ORGANIC COMPOUNDS

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Three Substituted 3-Amino-2-benzoylaminopropenoic Acid Derivatives

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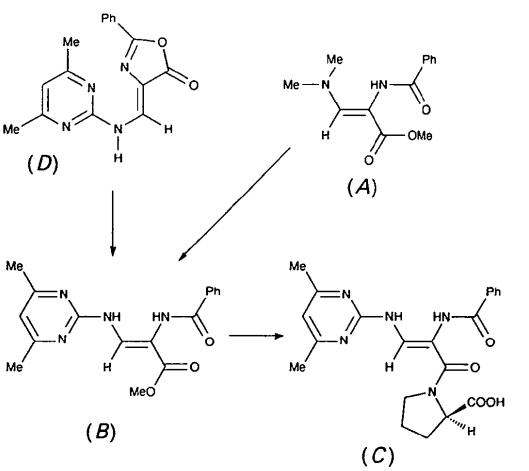
Abstract

The molecular structures of three substituted 3-amino-2-benzoylaminopropenoic acid derivatives, methyl (*Z*)-2-benzoylamino-3-dimethylaminopropenoate (*A*), methyl (*Z*)-2-benzoylamino-3-(4,6-dimethyl-2-pyrimidinylamino)propenoate (*B*) and *N*-[(*Z*)-2-benzoylamino-3-(4,6-dimethyl-2-pyrimidinylamino)propenoyl]-L-proline monohydrate (*C*), show that the configuration around the exocyclic C=C double bond is *Z*. The mechanisms of syntheses of (*B*) and (*C*) from (*A*) are confirmed as the *Z* configuration is preserved in the title compounds. The crystal structure of compound (*C*) is stabilized *via* hydrogen bonds from the solvent water molecules to the N atom bonded to the C=C double bond and to the two carbonyl O atoms in the molecule, each of the water molecules contributing to three hydrogen bonds. The bond lengths and angles agree with expected values.

Comment

Dehydroamino acids are of major interest in research on bioactive dehydropeptides and asymmetric hydrogenation (Schmidt, Häusler, Öhler & Poisel, 1979; Stammer, 1982; Kagan, 1985; El-Baba, Nuzillard, Paulin & Kagan, 1986; Schmidt, Lieberknecht & Wild, 1988).

Methyl (*Z*)-2-benzoylamino-3-dimethylaminopropenoate (*A*), prepared either in a two-step (Japan Kokai, 1975) or in a one-step synthesis from hippuric acid (Stanovnik, Svete, Tišler, Žorž, Hvala & Simonič, 1988), has been introduced recently as a versatile reagent for the synthesis of β-arylamino-α,β-dehydro-α-amino acid derivatives (Stanovnik, Urbanija, Svete & Tišler, 1989), β-heteroarylamino-α,β-dehydro-α-amino acids and dipeptides, such as (*B*) and (*C*) (Stanovnik *et al.*, 1988), as an alternative to the method where oxazolones, such as (*D*), are formed as intermediates (Stanovnik, Svete & Tišler, 1987; Svete, Stanovnik, Tišler, Golič & Leban, 1989), and monocyclic, bicyclic and polycyclic systems, where the α-amino acid structural element is incorporated into the ring systems, such as pyranones (Svete, Čadež, Stanovnik & Tišler, 1990), benzopyranones (Stanovnik, Svete & Tišler, 1989), pyranobenzopyranones (Ornik, Čadež, Stanovnik & Tišler, 1990), isomeric naphthopyranones and naphthodipyranones (Ornik, Stanovnik & Tišler, 1992*a*,*b*), pyranoazoles and pyranoazines (Stanovnik *et al.*, 1989; Stanovnik, Golič, Kmecl, Ornik, Svete & Tišler, 1991), including pyranoquinoline derivatives (Kmetič, Stanovnik & Tišler, 1993), and azolo- and azinopyrimidines (Stanovnik, van de Bovenkamp, Svete, Hvala, Simonič & Tišler, 1989).



