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Double-Layered Polytypic Structure of the B Form of Octadecanoic Acid, $C_{18}H_{36}O_2$

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Abstract

Two bimolecular layers forming a double-layered polytypic structure exist in a repeating unit along the stacking direction. One bimolecular layer has essentially the same structure as that of the ordinary single-layered type of the B form.

Comment

The structure determination of the orthorhombic modification of the B form of stearic acid (I) (octadecanoic acid) has been undertaken to confirm its

(I)
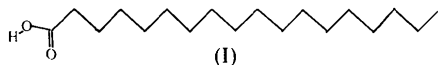
double-layered polytypic structure, which was indicated from a previous vibrational spectroscopic study. Stearic acid crystallizes in four polymorphic phases, A, B, C and E. In the previous vibrational spectroscopic work (Kobayashi, Kobayashi, Itoh & Sato, 1984), we found a new type of single crystal of the B form. This crystal exhibited essentially the same crystal morphology and vibrational spectra as those of the ordinary monoclinic modification (single-layered structure, referred as *Mon*) of the B form (Goto & Asada, 1978); however, large differences were observed in the low-frequency region of Raman spectra and in the bands due to the methyl groups. On the basis of the spectral features and the Weissenberg photograph, we concluded that this new crystal of the B form is an orthorhombic modification of the double-layered polytypic structure (referred as *Orth* II) that had been found in *n*-alkanes and *n*-alcohols (Amelinckz, 1955, 1956; Boistelle, Simon & Pepé, 1976; Kobayashi, Kobayashi, Itoh, Chatani & Tadokoro, 1980). The systematic differences in thermodynamic stability and mechanical properties between the *Mon* and *Orth* II types have been studied by Sato, Kobayashi & Morishita (1988) and Itoh & Kobayashi (1991).

The present structure analysis shows that the B form has a double-layered polytypic structure, as expected (Fig. 1). The *c* dimension [87.662 (9) Å] is twice the thickness of one bimolecular layer in the *Mon* type (43.87 Å), whose lattice parameters are $a = 5.587$, $b = 7.386$, $c = 49.33$ Å and $\beta = 117.24°$. The eight molecules in the unit cell form two bimolecular layers related to each other by a twofold *c*-screw axis operation. Thus, the acyl chain inclines from the *c* axis toward the [010] and [010] directions alternately, forming a herringbone structure. The arrangement of the methyl groups at the interface of the bimolecular layers is markedly different from that in the ordinary single-layered structure. In addition to the orientation of the terminal methyl groups, there is a systematic difference between the *Orth* II and *Mon* types in the distances between neighboring terminal methyls. The *c*-axis projection of the arrangement of the terminal methyls is depicted in Fig. 2, in comparison with that of the *Mon* type. In the *Orth* II type, a methyl C atom in one layer is located at the center of a dimple surrounded by four methyl C atoms in the opposite layer, that is, the methyl C atoms are placed at equal intervals along both the a_s and b_s directions. In case of the *Mon* type, the methyl C atom is displaced from the center along the b_s direction. The methyl terminals in the *Mon* and *Orth* II types are in different intermolecular force fields, giving rise to different vibrational frequencies of the methyl group.

