

& Camerman, 1978) and *N*-methyl-*N*-nitrosourea [1.231 (2) Å], *N,N'*-dimethyl-*N*-nitrosourea [1.227 (2) Å], 2-nitroso-2-azabicyclo[2.2.2]octan-3-one [1.227 (5) Å] and *N*-methyl-*N*-nitroso-*p*-nitrobenzamide [1.218 (4) Å] (Prout, Fail, Hernandez-Cassou & Ming Miao, 1982). However, a comparatively long nitroso N—O bond [1.240 (2) Å] and a short N(1)—N(5) bond [1.327 (2) Å] were observed in (II). These results and the N(1)—C(7) bond length [1.429 (2) Å] as well as the prolonged urea C—N bond length [C(2)—N(1) 1.487 (2) Å] suggest conjugation through the phenyl—N—N=O moiety instead of the urea moiety in (II). Intermolecular hydrogen bonds and unusual short non-bonded contacts are not observed.

References

JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

PROUT, K., FAIL, J., HERNANDEZ-CASSOU, S. H. & MING MIAO, F. (1982). *Acta Cryst.* **B38**, 2176–2181.

Rigaku Corporation (1985). RCRYSTAN. X-ray Analysis Program System. Rigaku Corporation, Tokyo, Japan.

SMITH, H. W. & CAMERMAN, A. (1978). *J. Med. Chem.* **21**, 468–471.

SUEYOSHI, S. & TANNO, M. (1985). *Chem. Pharm. Bull.* **33**, 488–496.

TANNO, M. & SUEYOSHI, S. (1987). *Chem. Pharm. Bull.* **35**, 1353–1359, 1360–1371.

TANNO, M., SUEYOSHI, S. & KAMIYA, S. (1990). *Chem. Pharm. Bull.* **38**, 49–54, 2644–2649.

TSUJIHARA, K., OZAKI, M., MORIKAWA, T. & ARAI, Y. (1981). *Chem. Pharm. Bull.* **29**, 2509–2515.

YAO, J.-X., ZHENG, C.-D., QIAN, J.-Z., HAN, F.-S., GU, Y.-X. & FAN, H.-F. (1985). SAP185. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Acta Cryst. (1992). **C48**, 1054–1057

Structure of the Low-Melting Phase of Petroselinic Acid

BY FUMITOSHI KANEKO AND MASAMICHI KOBAYASHI

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

YASUYUKI KITAGAWA AND YOSHIKI MATSUURA

Institute for Protein Research, Osaka University, Suita, Osaka 656, Japan

KIYOTAKA SATO

Faculty of Applied Biological Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 724, Japan

AND MASAO SUZUKI

Oil and Fats Research Laboratory, Nippon Oil and Fats Co., Ohama, Amagasaki 660, Japan

(Received 7 June 1991; accepted 28 October 1991)

Abstract. *cis*-6-Octadecenoic acid, $C_{18}H_{34}O_2$, $M_r = 282.47$, orthorhombic, $Pbca$, $a = 7.311 (1)$, $b = 5.565 (1)$, $c = 88.01 (1)$ Å, $V = 3581.1 (8)$ Å 3 , $Z = 8$, $D_x = 1.05$ g cm $^{-3}$, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 4.74$ cm $^{-1}$, $F(000) = 1264$, $T = 263$ K, $R(F) = 0.054$ for 1633 unique observed reflections with $F > 3\sigma(F)$. Two bimolecular layers forming a double-layered polytype structure exist within a repeating unit along the c axis. The *cis* olefin group [C(5)—C(6)=C(7)—C(8)] has a 157, 0, -160° conformation, deviating significantly from the standard skew, *cis*, skew' conformation. The hydrocarbon chains on either side of

the olefin group adopt all-*trans* conformations and form an orthorhombic polyethylene-type subcell.

Introduction. Petroselinic acid (*cis*-6-octadecenoic acid) is a naturally occurring *cis*-monounsaturated fatty acid with a rather unusual crystal structure. It contains an even-numbered hydrocarbon chain on the methyl-terminal side of the C=C bond, and its polymorphism differs from that of other *cis*-monounsaturated fatty acids (Sato, Yoshimoto, Suzuki, Kobayashi & Kaneko, 1990). There are two polymorphic phases: a low-melting (LM) and a high-

melting (HM) phase. The morphology of the LM phase is identical to that of the *B* and *E* forms of even-numbered *n*-fatty acids: lozenge-shaped plate crystals whose acute angle is 75°.

