bonds (1·366 to 1·387 Å) are intermediate between single and double bonds (Arriau, Deschamps, Duke, Epsztajn, Katritzky, Lunt, Mitchell, Rizvi & Roch, 1974). The bond distances in the triazinium imide indicate that, on the contrary, the canonical forms (i)–(iv) of (VII*a*) make important contributions to the resonance hybrid, due, presumably, to the presence of the electronegative N atoms at positions 2 and 4.

The molecular packing is shown in Fig. 2 viewed along the unit-cell *c* axis, Intermolecular H bonds are formed between the 1-imide N atom, N11, and N2 of a molecule related by the twofold symmetry operation $(1-x, -y, z)$; the N···N separation is 3·240 (2) Å. This type of intermolecular interaction presumably assists in stabilizing the 1-imide structure in the crystal. There are no other non-bonded contacts which are significantly closer than the sum of the corresponding van der Waals radii.

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Structure of Stearic Acid *E* Form

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Abstract. *E* form of octadecanoic acid, $C_{18}H_{36}O_2$, $M_r = 284{\cdot}48$, monoclinic, $P2_1/a$, $a = 5{\cdot}603$ (1), $b = 7{\cdot}360$ (1), $c = 50{\cdot}789$ (9) Å, $\beta = 119{\cdot}40$ (2)°, $V = 1824{\cdot}6$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}04$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}0$ cm^{-1}, $F(000) = 640$, $T = 283$ K, $R(F) = 0{\cdot}052$, $wR(F) = 0{\cdot}082$ for 2225 unique observed reflections with $F > 3\sigma(F)$. The polymethylene chain of the acyl group takes an all-*trans* conformation and forms an $O\perp$ type subcell with $a_s = 7{\cdot}36$, $b_s = 5{\cdot}02$, and $c_s = 2{\cdot}55$ Å. The a_s axis is parallel to the unique axis (*b* axis) and the c_s axis is tilted by about 26° from the normal of the basal plane toward the *a* axis.

Introduction. It is well known that even-numbered *n*-fatty acids crystallize into various modifications depending on the crystallization conditions. Holland & Nielson (1962) obtained single crystals of stearic acid (octadecanoic acid) from a diethyl ether solution. The crystal had a lozenge shape with an acute interedge angle of about 74° like the *B* form but showed an infrared spectrum different from those of any of the previously known modifications (*A*, *B* and *C* forms). They concluded that the crystal was of a new modification, and named it the *E* form. Based on the investigation of the infrared spectra and on the morphological observation, they derived the crystal structure of the *E* form as follows (Holland & Nielson, 1963):

(1) Molecules formed an *o*-PE type ($O\perp$) sublattice in the unit cell that belongs to a monoclinic system as in the *B* and *C* forms.

(2) The polymethylene chain took the all-*trans* conformation as in the *C* form and was inclined toward the basal plane in the same manner (the direction and the angle of inclination) as in the *B* form.

Except for the work carried out by Kobayashi, Kobayashi, Cho & Kaneko (1986) who came to the same conclusions through Raman spectroscopy,

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studies of the structure and the properties of the *E* form have not been carried out because this form is a metastable phase and the preparation conditions were uncertain. Recently, we succeeded in obtaining reproducible good single crystals of this form, and performed the structural analysis by X-ray diffraction using a four-circle diffractometer.

Experimental. The stearic acid sample used (with purity guaranteed greater than 99%) was purchased from Nakarai Chemical Co. Ltd. Crystals of *E* form were grown from diethyl ether solution by cooling.

Crystal structure analysis was carried out on a crystal with size about 0·5 × 0·5 × 0·05 mm; intensity data from Rigaku–Denki AFC-5 automated four-circle diffractometer equipped with Ni-filtered Cu $K\alpha$ radiation from a rotating anode; unit-cell parameters from angular values of 20 reflections in the range $40 < 2\theta < 75°$; 2734 unique reflections with $2\theta < 120°$ $(0 \le h \le 6,\ 0 \le k \le 8,\ -56 \le l \le 49)$ were measured by ω-scan mode with scan speed 4° min^{-1}, and scan ranges $(2{\cdot}0 + 0{\cdot}15\tan\theta)°$ for reflections with $4 \le 2\theta \le 60°$ and $(1{\cdot}2 + 0{\cdot}15\tan\theta)°$ for $60 < 2\theta \le 120°$; 2225 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 the C atoms set with reference to the three-dimensional Patterson map and the fractional coordinates of stearic acid *C* form (Malta, Celotti, Zannetti & Martelli, 1971); all other atoms located after several least-squares cycles and Fourier calculations; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for all non-H atoms; 36 H atoms refined isotropically; 325 parameters, $R = 0{\cdot}052$, $wR = 0{\cdot}082$, $S = 1{\cdot}89$, $w = [\sigma(F)^2 + 0{\cdot}001F^2]^{-1}$, max. $\Delta/\sigma = 0{\cdot}066$; largest features in $\Delta\rho$ map 0·2 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computation carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University; program *MFPA* (Tanaka & Yasuoka, 1979) for Patterson map, *HBLS*-V and *FMLS* (Ashida, 1979) for the least-squares refinements, *ORTEP*II (Johnson, 1976) for plotting molecular and crystal structures.

