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The Crystal Structure of the A′-form of Tridecanoic Acid

Midori Goto* and Eiichi Asada

National Chemical Laboratory for Industry, 1-1, Higashi, Yatabe, Ibaraki 305

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The A′-form of tridecanoic acid is triclinic, with the space group $P\bar{1}$ and with $a=4.273(1)$, $b=4.972(1)$, $c=37.69(1)$ Å, $\alpha=90.36(2)$, $\beta=109.44(2)$, and $\gamma=112.43(2)°$. The structure was determined by the Patterson method. Refinement by block-diagonal least-squares methods gave a final R factor of 0.071.

Odd-numbered fatty acids are known to crystallize in three polymorphic forms, named A′, B′, and C′.[1] Their crystal structures have been studied by von Sydow in only one projection (the A′-form[2] and the B′-form[3] of pentadecanoic acid; the C′-form[4] of undecanoic acid). We have now been able to obtain fairly good single crystals of the A′-form of tridecanoic acid; we also investigated its crystal structure.

Experimental

The tridecanoic acid was prepared by the Ajinomoto Co., Ltd. The A′-form crystal was obtained by crystallization in a 2,2,4-trimethylpentane solution. The crystal data and the diffraction intensities were measured on a Rigaku-Denki four-circle diffractometer by using graphite monochromated Cu $K\alpha$ radiation at room temperature (about 20 °C).

Table 1. Crystal data

n-Tridecanoic acid		A′-form	
Molecular formula:		$C_{13}H_{26}O_2$	
Molecular weight:		214	
Transition point:		34 °C	
Triclinic;		$P\bar{1}$	
$z=2$			
a(/Å)	4.273(1)	α(/°)	90.36(2)
b	4.972(1)	β	109.44(2)
c	37.686(8)	γ	112.43(2)

The crystal data are listed in Table 1. The total number of observed reflections was 533 out of 1415 possible reflections within the 2θ angle of 120 °.

Structure Determination

The positions of the carbon atoms were obtained by taking into account the 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 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).[5]

The R-value was reduced to 0.071. The final atomic parameters obtained are listed in Table 2. The large temperature factors, especially at the end carboxyl groups, may be caused by the proximity of the experimental temperature to the transition point of the acid.

Results and Discussion

The structure of the A′-form of tridecanoic acid reveals a layer characteristic and is not significantly different from that of the A′-form[2] of pentadecanoic acid.

The bond lengths, bond angles, and internal rotation angles are shown in Table 3. Figure 1 is an ORTEP drawing.[7] Table 4 reveals that the molecule may be slightly bowed. The dihedral angle between the plane of the carbon main chain and the plane containing the carboxyl group is calculated to be 15°, nearly the same as that in the A_1-form[8] or the A-super form[9] of lauric acid.

Table 2(a). Fractional atomic coordinates and anisotropic temperature factors for C and O atoms

	$x(\times10^4)$	$y(\times10^4)$	$z(\times10^4)$	$B_{11}(\times10^4)$	$B_{22}(\times10^4)$	$B_{33}(\times10^4)$	$B_{12}(\times10^4)$	$B_{13}(\times10^4)$	$B_{23}(\times10^4)$
C1	−618(35)	3317(22)	447(3)	2363(192)	578(75)	17(2)	764(103)	86(15)	23(9)
C2	−1440(27)	1914(20)	772(3)	975(124)	463(63)	11(1)	83(75)	34(12)	19(7)
C3	−405(27)	4060(21)	1124(3)	937(115)	734(73)	7(1)	467(79)	26(10)	13(7)
C4	−926(29)	2521(20)	1459(3)	1532(148)	478(65)	10(1)	334(83)	70(12)	14(7)
C5	37(27)	4597(21)	1806(3)	934(119)	658(69)	16(2)	532(79)	76(12)	41(8)
C6	−488(29)	3116(22)	2141(3)	1332(136)	729(76)	10(1)	484(87)	57(12)	19(8)
C7	623(29)	5161(21)	2508(3)	1125(133)	646(74)	13(1)	293(85)	41(12)	20(8)
C8	57(30)	3686(21)	2841(3)	1360(143)	513(68)	17(2)	362(87)	82(13)	30(9)
C9	1265(31)	5763(21)	3200(3)	1511(148)	501(70)	12(2)	191(88)	57(13)	12(8)
C10	740(30)	4282(22)	3536(3)	1237(143)	694(77)	10(1)	290(89)	33(12)	19(8)
C11	1977(32)	6348(23)	3895(3)	1690(163)	677(77)	14(2)	341(97)	77(14)	11(9)
C12	1608(36)	5000(27)	4232(3)	2137(195)	1157(104)	16(2)	795(121)	109(16)	50(11)
C13	2739(40)	7088(31)	4589(3)	2657(225)	1750(137)	12(2)	1289(152)	93(11)	40(12)
O1	−559(41)	2008(23)	194(3)	8323(329)	1779(101)	33(2)	3234(158)	416(24)	158(12)
O2	−537(31)	5709(18)	404(3)	4477(114)	910(61)	22(1)	1205(93)	227(14)	59(7)