X-ray structure analysis of (*D*) (Leban, Svete, Stanovnik & Tišler, 1991) showed that the configuration of the heteroaryl amino group and the N atom of the oxazolinone ring is *Z* around the exocyclic C=C double bond. The crystal structure determination was undertaken to elucidate the molecular structures and synthetic mechanisms of the title compounds.

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Views of the molecules in the same orientation along with the atomic numbering are shown in Figs. 1–3. The observed bond distances and angles are within the expected values when compared to those reported in *Tables of Bond Lengths Determined by X-ray and Neutron Diffraction*, Part I (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

The observed configuration of N atoms around the C=C bond is *Z* in all three compounds. The C=C bond distances in compounds (*A*) and (*B*) are somewhat longer [1.350 (5) and 1.332 (3) Å, respectively] when compared to the same distances of the two molecules of compound (*C*) in the asymmetric unit [1.325 (5) and 1.317 (5) Å for (I) and (II),

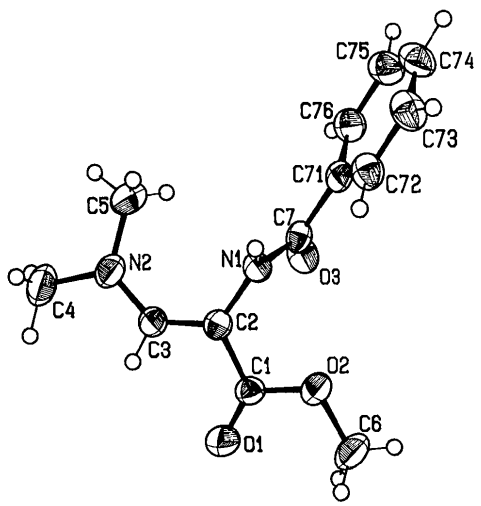

Fig. 1. *ORTEP* diagram (Johnson, 1965) showing the molecular structure and atom-labelling system of molecule (*A*). Non-H atoms are shown as 50% probability ellipsoids.

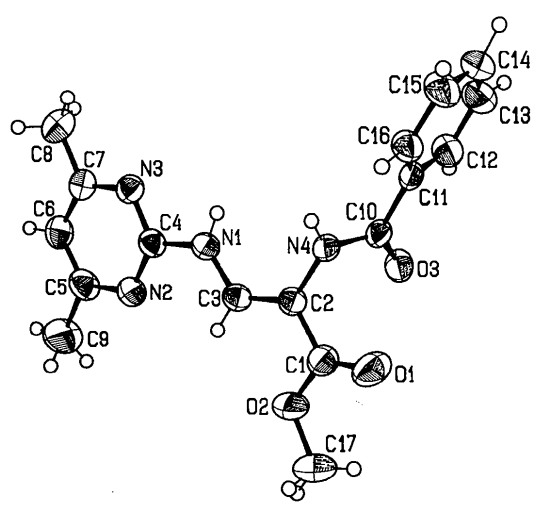

Fig. 2. *ORTEP* diagram (Johnson, 1965) showing the molecular structure and atom-labelling system of molecule (*B*). Non-H atoms are shown as 50% probability ellipsoids.

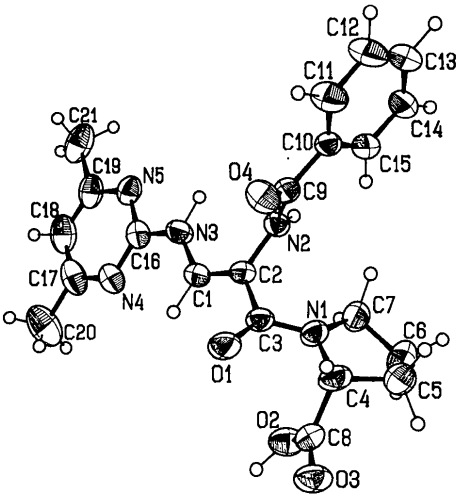

Fig. 3. *ORTEP* diagram (Johnson, 1965) showing the molecular structure and atom-labelling system of molecule (I) of the asymmetric unit of (*C*). Non-H atoms are shown as 50% probability ellipsoids.