One bimolecular layer in the *Orth* II type of the B form has essentially the same structure as that of the
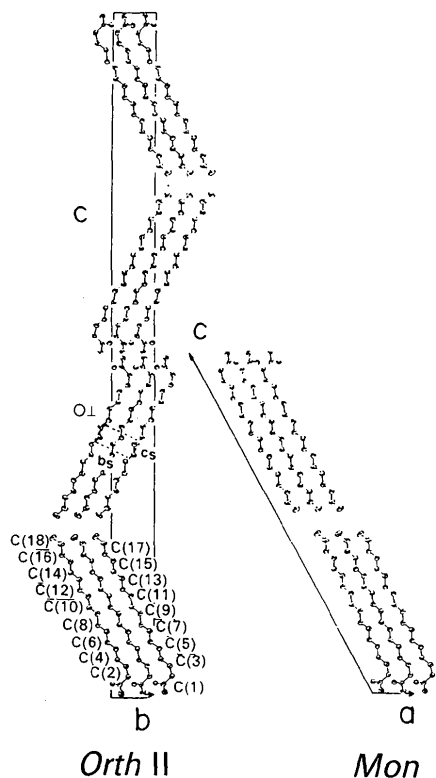
Fig. 1. *ORTEP*II view of the *Orth* II type of stearic acid B form. Thermal ellipsoids are at the 50% probability level.
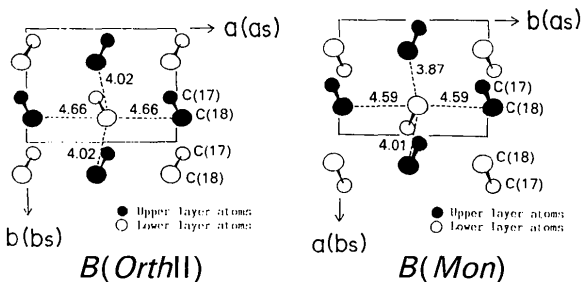

Fig. 2. Projection of the terminal methyls onto the basal (*ab*) plane.

Mon type, where two dimers are related to each other by a *b*-glide operation. The hydrocarbon segment is not fully extended but twisted about the C(2)—C(3) bond, of which the torsion angle is 70°, adopting a *gauche* conformation. The straight part of the acyl chain constructs the orthorhombic polyethylene subcell with a perpendicular arrangement of the skeletal planes (O⊥), whose average subcell parameters are $a_s = 7.40$, $b_s = 4.97$ and $c_s = 2.55$ Å [the setting of the axes is made in accordance with orthorhombic polyethylene determined by Bunn (1939)]. The setting angle of the zigzag plane to the $a_s c_s$ plane is 44.6°. The direction of the a_s axis agrees

with that of the *a* axis of the main lattice and the c_s axis tilts towards the *b* axis by about 27°. In other words, the (011) plane of the subcell is nearly parallel to the basal (*ab*) plane. The thermal factors of the C atoms increase gradually from the C(14) atom toward the terminal methyl groups, as in the other polymorphs of *n*-fatty acids.

The carboxyl plane is nearly coplanar with the C(1)—C(2)—C(3) plane. The C(1)—O(2) bond length is in the range normally found for C=O bonds. The carbonyl group and the C(2)—C(3) bond adopt *cis* geometry about the C(1)—C(2) bond. The distance between the hydrogen-bonded O atoms is 2.681 (3) Å. The *cis–trans* tautomerism in the dimerized carboxyl groups has not been observed in the B form (Kobayashi, Kobayashi, Cho & Kaneko, 1986), in contrast to the C form of *n*-fatty acids (Hayashi & Umemura, 1975). The O···O hydrogen-bond distance in a hydrogen-bond system is considered to be related to the occurrence of tunneling exchange of the H atom and the probability of proton transfer is quite small for O···O distances greater than 2.64 Å (Matsushita & Matsubara, 1982). The large O···O distance of 2.681 Å suggests that no proton exchange by tunneling takes place in the *Orth* II type of the B form.

Experimental

Crystal data

$C_{18}H_{36}O_2$	Cu $K\alpha$ radiation
$M_r = 284.48$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 25
Pbca	reflections
$a = 7.404$ (1) Å	$\theta = 21-38°$
$b = 5.591$ (1) Å	$\mu = 0.468$ mm^{-1}
$c = 87.662$ (9) Å	$T = 296$ K
$V = 3628.7$ (7) Å^3	Plate
$Z = 8$	0.55 × 0.40 × 0.10 mm
$D_x = 1.04$ Mg m^{-3}	Colorless
$D_m = 1.03$ Mg m^{-3}	Crystal source: grown from
Density measured by flotation	hexane solution