Discussion. Atomic coordinates are given in Table 1* and the overall crystal structure is drawn in Fig. 1. The bond lengths, bond angles and internal rotation angles are given in Table 2.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the non*-H *atoms*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	−0·2298 (5)	0·1254 (3)	0·00708 (4)	5·26
O(2)	0·1023 (5)	−0·0655 (4)	0·03639 (5)	4·85
C(1)	−0·0879 (5)	0·0331 (3)	0·03216 (5)	3·95
C(2)	−0·1800 (5)	0·0659 (3)	0·05467 (5)	4·54
C(3)	−0·0204 (5)	−0·0278 (3)	0·08508 (5)	4·12
C(4)	−0·1193 (5)	0·0360 (3)	0·10639 (5)	4·18
C(5)	0·0288 (5)	−0·0439 (3)	0·13802 (5)	4·13
C(6)	−0·0725 (5)	0·0335 (3)	0·15848 (5)	4·17
C(7)	0·0663 (5)	−0·0435 (3)	0·19025 (5)	4·12
C(8)	−0·0402 (5)	0·0368 (3)	0·21011 (5)	4·11
C(9)	0·0952 (5)	−0·0401 (3)	0·24196 (5)	4·10
C(10)	−0·0138 (5)	0·0395 (3)	0·26165 (5)	4·12
C(11)	0·1177 (5)	−0·0387 (3)	0·29329 (5)	4·19
C(12)	0·0088 (5)	0·0404 (3)	0·31300 (5)	4·20
C(13)	0·1411 (5)	−0·0387 (4)	0·34456 (5)	4·25
C(14)	0·0333 (6)	0·0401 (4)	0·36445 (5)	4·33
C(15)	0·1673 (6)	−0·0394 (4)	0·39593 (6)	4·52
C(16)	0·0634 (8)	0·0387 (6)	0·41630 (7)	4·73
C(17)	0·1961 (4)	−0·0433 (3)	0·44741 (3)	5·71
C(18)	0·0962 (4)	0·0374 (2)	0·46795 (3)	7·25

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

C(1)—O(1)	1·312 (3)	C(9)—C(10)	1·522 (4)
C(1)—O(2)	1·218 (3)	C(10)—C(11)	1·514 (4)
C(1)—C(2)	1·487 (3)	C(11)—C(12)	1·522 (4)
C(2)—C(3)	1·518 (4)	C(12)—C(13)	1·514 (4)
C(3)—C(4)	1·513 (4)	C(13)—C(14)	1·524 (4)
C(4)—C(5)	1·518 (4)	C(14)—C(15)	1·511 (4)
C(5)—C(6)	1·518 (4)	C(15)—C(16)	1·527 (4)
C(6)—C(7)	1·516 (4)	C(16)—C(17)	1·504 (4)
C(7)—C(8)	1·521 (4)	C(17)—C(18)	1·526 (5)
C(8)—C(9)	1·519 (4)		

C(2)—C(1)—O(1)	112·8 (2)	C(8)—C(9)—C(10)	113·9 (2)
C(2)—C(1)—O(2)	124·4 (2)	C(9)—C(10)—C(11)	114·1 (2)
O(1)—C(1)—O(2)	122·8 (2)	C(10)—C(11)—C(12)	114·2 (2)
C(1)—C(2)—C(3)	117·1 (2)	C(11)—C(12)—C(13)	113·8 (2)
C(2)—C(3)—C(4)	110·3 (2)	C(12)—C(13)—C(14)	114·1 (2)
C(3)—C(4)—C(5)	115·8 (2)	C(13)—C(14)—C(15)	113·7 (2)
C(4)—C(5)—C(6)	112·7 (2)	C(14)—C(15)—C(16)	114·5 (2)
C(5)—C(6)—C(7)	114·8 (2)	C(15)—C(16)—C(17)	113·8 (2)
C(6)—C(7)—C(8)	113·4 (2)	C(16)—C(17)—C(18)	113·8 (3)
C(7)—C(8)—C(9)	114·1 (2)		

C(1)—C(2)—C(3)—C(4)	173·7 (2)	C(10)—C(11)—C(12)—C(14)	179·9 (2)
C(2)—C(3)—C(4)—C(5)	−178·5 (2)	C(11)—C(12)—C(13)—C(14)	179·9 (2)
C(3)—C(4)—C(5)—C(6)	177·2 (2)	C(12)—C(13)—C(14)—C(15)	−179·9 (2)
C(4)—C(5)—C(6)—C(7)	179·3 (2)	C(13)—C(14)—C(15)—C(16)	179·6 (2)
C(5)—C(6)—C(7)—C(8)	−180·0 (2)	C(14)—C(15)—C(16)—C(17)	179·3 (2)
C(6)—C(7)—C(8)—C(9)	179·5 (2)	C(15)—C(16)—C(17)—C(18)	178·9 (3)
C(7)—C(8)—C(9)—C(10)	−179·5 (2)	O(1)—C(1)—C(2)—C(3)	−177·2 (2)
C(8)—C(9)—C(10)—C(11)	179·2 (2)	O(2)—C(1)—C(2)—C(3)	1·3 (4)
C(9)—C(10)—C(11)—C(12)	−179·9 (2)		