respectively]. The geometric parameters of the phenyl rings in all four molecules can be considered to be equal within the limits of experimental error. While in compounds (*A*) and (*B*) the carbonyl groups adjacent to the phenyl ring are oriented under the plane defined by the N—C=C—N moiety, free rotation around the C—N bond in compound (*C*) is 'clipped' at the point where the carbonyl group is above this plane, as seen Figs. 1–3. This conformation might be explained by hydrogen-bonding interactions of carbonyl atoms O(1) and O(4) with O atoms of the water molecules O(10) and O(20) [for molecules (I) and (II) of the asymmetric unit, see Table 7], stabilizing the molecular structure. The influence of this hydrogen bond is also reflected by the carbonyl C—O bond distance which is longer in compound (*C*) [1.235 (4) and 1.230 (4) Å, C(9)—O(4)] with respect to the bond lengths in compounds (*A*) and (*B*) [1.226 (4) Å, C(7)—O(3) and 1.231 (2) Å, C(10)—O(3)], respectively. The same carbonyl O atom seems also to have a structural role in compound (*B*) where it is involved in hydrogen-bonding interactions with the N atoms around the C=C double bond of symmetry-related molecules. In the crystal structure of (*C*) the solvent molecules also take part in hydrogen bonding to the peptide N atoms N(2): O(10) interacts with the N(2) atom of molecule (II), while O(20) is within hydrogen-bonding distance of N(2) of the symmetrically related molecule (I), contributing to the stability of the crystal structure of compound (*C*).

The energy difference between *cis* and *trans* isomers in di-, tri- and polypeptide chains is about 8.4 kJ mol^{-1}, the *trans* isomer having the lower energy (Ramachandran, Ramakrishnan & Sasisek-

haran, 1963). In proline the difference is smaller due to the reduction in the contact between C^{α_i} and $C^{\delta_{i+1}}$ during the transformation from *cis* to *trans*. This is the reason for the occurrence of *cis* bonds in small cyclic peptides at the N-terminal end of proline (Wieland & Birr, 1976), as well as in some isolated cases in globular protein structures (Epp, Lattman, Schiffer, Huber & Palm, 1975). In the structure of (*C*), the proline is found to have the *trans* conformation. The angle C(2)—C(3)—N(1) is 118.2 (3) and 117.9 (3)° for molecules (I) and (II), respectively, of the asymmetric unit, agreeing with the normal value of 118° (Pauling, 1960). The angle O(1)—C(3)—N(1) is 121.8 (3) and 120.8 (3)° in (I) and (II), respectively, comparable to the mean value of 120.3° found in some oligopeptides (Ashida & Kakudo, 1974).

Proline rings can also be divided in two classes with respect to the torsion angle χ_1. In class A the torsion angle χ_1 takes negative values, while in class B the values are positive (Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1971). In compound (*C*) the proline ring has the B conformation with the χ_1 torsion angles defined by N(1)—C(4)—C(5)—C(6) of 28.6 (5) and 21.6 (6)° for molecules (I) and (II), respectively.

The rotations around the N—C^α and C^α—C bonds of the peptide linkage are denoted by φ and ψ torsional angles (Ramachandran & Ramakrishnan, 1965). In our compounds the C^α atom is sp^2 hybridized and the torsion angles for compound (*C*) are: $\varphi = -62.7$ (4), -73.4 (4)° [C(9)—N(2)—C(2)—C(3)]; $\psi = 39.6$ (4), 44.6 (4)° [N(2)—C(2)—C(3)—N(1)] for the two molecules in the asymmetric unit. The corresponding values of φ in compounds (*A*) and (*B*) are 75.7 (5) [C(7)—N(1)—C(2)—C(1)] and 62.3 (3)° [C(10)—N(4)—C(2)—C(1)], respectively, reflecting again the different orientation of the carbonyl group linked to the phenyl ring.