Table 2(b). Fractional atomic coordinates and isotropic temperature factors for H atoms

	$x(\times 10^3)$	$y(\times 10^3)$	$z(\times 10^4)$	$B(/Å^2)$
H(C 2)	14(27)	59(21)	881(27)	11.8(3.2)
H(C′ 2)	−436(25)	46(19)	664(25)	9.9(2.8)
H(C 3)	−227(22)	515(17)	1061(23)	8.0(2.4)
H(C′ 3)	270(23)	550(18)	1204(24)	8.9(2.6)
H(C 4)	84(22)	134(17)	1527(23)	8.1(2.5)
H(C′ 4)	−368(22)	95(17)	1376(23)	8.1(2.4)
H(C 5)	−183(18)	572(14)	1729(19)	4.4(1.8)
H(C′ 5)	292(24)	601(19)	1891(24)	9.4(2.7)
H(C 6)	107(24)	178(19)	2197(24)	9.4(2.7)
H(C′ 6)	−333(23)	171(18)	2053(24)	8.8(2.6)
H(C 7)	−75(24)	646(19)	2440(25)	9.3(2.7)
H(C′ 7)	354(20)	658(16)	2604(21)	6.5(2.2)
H(C 8)	165(20)	233(16)	2902(21)	6.5(2.2)
H(C′ 8)	−282(24)	224(19)	2751(24)	9.5(2.7)
H(C 9)	−30(21)	704(17)	3147(22)	7.5(2.4)
H(C′ 9)	415(20)	727(16)	3279(21)	6.5(2.2)
H(C 10)	225(23)	299(18)	3592(23)	8.1(2.4)
H(C′ 10)	−225(22)	276(17)	3443(23)	7.5(2.3)
H(C 11)	29(22)	769(17)	3824(23)	8.1(2.4)
H(C′ 11)	477(22)	785(17)	3970(23)	8.2(2.5)
H(C 12)	299(23)	361(18)	4300(24)	9.1(2.6)
H(C′ 12)	−130(21)	352(16)	4147(21)	6.9(2.3)
H(C 13)	251(23)	600(18)	4682(26)	10.7(3.0)
H(C′ 13)	575(23)	845(20)	4682(26)	10.7(3.0)
H(C″ 13)	126(27)	844(22)	4554(28)	12.4(3.3)

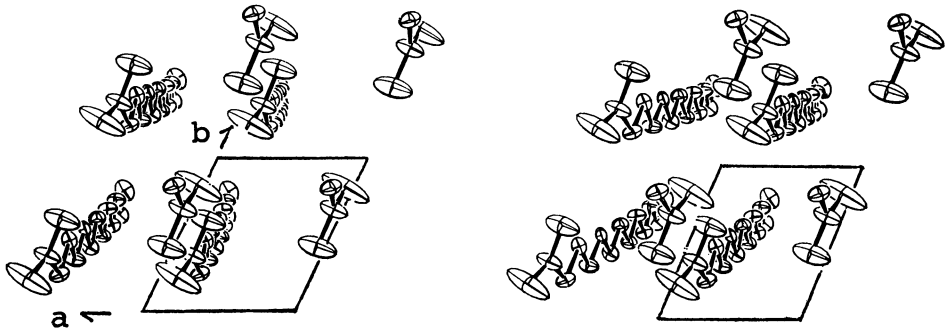

Fig. 1. A perspective view along the c-direction drawn by ORETP.
Only C2, C1, O1, O2 atoms were shown in the one molecule of the pair joined by the hydrogen bond.

Table 3. Bond lengths, angles and internal rotation angles

Bond lengths (/Å)			
C1–C2	1.49(2)	C 6–C 7	1.53(2)
C1–O1	1.16(2)	C 7–C 8	1.50(2)
C1–O2	1.19(2)	C 8–C 9	1.51(2)
C2–C3	1.53(1)	C 9–C10	1.51(2)
C3–C4	1.52(2)	C10–C11	1.50(2)
C4–C5	1.50(2)	C11–C12	1.47(2)
C5–C6	1.51(2)	C12–C13	1.51(2)
Bond angles (/°)			
C2–C1–O1	122(1)	C 7–C 6–C 5	116(1)
C2–C1–O2	121(1)	C 8–C 7–C 6	116(1)
O1–C2–O2	116(1)	C 9–C 8–C 7	115(1)
C3–C2–C1	115(1)	C10–C 9–C 8	115(1)
C4–C3–C2	113(1)	C11–C10–C 9	115(1)
C5–C4–C3	113(1)	C12–C11–C10	117(1)
C6–C5–C4	113(1)	C13–C12–C11	116(1)
Internal rotation angles (/°)			
C 3–C 2–C 1–O2	−28		
C 4–C 3–C 2–C1	−174		
C 6–C 5–C 4–C3	179		
C 8–C 7–C 6–C5	179		
C10–C 9–C 8–C7	−179		
C12–C11–C10–C9	−179		
C 3–C 2–C 1–O1	164		
C 5–C 4–C 3–C2	−179		
C 7–C 6–C 5–C4	177		
C 9–C 8–C 7–C6	178		
C11–C10–C 9–C8	179		

