki 305
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Synopsis. X-Ray structural determination of the B′-form of heptadecanoic acid showed that the unit cell contains two crystallographically independent molecules. All-trans zigzag chains are found in both molecules.

Odd numbered fatty acids are known to crystallize in three polymorphic forms, named A′, B′, and C′.[1] Informations relating to the properties of these are collected in Table 1. The B′-form of pentadecanoic acid has been studied by von Sydow using two-dimentional X-ray diffraction data.[2] We have now been able to obtain fairly good single crystals of the B′-form of heptadecanoic acid and investigated its crystal structure.

Experimental

The heptadecanoic acid was prepared from methyl heptadecanoate by hydrolysis. The B′-form crystals were obtained by crystallization from a 2,2,4-trimethylpentane solution. A crystal with dimensions of $0.6\times0.3\times0.05$ mm^3 was used for the structure determination. The cell dimensions and the diffraction intensities were measured on a Rigaku-Denki four circle diffractometer by using graphite monochromated Cu-$K\alpha$ radiation at room temperature. Crystal data are as follows: $C_{17}H_{34}O_2$ (B′-form); M.W=270.46; triclinic, $P\bar{1}$; a=5.561(1), b=8.018(1), c=47.90(1)Å; α=114.18(1), β=114.96(1), γ=80.22(1)°; D_x=1.017 g cm^{-3}. All independent reflections within the range of $2\theta\leqq120°$ were collected by the use of the 2θ—ω scan mode with a scanning rate 4° (2θ) min^{-1}. Correction for absorption was not applied. A total 1028 independent reflections with $|F_o|\geqq3\sigma(|F_o|)$ were obtained.

Structure Determination

The positions of the carbon atoms were obtained from three dimensional Patterson maps. The positions of the oxygen atoms were obtained by difference synthesis. The positions of the hydrogen atoms, with the exception of carboxyl hydrogen atoms, were calculated by assuming C–H distances of 1.10 Å and a tetrahedral arrangement. The structure was refined

TABLE 1. POLYMORPHISM OF SATURATED ODD-NUMBERED FATTY ACIDS

Number of carbon atoms		11	13	15	17
Crystal form A′			t[6]	t*[10]	t*[10]
B′				t[2,8]	t
and subcell C′		m[9]	m*[10]	m*[10]	m*[10]
Crystal form	from 2,2,4-trimethyl pentane	(stable form at room temp)	A′	B′	B′
	from melt	C′[10]	A′	B′	B′
Transition on heating			C′	C′	C′

t; triclinic, m; monoclinic t*, m*; The crystal structure has not been determined; The crystal system was deduced from powder diffraction data.[10]

TABLE 2. FRACTIONAL ATOMIC COORDINATES (×10^4) AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS

$$B_{eq}=\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j.$$

Atom	X	Y	Z	B_{eq}/Å^2
C17	3346(30)	6513(24)	4636(3)	10.0
C16	4627(27)	5606(20)	4379(3)	8.0
C15	3499(22)	6244(17)	4094(3)	5.7
C14	4801(22)	5256(16)	3840(3)	5.5
C13	3623(21)	5933(16)	3549(2)	4.8
C12	4992(20)	4974(15)	3305(2)	4.7
C11	3823(20)	5658(15)	3010(2)	4.5
C10	5178(20)	4698(15)	2760(2)	4.5
C9	4026(20)	5393(15)	2470(2)	4.4
C8	5346(20)	4414(15)	2218(2)	4.4
C7	4248(20)	5131(15)	1938(3)	4.6
C6	5547(19)	4152(15)	1682(2)	4.4
C5	4539(19)	4880(15)	1409(2)	4.1
C4	5854(20)	3919(15)	1154(2)	4.4
C3	4907(18)	4653(14)	877(2)	3.5
C2	6537(19)	3737(14)	661(2)	4.0
C1	5818(19)	4351(14)	372(2)	3.7
O1	4073(13)	5459(9)	315(2)	4.4
O2	7309(12)	3608(9)	201(2)	4.5
C34	-837(34)	1505(23)	4669(3)	10.5
C33	-1774(26)	511(19)	4305(3)	7.1
C32	-406(23)	1198(16)	4151(3)	5.8
C31	-1472(20)	238(16)	3771(2)	4.8
C30	-132(21)	934(15)	3619(2)	4.7
C29	-1251(20)	-30(15)	3230(2)	4.6
C28	113(20)	681(15)	3083(2)	4.4
C27	-1019(20)	-289(15)	2697(3)	4.8
C26	338(19)	431(15)	2547(2)	4.1
C25	-748(20)	-549(15)	2168(2)	4.5
C24	559(19)	165(14)	2003(2)	4.2
C23	-508(19)	-848(14)	1630(2)	4.1
C22	714(20)	-141(15)	1457(2)	4.4
C21	-476(20)	-1190(15)	1083(2)	4.3
C20	573(19)	-479(14)	897(2)	4.2
C19	-899(20)	-1521(15)	523(2)	4.4
C18	-392(20)	-790(14)	308(3)	4.4
O3	1587(13)	194(10)	416(2)	5.3
O4	-2078(14)	-1287(11)	3(2)	6.1