The peptide bond is in *trans* conformation in all three compounds, with the ω angles ranging from 173.9 (3) to 179.8 (2)°. The same *trans* conformation is also evident in the second peptide linkage of compound (*C*), where the ω angles [C(10)—C(9)—N(2)—C(2)] are 173.6 (3) and 176.0 (3)° for (I) and (II), respectively. The φ angles for the terminal proline residue of compound (*C*) [C(3)—N(1)—C(4)—C(8)] are 62.8 (4) and 58.1 (4)° for (I) and (II), respectively.

The orientation of the substituents around the C=C double bond in the three compounds is similar. The two C atoms and the two bonded N atoms are nearly coplanar with the heterocyclic ring in compounds (*B*) and (*C*); the heterocyclic ring plane and the N—C=C—N plane form angles of 10.1 (1)° for (*B*), and 7.9 (1) and 8.0 (1)° for (*C*); the dimethylamino group of compound (*A*), defined by atoms N(2), C(4) and C(5), forms an angle of 9.0 (4)° with the N—C=C—N plane. Similarly, the phenyl rings in (*A*), (*B*) and (*C*) form angles of 65.3 (2), 83.7 (1), 90.2 (2) and 105.3 (2)° with the N—C=C—N plane, respectively, while the pyrrolidine ring forms angles of 51.7 (2) and 53.7 (2)° with this plane in the two molecules of the asymmetric unit of compound (*C*).

Experimental

Compound (*A*)

Crystal data

$C_{13}H_{16}N_2O_3$
$M_r = 248.28$
Orthorhombic
*Fdd*2
$a = 41.505$ (6) Å
$b = 19.450$ (2) Å
$c = 6.338$ (1) Å
$V = 5117$ (2) Å^3
$Z = 16$
$D_x = 1.289$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 50 reflections
$\theta = 6.16$–$12.51°$
$\mu = 0.866$ mm^{-1}
$T = 293$ K
Prismatic
0.40 × 0.24 × 0.08 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6231 measured reflections
1676 independent reflections
822 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.040$
$\theta_{max} = 28°$
$h = 0 \rightarrow 54$
$k = -25 \rightarrow 25$
$l = -8 \rightarrow 8$
3 standard reflections
frequency: 125 min
intensity variation: 1.8%

Refinement

Refinement on F
$R = 0.029$
$wR = 0.032$
$S = 1.139$
1042 reflections
227 parameters
All H-atom parameters refined
$(\Delta/\sigma)_{max} = 0.69$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: $2.6\,(3) \times 10^5$

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O(1)	0.53141 (6)	0.1144 (1)	0.65034	0.0584 (9)
O(2)	0.58115 (5)	0.0987 (1)	0.7767 (6)	0.0481 (7)
O(3)	0.62173 (5)	0.0707 (1)	0.3496 (6)	0.0471 (7)
N(1)	0.60952 (5)	0.1753 (1)	0.4827 (6)	0.0334 (7)
N(2)	0.56185 (7)	0.2324 (1)	0.1552 (6)	0.0453 (9)
C(1)	0.55988 (7)	0.1248 (1)	0.6385 (7)	0.0365 (9)
C(2)	0.57532 (7)	0.1666 (1)	0.4758 (7)	0.0344 (8)
C(3)	0.55590 (7)	0.1955 (1)	0.3296 (7)	0.0361 (9)
C(4)	0.5351 (1)	0.2603 (2)	0.0355 (9)	0.065 (2)
C(5)	0.5940 (1)	0.2447 (2)	0.0717 (8)	0.057 (1)
C(6)	0.5679 (1)	0.0561 (2)	0.9405 (8)	0.061 (1)
C(7)	0.63042 (7)	0.1258 (1)	0.4241 (6)	0.0332 (8)

C(71)	0.66549 (7)	0.1429 (1)	0.4490 (6)	0.0352 (8)
C(72)	0.67718 (8)	0.1820 (2)	0.6179 (8)	0.043 (1)
C(73)	0.70987 (8)	0.1951 (2)	0.6327 (8)	0.052 (1)
C(74)	0.73067 (7)	0.1710 (2)	0.4844 (9)	0.0550 (1)
C(75)	0.71939 (9)	0.1334 (2)	0.3150 (8)	0.0550 (1)
C(76)	0.68685 (8)	0.1183 (2)	0.2996 (8)	0.0460 (1)