Data collection

Rigaku AFC-5 four-circle diffractometer	$R_{int} = 0.038$
	$\theta_{max} = 62.5°$
ω scans	$h = 0 \rightarrow 9$
Absorption correction: none	$k = -7 \rightarrow 7$
	$l = -101 \rightarrow 101$
13 071 measured reflections	3 standard reflections
2921 independent reflections	frequency: 45 min
2198 observed reflections	intensity variation: 3%
$[F > 3\sigma(F)]$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0008F^2]$
$R = 0.062$	$(\Delta/\sigma)_{max} = 0.005$

$wR = 0.086$
$S = 1.66$
2198 reflections
325 parameters
All H-atom parameters refined

$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.10$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.1305 (3)	0.2597 (4)	0.00482 (2)	5.25
O(2)	−0.0772 (3)	0.0557 (4)	0.01777 (2)	4.96
C(1)	0.0246 (4)	0.2249 (5)	0.01663 (3)	4.16
C(2)	0.0432 (5)	0.4184 (6)	0.02851 (3)	4.75
C(3)	−0.0499 (5)	0.3674 (6)	0.04353 (3)	4.50
C(4)	0.0378 (5)	0.1714 (6)	0.05299 (3)	4.30
C(5)	−0.0415 (5)	0.1497 (6)	0.06895 (3)	4.42
C(6)	0.0401 (5)	−0.0489 (6)	0.07853 (3)	4.36
C(7)	−0.0395 (5)	−0.0651 (6)	0.09445 (3)	4.60
C(8)	0.0399 (5)	−0.2643 (6)	0.10415 (3)	4.50
C(9)	−0.0392 (5)	−0.2773 (6)	0.12021 (3)	4.59
C(10)	0.0404 (5)	−0.4751 (6)	0.12989 (3)	4.60
C(11)	−0.0382 (5)	−0.4869 (6)	0.14598 (3)	4.58
C(12)	0.0402 (5)	−0.6833 (6)	0.15582 (4)	4.70
C(13)	−0.0391 (5)	−0.6935 (6)	0.17176 (4)	4.67
C(14)	0.0387 (5)	−0.8902 (6)	0.18182 (4)	4.92
C(15)	−0.0396 (5)	−0.8982 (6)	0.19754 (4)	5.1
C(16)	0.0383 (5)	−1.0917 (6)	0.20795 (4)	5.12
C(17)	−0.0419 (6)	−1.0968 (7)	0.22360 (4)	6.1
C(18)	0.0378 (9)	−1.288 (1)	0.23382 (6)	7.8

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(1)	1.313 (3)	C(2)—C(3)	1.513 (5)
O(2)—C(1)	1.214 (3)	C(3)—C(4)	1.520 (4)
C(1)—C(2)	1.508 (4)		
O(1)—C(1)—C(2)	112.6 (3)	C(1)—C(2)—C(3)	115.1 (3)
O(2)—C(1)—C(2)	124.0 (3)	C(2)—C(3)—C(4)	114.6 (3)
O(1)—C(1)—O(2)	123.5 (3)	C(3)—C(4)—C(5)	113.3 (3)
O(1)—C(1)—C(2)—C(3)	−169.8 (3)	C(2)—C(3)—C(4)—C(5)	171.5 (3)
O(2)—C(1)—C(2)—C(3)	10.5 (4)	C(3)—C(4)—C(5)—C(6)	178.5 (3)
C(1)—C(2)—C(3)—C(4)	70.3 (4)		

A relatively small ω-scan width of 0.8° was used in order to avoid overlapping of neighboring reflections; the ω-scan rate was 4.0° min^{-1} and background counts were made for 4 s on each side of every scan. The molecular model was initially built for 18 C and two O atoms by reference to the structure of the *Mon* type of the B form of stearic acid. Refinement was by full-matrix least-squares methods. Data collection: Rigaku AFC-5 with software *AFCM* of the Research Center for Protein Engineering, Institute for Protein Research Center, Osaka University, Japan. Program(s) used to refine structure: *HBLS-V FMLS* (Ashida, 1979). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *POTP* (Yasuoka, Kimura & Mizuma, 1979); *DAPH* (Ashida, 1979).

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Double-Layered Polytypic Structure of the E Form of Octadecanoic Acid, C$_{18}$H$_{36}$O$_2$

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