The structure of the *E* form agrees with the results derived by Holland & Neilson (1962, 1963) and Kobayashi *et al.* (1986). The polymethylene chain assumes an all-*trans* conformation constructing the $O\perp$ type subcell whose averaged dimensions are $a_s = 7{\cdot}36$, $b_s = 5{\cdot}02$, $c_s = 2{\cdot}55$ Å [the setting of the axes is made in accordance with orthorhombic polyethylene determined by Bunn (1939)]. The direction of the a_s axis coincides with the unique axis (the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52777 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

b axis) of the main lattice, and the c_s axis tilts toward the *a* axis by about 26°. In other words, the (011) plane of the sublattice is nearly parallel to the basal plane as in the *B* form (Goto & Asada, 1978). The most prominent difference between the structures of the *E* and *B* forms is in the conformation in the vicinity of the carboxyl group. The *E* form has a straight acyl chain, while the C(2)—C(3) bond in the *B* form takes a *gauche* conformation. The arrangement of the carboxyl groups projected onto the basal plane is shown in Fig. 2. The interatomic distances between the neighbouring carboxyl groups are slightly larger than those in the *B* form (see Fig. 3 of Goto & Asada, 1978).

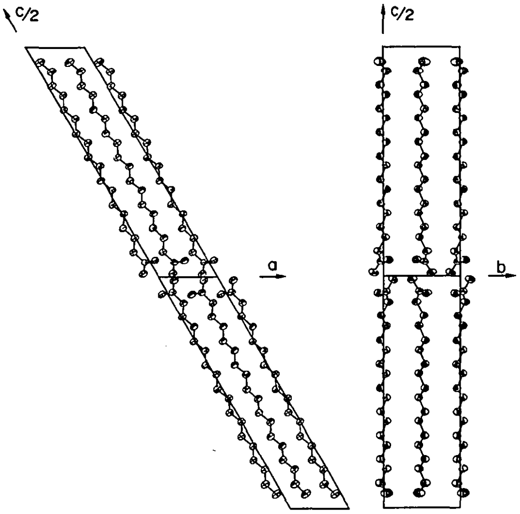

Fig. 1. *ORTEP* view of stearic acid *E* form. Thermal ellipsoids are plotted at the 50% probability level.

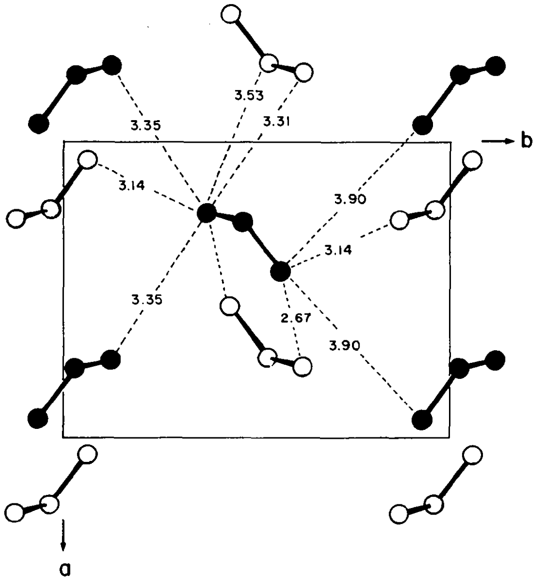

Fig. 2. Projection of carboxyl groups along the normal of the basal (*ab*) plane. Upper layer atoms ●, lower layer atoms ○.

The carboxyl group is nearly coplanar with the skeletal plane of the hydrocarbon chain. The bond lengths of C(1)—O(1) and C(1)—O(2) are 1·312 (3) and 1·218 (3) Å, respectively, which are the standard bond lengths of C—O and C═O bonds. Thus, the C(3)—C(2)—C(1)═O group assumes the *cis* conformation. The distance between the hydrogen-bonded O atoms is 2·670 (2) Å. Kobayashi *et al.* (1986) examined the temperature dependence of the conformation of the carboxyl groups by means of vibrational spectroscopy and concluded that no conformational changes occurred in the range from room temperature to liquid-N_2 temperature in contrast with the case of the *C* form where both *cis* and *trans* forms coexisted in a tautomeric equilibrium and the *trans* content increased with decreasing temperature (Hayashi & Umemura, 1975). The O···O length in a dimeric system of carboxyl groups is considered to be related to the occurrence of tunnelling exhange of the H atom (Matusushita & Matsubara, 1982). The probability of occurrence of the tunnelling motion is quite small for O···O distances greater than 2·64 Å. The large O···O length (2·67 Å) of the *E* form suggests that no proton exchange by tunnelling takes place, consistent with the conclusion obtained by the previous spectroscopic work.

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