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

O(1)—C(1)	1.202 (4)	C(1)—C(2)	1.460 (5)
O(2)—C(1)	1.343 (5)	C(2)—C(3)	1.350 (5)
O(2)—C(6)	1.438 (6)	C(7)—C(71)	1.501 (4)
O(3)—C(7)	1.226 (4)	C(71)—C(76)	1.382 (5)
N(1)—C(7)	1.348 (4)	C(71)—C(72)	1.400 (5)
N(1)—C(2)	1.430 (4)	C(72)—C(73)	1.384 (5)
N(2)—C(3)	1.341 (5)	C(73)—C(74)	1.359 (6)
N(2)—C(4)	1.449 (6)	C(74)—C(75)	1.382 (7)
N(2)—C(5)	1.454 (5)	C(75)—C(76)	1.385 (5)
C(1)—O(2)—C(6)	115.9 (3)	O(3)—C(7)—N(1)	122.8 (3)
C(7)—N(1)—C(2)	123.1 (2)	O(3)—C(7)—C(71)	121.3 (3)
C(3)—N(2)—C(4)	119.4 (3)	N(1)—C(7)—C(71)	115.9 (2)
C(3)—N(2)—C(5)	123.8 (3)	C(76)—C(71)—C(72)	119.3 (3)
C(4)—N(2)—C(5)	116.7 (4)	C(76)—C(71)—C(7)	118.3 (3)
O(1)—C(1)—O(2)	122.8 (3)	C(72)—C(71)—C(7)	122.4 (3)
O(1)—C(1)—C(2)	124.7 (3)	C(73)—C(72)—C(71)	119.5 (4)
O(2)—C(1)—C(2)	112.5 (3)	C(74)—C(73)—C(72)	120.8 (4)
C(3)—C(2)—N(1)	124.3 (3)	C(73)—C(74)—C(75)	120.3 (3)
C(3)—C(2)—C(1)	117.0 (3)	C(74)—C(75)—C(76)	119.8 (4)
N(1)—C(2)—C(1)	118.7 (3)	C(71)—C(76)—C(75)	120.3 (4)
N(2)—C(3)—C(2)	132.7 (3)		

Compound (*B*)

Crystal data

$C_{17}H_{18}N_4O_3$
M_r = 326.36
Monoclinic
Cc
a = 36.050 (5) Å
b = 4.943 (1) Å
c = 19.793 (3) Å
β = 108.72 (1)°
V = 3340 (2) Å^3
Z = 8
D_x = 1.298 Mg m^{-3}

Mo *K*α radiation
λ = 0.71069 Å
Cell parameters from 100 reflections
θ = 7.2–12.4°
μ = 0.856 mm^{-1}
T = 293 K
Prismatic
0.6 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
8890 measured reflections
4454 independent reflections
1387 observed reflections [$I > 2.5\sigma(I)$]

R_{int} = 0.045
θ_{max} = 28°
h = −47 → 47
k = −6 → 0
l = −26 → 26
3 standard reflections
frequency: 166.67 min
intensity variation: 3.8%

Refinement

Refinement on *F*
R = 0.038
wR = 0.048
S = 1.130
2317 reflections
290 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{max}$ = 0.86
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 1.94 (7) × 10^5