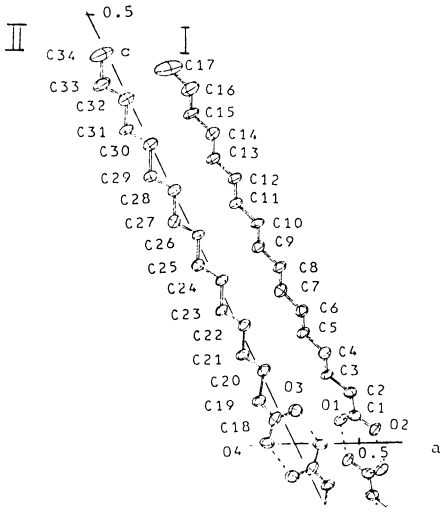

Fig. 1. ORTEP drawing along the b-direction and the numbering system of atoms.
The ellipsoids are drawn to enclose 40% probability.

†Present address: Toyohashi University of Technology 1-1, Hibarigaoka, Tenpaku-cho, Toyohashi, Aichi 440.

by the block-diagonal least-squares method using the UNICS III system.[3] The R-value was reduced to 0.077. The final atomic parameters[4] are listed in Table 2.

Results and Discussion

The B′-form of heptadecanoic acid has a characteristic layer structure, such as is usually found in fatty acids. As shown in Fig. 1, the molecules form all-trans zigzag chains, in contrast to the case of the B-form of stearic acid,[5] in which the bond between the second and third carbon atoms takes a gauche conformation. The structural parameters are shown in Table 3. The subcell, *i.e.* the cell which describes the repetition in the hydrocarbon chains,[1] was found to be orthorhombic, with the following dimensions: a_s=5.0 Å, b_s= 7.4 Å, and c_s=2.54 Å, similar to that of the B-form of stearic acid.[5]

The conformations of the two molecules (I, II) in the asymmetric unit are similar to each other. These molecules are joined in pairs by hydrogen bonds between the carboxyl groups with the O···O distances of 2.64(1) Å (I–I) and 2.62(1) Å (II–II). The dihedral angles between the planes containing the carboxyl groups was 11° (I–I), and 21° (II–II), nearly the same as those in the other fatty acids.[6,7] The second closest oxygen contact distance is 3.2 Å as shown in Fig. 2.

TABLE 3. STRUCTURAL PARAMETERS

Interatomic distance (l/Å)

C34 - C33	1.49(2)	C22 - C21	1.52(1)	C11 - C10	1.55(2)
C33 - C32	1.54(2)	C21 - C20	1.53(1)	C10 - C9	1.56(2)
C32 - C31	1.55(2)	C20 - C19	1.53(2)	C9 - C8	1.54(2)
C31 - C30	1.53(2)	C19 - C18	1.51(2)	C8 - C7	1.52(2)
C30 - C29	1.52(2)	C18 - O3	1.26(1)	C7 - C6	1.55(2)
C29 - C28	1.52(2)	C18 - O4	1.29(2)	C6 - C5	1.50(2)
C28 - C27	1.52(2)	C17 - C16	1.54(2)	C5 - C4	1.55(2)
C27 - C26	1.54(2)	C16 - C15	1.51(2)	C4 - C3	1.52(2)
C26 - C25	1.53(2)	C15 - C14	1.55(2)	C3 - C2	1.54(2)
C25 - C24	1.57(2)	C14 - C13	1.54(2)	C2 - C1	1.53(2)
C24 - C23	1.51(1)	C13 - C12	1.53(2)	C1 - O1	1.22(1)
C23 - C22	1.57(2)	C12 - C11	1.57(2)	C1 - O2	1.31(1)

Bond angle (ϕ/°)