Recently, we have reported evidence indicating that the LM phase is formed from an orthorhombic polyethylene-type ($O\perp$) subcell (Kaneko, Nishi, Kobayashi, Sato & Suzuki, 1987). Since this was the first report of an $O\perp$ -type subcell in a *cis*-unsaturated fatty acid, and as it seemed difficult to construct $O\perp$ subcell packing with *cis*-formed unsaturated acyl chains, we determined the crystal structure of this phase to allow the characteristic behavior of petroselinic acid to be understood from a structural point of view.

Experimental. Petroselinic acid supplied by the Nippon Oil and Fats Co. Crystals of the low-melting phase were prepared from an acetonitrile solution at 278 K by slow evaporation. A lozenge-shaped crystal of dimensions $0.7 \times 0.5 \times 0.2$ mm was used for intensity measurements. Specimen cooled with a stream of dry air. Intensity data from a Rigaku-Denki AFC-5 automated four-circle diffractometer with Ni-filtered $Cu K\alpha$ radiation from a rotating anode. Lattice parameters refined using the 2θ values of 25 reflections in the range $20 < 2\theta < 50^\circ$. Reflections with $3 < 2\theta < 100^\circ$ ($-7 \leq h \leq 7$, $0 \leq k \leq 5$, $-87 \leq l \leq 87$) measured by ω -scan mode with scan speed 6° min^{-1} ($60 < 2\theta \leq 100^\circ$) or $12^\circ \text{ min}^{-1}$ ($3 < 2\theta \leq 60^\circ$); in order to avoid overlapping of neighboring reflections, four scan-width ranges were used, $(1.7 + 0.15\tan\theta)^\circ$ for reflections with $3 < 2\theta \leq 40^\circ$, $(1.2 + 0.15\tan\theta)^\circ$ for reflections with $40 < 2\theta \leq 60^\circ$, $(0.9 + 0.15\tan\theta)^\circ$ for reflections with $60 < 2\theta \leq 85^\circ$ and $(0.7 + 0.15\tan\theta)^\circ$ for reflections with $85 < 2\theta \leq 100^\circ$; 6894 observed reflections were collected, of which 1846 were unique ($R_{\text{int}} = 0.066$). 1633 reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the refinement; no significant intensity variation for three standard reflections; no absorption correction. The initial coordinates of C atoms were set based on *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) results with reference to the fractional coordinates of the *E* form of octadecanoic acid (Kaneko, Kobayashi, Kitagawa & Matsuura, 1990); all other non-H atoms located after several cycles of block-diagonal least-squares refinement and Fourier calculations; H atoms located by difference Fourier syntheses; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for all non-H atoms; 34 H atoms refined isotropically; 317 parameters, $R = 0.052$, $wR = 0.082$, $S = 1.36$, $w = [\sigma(F)^2 + 0.003F^2]^{-1}$, maximum $\Delta/\sigma = 0.055$, largest features in $\Delta\rho$ map $0.14 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography*

(1974, Vol. IV). Computations were carried out on an ACOS-S930 system at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. Programs *HBLS-V* and *FMLS* (Ashida, 1979) were used for the least-squares refinement, and *ORTEPII* (Johnson, 1971) for plotting the crystal structure.

Discussion. The atomic coordinates for the non-H atoms are given in Table 1* and the overall crystal structure is shown in Fig. 1. The bond lengths, bond angles and torsion angles are given in Table 2.

The LM phase has a double-layered polytype structure, Orth II, previously found in monoclinic *n*-alkanes (Boistelle, Simon & Pepe, 1976; Kobayashi, Kobayashi, Itoh, Chatani & Tadokoro, 1980) and the *B* form of stearic acid (Kobayashi, Kobayashi, Itoh & Sato, 1984). The eight molecules in the unit cell form two bimolecular layers related to each other by a twofold *c*-screw axis. The two hydrocarbon chains linked to the *cis* olefin group adopt all-*trans* conformations forming an $O\perp$ -type subcell. This is the first time that this subcell structure has been found in a *cis*-monounsaturated fatty acid. The average subcell parameters in the methyl-terminal chain are $a_s = 7.31$, $b_s = 4.98$ and $c_s = 2.54 \text{ \AA}$ [axes set in accordance with orthorhombic polyethylene, Bunn (1939)]. For the carboxyl-terminal chain, which has only four methylene units, the subcell is rather distorted, with average dimensions $a_s = 7.31$, $b_s = 5.19$, $c_s = 2.53 \text{ \AA}$ and $\alpha_s = 85^\circ$. The a_s axis is parallel to the a axis of the main lattice on both sides of the *cis* C=C bond, and the chains tilt towards the b axis by 26° on the methyl-terminal side and by 22° on the carboxyl-terminal side. In other words, the (011) plane of the subcell of the methyl-terminal chain is nearly parallel to the basal plane as in the *B* and *E* forms of even-numbered *n*-fatty acids.