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

Carbon chain	Carboxyl group
$Lx+My+Nz=D$	$Lx+My+Nz=D$
$L=0.88$	$L=0.87$
$M=-0.37$	$M=-0.06$
$N=0.35$	$N=0.50$
$D=-1.77$	$D=-0.14$

The equation expressed in the orthogonal Cartesian system:

Atom	Deviation(/Å)	Atom	Deviation(/Å)
C 2	0.07	C 2	−0.02
C 3	0.02	C 1	0.05
C 4	0.03	O 1	−0.02
C 5	−0.03	O 2	−0.02
C 6	−0.04		
C 7	−0.04		
C 8	−0.06		
C 9	−0.03		
C10	−0.03		
C11	0.02		
C12	0.05		
C13	0.05		
C 1[a)]	0.21		
O 1[a)]	0.53		
O 2[a)]	−0.20		

a) These atoms are not included in the least-squares calculation.

Table 5. Dimensions of the triclinic subcell[a)]

	a_s(/Å)	b_s(/Å)	c_s(/Å)	α(/°)	β(/°)	γ(/°)	V(/Å^3)
Tridecanoic acid A'-form	4.27	5.20	2.51	79	109	118	46.4
Lauric acid A-super form[8)]	4.33	5.42	2.52	76	109	122	47.1
Lauric acid A_1-form[7)]	4.25	5.41	2.45	75	108	122	47.4
Trilaurin[11)]	4.27	5.40	2.45	75	108	117	47.4

a) The triclinic packing was found in the branched-chain fatty acids. In these compounds, the subcell data vary considerably and show a distorted packing; the structures were studied in only one projection and could not be discussed in detail.

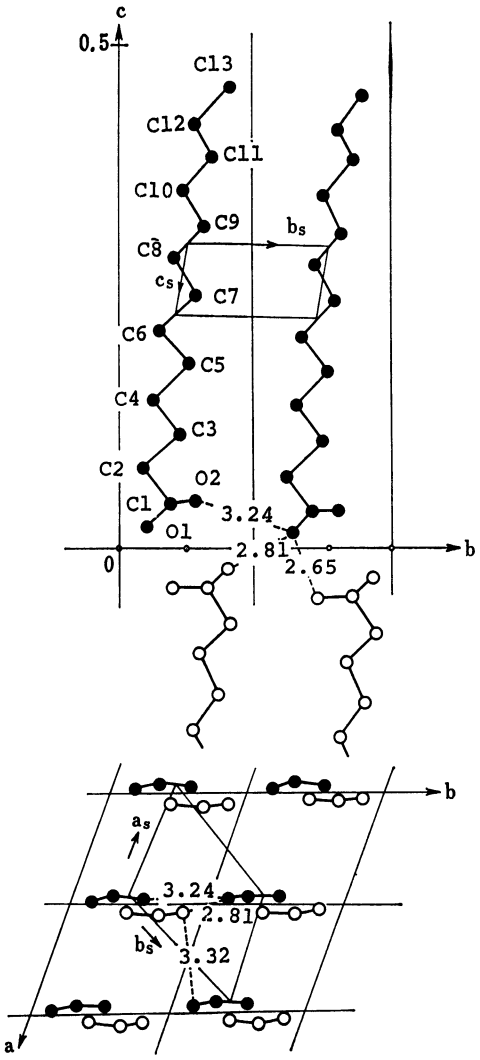

Fig. 2. The crystal structure.
a): Projection along the a*-axis, b): carboxyl groups projected along the c*-axis.

The arrangement of the chain and the end carboxyl group is shown in Fig. 2. The hydrogen bond length is 2.65 Å, and the second closest oxygen contact distance (except for the hydrogen bond) is 2.81 Å. This distance appears to be short compared with that of the other fatty acid,[9,10)] 3.13 Å.

The packing of the zig-zag chains of the carbon atoms is triclinic ($T_{//}$). The dimensions of the subcell are given in Table 5, together with the dimensions in other compounds with triclinic packing.

The structures of the B[10)] and C[11)] forms of the fatty acids reveal a typical layer structure, one in which the carboxyl groups and the methyl groups respectively are situated in alternate layers (parallel to 001). A-forms with the triclinic packing, both A_1[8)]- and A-super[9)] forms of lauric acid, have a structure in which the carboxyl and methyl groups appear mixed in the same layers in the crystal. However, the A'-form of tridecanoic acid has the typical layer structure, just as B-[10)] or C-[11)] forms.

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