C32	C33	C34	111.9(13)	C15 - C16 - C17	113.1(12)
C31	C32	C33	112.2(10)	C14 - C15 - C16	111.7(11)
C30	C31	C32	112.1(10)	C13 - C14 - C15	111.1(9)
C29	C30	C31	112.0(9)	C12 - C13 - C14	110.5(9)
C28	C29	C30	111.2(9)	C11 - C12 - C13	110.9(9)
C27	C28	C29	110.5(9)	C10 - C11 - C12	111.1(9)
C26	C27	C28	110.7(9)	C 9 - C10 - C11	110.9(9)
C25	C26	C27	110.6(9)	C 8 - C16 - C17	111.0(9)
C24	C25	C26	112.3(9)	C 7 - C15 - C16	111.6(9)
C23	C24	C25	111.2(9)	C 6 - C14 - C15	111.2(9)
C22	C23	C24	112.3(9)	C 5 - C13 - C14	111.8(9)
C21	C22	C23	110.0(9)	C 4 - C12 - C13	112.0(9)
C20	C21	C22	112.0(9)	C 3 - C11 - C12	113.2(9)
C19	C20	C21	108.8(9)	C 2 - C10 - C11	108.5(9)
C18	C19	C20	114.1(9)	C 1 - C 2 - C 3	114.6(9)
C18	C19	O3	122.1(9)	C 1 - C 2 - O 1	112.7(10)
C18	C19	O4	115.7(10)	C 1 - C 2 - O 2	113.2(9)
O3	C19	O4	122.2(9)	O 2 - C 1 - O 1	124.1(12)

Torsion angle (ϕ/°)

C17	C16	C15	C14	-178(1)	C34	C33	C32	C31	-177.1(
C16	C15	C14	C13	-180(1)	C33	C32	C31	C30	179(1)
C15	C14	C13	C12	178(1)	C32	C31	C30	C29	-179(1)
C14	C13	C12	C11	-179(1)	C31	C30	C29	C28	-180(1)
C13	C12	C11	C10	-180(1)	C30	C29	C28	C27	180(1)
C12	C11	C10	C9	-179(1)	C29	C28	C27	C26	180(1)
C11	C10	C9	C8	-179(1)	C28	C27	C26	C25	179(1)
C10	C9	C8	C7	-180(1)	C27	C26	C25	C24	179(1)
C9	C8	C7	C6	-180(1)	C26	C25	C24	C23	179(1)
C8	C7	C6	C5	-178(1)	C25	C24	C23	C22	179(1)
C7	C6	C5	C4	179(1)	C24	C23	C22	C21	-179(1)
C6	C5	C4	C3	-179(1)	C23	C22	C21	C20	178(1)
C5	C4	C3	C2	175(1)	C22	C21	C20	C19	-176(1)
C4	C3	C2	C1	-180(1)	C21	C20	C19	C18	171(1)
C3	C2	C1	O1	-1(2)	C20	C19	C18	O3	19(1)
C3	C2	C1	O2	177(1)	C20	C19	C18	O4	-162(1)

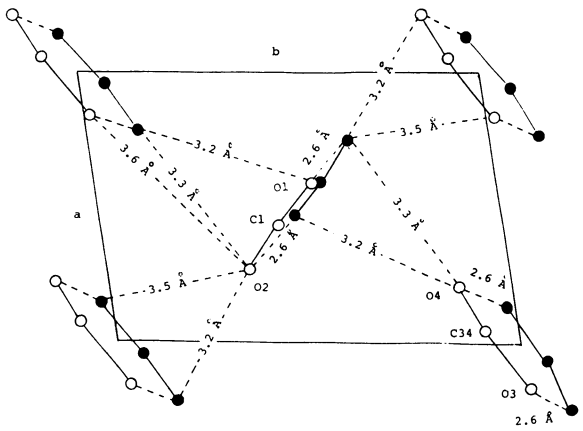

Fig. 2. Carboxyl groups projected along the c* axis.

This value agrees well with that of the B-form of stearic acid.[5] Von Sydow[2] reported that the hydrogen bond was formed between the crystallographically independent molecules (such as I–II) in the structure of the B′-form of pentadecanoic acid. We reinvestigated it and found that the hydrogen bond is formed between the two molecules related by a center of symmetry as in the B′-form of heptadecanoic acid.[8]

It is known that in the odd-numbered fatty acids a transition B′⇄C′ is reversible but in the even numbered ones a transition B⇄C is not.[1] This difference may be related to the fact that in the odd members the molecular conformation of the B′-form is similar to that of the C′-form because both of them have all-trans zigzag chains but in the even members the B-form has a bond of gauche conformation whereas the C-form does not.[5]

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