One bimolecular layer structure of the LM phase belongs to a monoclinic system where two dimers are related to each other by a b -glide operation. In the γ phase of oleic acid, two dimers in the unit cell are also related to each other by a glide operation, but the acyl chains form a specific $O' \parallel$ -type subcell (Abrahamsson & Ryderstedt-Nahringbauer, 1962).† The difference in subcell structure between the LM phase of petroselinic acid and the γ phase of oleic acid arises from the conformation around the *cis*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54797 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0516]

† The low-melting form of oleic acid reported by Abrahamsson & Ryderstedt-Nahringbauer is referred to here as the γ phase.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors (Å²) for non-H atoms*

	$B_{eq} = \frac{4}{3} \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$	x	y	z	B_{eq}
C(1)	0.0339 (4)	-0.2294 (4)	0.01625 (3)		4.80
C(2)	0.0623 (3)	-0.4192 (4)	0.02790 (2)		5.37
C(3)	-0.0296 (4)	-0.3842 (6)	0.04291 (3)		5.27
C(4)	0.0328 (6)	-0.5767 (7)	0.05414 (4)		5.34
C(5)	-0.0470 (5)	-0.5539 (7)	0.06984 (4)		6.35
C(6)	0.0227 (5)	-0.7425 (6)	0.08055 (4)		6.01
C(7)	0.0249 (6)	-0.7243 (7)	0.09535 (4)		5.66
C(8)	-0.0399 (5)	-0.5170 (6)	0.10464 (4)		5.61
C(9)	0.0359 (5)	-0.5089 (6)	0.12053 (4)		4.86
C(10)	-0.0396 (6)	-0.3074 (7)	0.13035 (4)		4.87
C(11)	0.0387 (5)	-0.2994 (6)	0.14611 (4)		4.61
C(12)	-0.0393 (5)	-0.1009 (6)	0.15601 (4)		4.63
C(13)	0.0378 (5)	-0.0925 (6)	0.17198 (4)		4.66
C(14)	-0.0393 (5)	0.1057 (6)	0.18193 (3)		4.66
C(15)	0.0397 (5)	0.1104 (6)	0.19785 (4)		4.66
C(16)	-0.0385 (5)	0.3065 (6)	0.20796 (4)		4.95
C(17)	0.0422 (5)	0.3099 (6)	0.22371 (3)		5.68
C(18)	-0.0362 (5)	0.5066 (6)	0.23280 (4)		6.92
O(1)	0.1268 (6)	-0.2659 (7)	0.00378 (4)		5.84
O(2)	-0.0652 (7)	-0.0563 (8)	0.01819 (5)		5.51

Table 2. *Selected bond distances (Å), bond angles (°) and torsion angles (°) with e.s.d.'s in parentheses*

C(1)—O(1)	1.307 (4)	C(1)—O(2)	1.217 (4)
C(1)—C(2)	1.487 (5)	C(2)—C(3)	1.495 (5)
C(3)—C(4)	1.528 (5)	C(4)—C(5)	1.505 (5)
C(5)—C(6)	1.500 (5)	C(6)—C(7)	1.306 (5)
C(7)—C(8)	1.492 (5)	C(8)—C(9)	1.505 (5)
C(2)—C(1)—O(1)	113.3 (3)	C(2)—C(1)—O(2)	123.3 (3)
O(1)—C(1)—O(2)	123.4 (3)	C(1)—C(2)—C(3)	117.0 (3)
C(2)—C(3)—C(4)	110.3 (3)	C(3)—C(4)—C(5)	114.8 (3)
C(4)—C(5)—C(6)	112.7 (3)	C(5)—C(6)—C(7)	125.2 (3)
C(6)—C(7)—C(8)	127.0 (3)	C(7)—C(8)—C(9)	114.5 (3)
O(1)—C(1)—C(2)—C(3)	176.3 (3)	C(4)—C(5)—C(6)—C(7)	157.1 (4)
O(2)—C(1)—C(2)—C(3)	-3.2 (5)	C(5)—C(6)—C(7)—C(8)	0.1 (6)
C(1)—C(2)—C(3)—C(4)	-172.8 (3)	C(6)—C(7)—C(8)—C(9)	-160.2 (4)
C(2)—C(3)—C(4)—C(5)	178.2 (3)	C(7)—C(8)—C(9)—C(10)	-176.2 (3)
C(3)—C(4)—C(5)—C(6)	-178.3 (3)		

double bond. In case of the γ phase, the torsion angles of the C—C=C—C group are typical of a skew, *cis*, skew' conformation, so that the skeletal zigzag planes of the hydrocarbon chains of the two sides are located perpendicular to the glide plane, and the zigzag planes of the neighboring molecules related by the glide operation are parallel to each other (forming the O'II subcell). In case of the LM phase, the dihedral angles of the C(5)—C(6)=C(7)—C(8) group are 157, 0, -160°, deviating significantly from the standard skew, *cis*, skew' form, so that the skeletal plane makes an angle of 43.6° on the methyl-terminal side and 40.6° on the carboxyl-terminal side with the b -glide plane, and the zigzag planes of the neighboring molecules become nearly perpendicular to each other (forming the O \perp subcell). The olefin planes themselves make an angle of 24.0° with the glide plane.

The important factor stabilizing the O \perp packing is the structure of the methyl-end interface. Since petroselinic acid has an even number of C atoms in the methyl-terminal hydrocarbon chain, in contrast

to the odd number of C atoms in oleic acid, it is possible to construct the methyl-end packing in the same manner as even-numbered *n*-fatty acids having an O \perp -type subcell. Indeed, the structure in the vicinity of the methyl groups is nearly the same as that of the *E* and *B* forms of stearic acid. Kobayashi, Kobayashi, Cho & Kaneko (1986) showed that the interfacial energy is nearly the same between single- and double-layered (Orth II) polytype structures in the case of the *B* form, in contrast to the large difference observed for the *C* form, whose Orth II-type structure has not been found. Thus, it is concluded that the even-odd effect of the methyl-terminal chain is also related to the formation of the double-layered polytype structure.

The thermal factors of the C atoms at the 5–8 (the olefin group) and 17–18 (methyl-end) positions are larger than those of the other atoms. It should also be noted that the thermal factors are larger in the carboxyl-terminal chain than in most of the methyl-terminal chain (positions 9–16). This indicates that the *cis* olefin group induces the mobility in the acyl chain. However, the long chain segment, the O \perp subcell structure and stable methyl packing at the interface depress the mobility of the methyl-terminal chain. It seems that the structure and dynamical properties of the acyl chains in the LM phase are closely related to the lack of reversible phase-

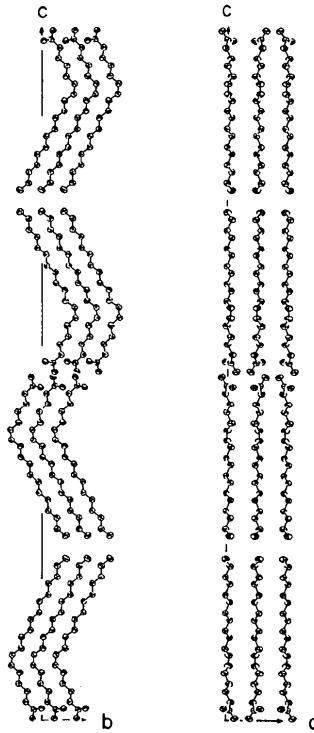


Fig. 1. ORTEP view of the low-melting phase of petroselinic acid. Thermal ellipsoids are plotted at the 50% probability level.

transition characteristics of *cis*-monounsaturated acids, which is induced by conformational disordering in the methyl-terminal chain (Kobayashi, Kaneko, Sato & Suzuki, 1986).

The carboxyl group is nearly coplanar with the skeletal plane of the carboxyl-terminal hydrocarbon chain, and the C—C=C=O group of the LM phase is recognized to have a *cis* conformation. The distance between the hydrogen-bonded O atoms is 2.68 (1) Å.

References

ABRAHAMSSON, S. & RYDERSTEDT-NAHRINGBAUER, I. (1962). *Acta Cryst.* **15**, 1261–1268.

ASHIDA, T. (1979). *HBLS-V and FMLS. The Universal Crystallographic Computing System – Osaka*, pp. 53–60. The Computation Center, Osaka Univ., Japan.

BOISTELLE, R., SIMON, B. & PEPE, G. (1976). *Acta Cryst.* **B32**, 1240–1243.

BUNN, C. W. (1939). *Trans. Faraday Soc.* **35**, 482–491.

JOHNSON, C. K. (1971). *ORTEPII. Report ORNL-3794*, revised. Oak Ridge National Laboratory, Tennessee, USA.

KANEKO, F., KOBAYASHI, M., KITAGAWA, Y. & MATSUURA, Y. (1990). *Acta Cryst.* **C46**, 1490–1492.

KANEKO, F., NISHI, I., KOBAYASHI, M., SATO, K. & SUZUKI, M. (1987). *Prep. Mol. Struct. Symp.*, Kanazawa, pp. 116–117.

KOBAYASHI, M., KANEKO, F., SATO, K. & SUZUKI, M. (1986). *J. Phys. Chem.* **90**, 6371–6378.

KOBAYASHI, M., KOBAYASHI, T., CHO, Y. & KANEKO, F. (1986). *Makromol. Chem. Macromol. Symp.* **5**, 1–20.

KOBAYASHI, M., KOBAYASHI, T., ITOH, Y., CHATANI, Y. & TADOKORO, H. (1980). *J. Chem. Phys.* **72**, 2024–2031.

KOBAYASHI, M., KOBAYASHI, T., ITOH, Y. & SATO, K. (1984). *J. Chem. Phys.* **80**, 2897–2903.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

SATO, K., YOSHIMOTO, N., SUZUKI, M., KOBAYASHI, M. & KANEKO, F. (1990). *J. Phys. Chem.* **94**, 3180–3185.

Acta Cryst. (1992). **C48**, 1057–1060

Structure of the High-Melting Phase of Petroselinic Acid

BY FUMITOSHI KANEKO AND MASAMICHI KOBAYASHI

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

YASUYUKI KITAGAWA AND YOSHIKI MATSUURA

Institute for Protein Research, Osaka University, Suita, Osaka 565, Japan

KIYOTAKA SATO

Faculty of Applied Biological Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 724, Japan

AND MASAO SUZUKI

Oil and Fats Research Laboratory, Nippon Oil and Fats Co., Ohama, Amagasaki 660, Japan

(Received 17 July 1991; accepted 4 November 1991)

Abstract. *cis*-6-Octadecenoic acid, $C_{18}H_{34}O_2$, $M_r = 282.47$, triclinic, $P\bar{1}$, $a = 5.359$ (1), $b = 8.874$ (2), $c = 41.391$ (5) Å, $\alpha = 90.49$ (1), $\beta = 89.12$ (2), $\gamma = 113.81$ (2)°, $V = 1800.7$ (6) Å³, $Z = 4$, $D_x = 1.04$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 4.7$ cm⁻¹, $F(000) = 632$, $T = 263$ K, $R(F) = 0.068$, $wR(F) = 0.087$ for 3927 unique observed reflections with $F > 3\sigma(F)$. There are two crystallographically independent molecules *A* and *B* in the asymmetric unit. The methyl-terminal hydrocarbon chains of both molecules form a monoclinic subcell with parallel skeletal planes. Torsion angles of the C—C=C—C olefin group are 91, 1 and 130° from the carboxyl side for molecule *A*, and 137, 1 and 119° for molecule *B*.

Introduction. Recently, we have demonstrated that *cis*-monounsaturated fatty acids crystallize in various modifications and that they undergo several types of solid-state phase transition (Kobayashi & Kaneko, 1990). Most *cis*-monounsaturated fatty acids whose methyl-terminal hydrocarbon chains contain an odd number of C atoms have two crystalline phases α and γ in common. Between the α and γ phases, there is a reversible phase transition accompanied by conformational disorder in the vicinity of the methyl terminal. We found an additional order-disorder phase transition between the α_1 and γ_1 phases of erucic acid (Suzuki, Sato, Yoshimoto, Tanaka & Kobayashi, 1988). These phase transitions are one of the important characteristics of *cis*-monoenoic acids.