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (*B*)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
C(1)	0.07253 (8)	−0.0017 (5)	0.6469 (1)	0.0494 (9)
O(1)	0.07417 (7)	−0.1088 (5)	0.7019 (1)	0.0749 (9)
O(2)	0.04308 (6)	−0.0465 (5)	0.5860 (1)	0.0726 (8)
C(2)	0.10112 (7)	0.1918 (5)	0.6367 (1)	0.0400 (7)
C(3)	0.09432 (7)	0.3329 (5)	0.5766 (1)	0.0418 (7)
N(1)	0.11784 (6)	0.5293 (4)	0.56494 (9)	0.0448 (7)
C(4)	0.11205 (7)	0.6621 (5)	0.5005 (1)	0.0417 (8)
N(2)	0.08234 (6)	0.5822 (5)	0.4446 (1)	0.0506 (7)
C(5)	0.07962 (8)	0.7083 (6)	0.3828 (1)	0.0563 (9)
C(6)	0.10588 (8)	0.9053 (6)	0.3790 (1)	0.0556 (9)
C(7)	0.13538 (7)	0.9749 (5)	0.4412 (1)	0.0468 (8)
N(3)	0.13870 (6)	0.8515 (4)	0.5028 (1)	0.0453 (7)
C(8)	0.16535 (9)	1.1849 (6)	0.4424 (2)	0.062 (1)
C(9)	0.0472 (1)	0.6161 (9)	0.3181 (2)	0.093 (1)
N(4)	0.13563 (6)	0.2308 (4)	0.69611 (9)	0.0417 (6)
C(10)	0.16119 (7)	0.0286 (4)	0.7235 (1)	0.0403 (8)
O(3)	0.15630 (6)	−0.2020 (3)	0.69879 (9)	0.0552 (6)
C(11)	0.19622 (7)	0.0928 (5)	0.7859 (1)	0.0385 (7)
C(12)	0.22914 (8)	−0.0678 (6)	0.7973 (1)	0.0524 (9)
C(13)	0.26262 (8)	−0.0195 (7)	0.8541 (2)	0.063 (1)
C(14)	0.26311 (8)	0.1856 (6)	0.9011 (1)	0.061 (1)
C(15)	0.23056 (9)	0.3441 (6)	0.8915 (1)	0.062 (1)
C(16)	0.19707 (8)	0.3008 (5)	0.8334 (1)	0.0498 (8)
C(17)	0.0123 (1)	−0.223 (1)	0.5914 (3)	0.097 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (*B*)

C(1)—O(1)	1.195 (3)	C(6)—C(7)	1.387 (3)
C(1)—O(2)	1.344 (3)	C(7)—N(3)	1.334 (3)
C(1)—C(2)	1.467 (4)	C(7)—C(8)	1.493 (4)
O(2)—C(17)	1.442 (5)	N(4)—C(10)	1.350 (3)
C(2)—C(3)	1.332 (3)	C(10)—O(3)	1.231 (2)
C(2)—N(4)	1.424 (3)	C(10)—C(11)	1.490 (3)
C(3)—N(1)	1.357 (3)	C(11)—C(12)	1.385 (4)
N(1)—C(4)	1.389 (3)	C(11)—C(16)	1.388 (3)
C(4)—N(2)	1.329 (3)	C(12)—C(13)	1.381 (4)
C(4)—N(3)	1.332 (3)	C(13)—C(14)	1.372 (5)
N(2)—C(5)	1.348 (3)	C(14)—C(15)	1.372 (4)
C(5)—C(6)	1.377 (4)	C(15)—C(16)	1.391 (3)
C(5)—C(9)	1.501 (4)		
O(1)—C(1)—O(2)	122.5 (3)	N(3)—C(7)—C(6)	121.1 (2)
O(1)—C(1)—C(2)	125.6 (2)	N(3)—C(7)—C(8)	116.8 (2)
O(2)—C(1)—C(2)	111.8 (2)	C(6)—C(7)—C(8)	122.1 (3)
C(1)—O(2)—C(17)	116.0 (3)	C(4)—N(3)—C(7)	116.0 (2)
C(3)—C(2)—N(4)	121.9 (2)	C(10)—N(4)—C(2)	122.3 (2)
C(3)—C(2)—C(1)	121.9 (2)	O(3)—C(10)—N(4)	122.3 (2)
N(4)—C(2)—C(1)	116.2 (2)	O(3)—C(10)—C(11)	120.1 (2)
C(2)—C(3)—N(1)	125.5 (2)	N(4)—C(10)—C(11)	117.6 (2)
C(3)—N(1)—C(4)	125.2 (2)	C(12)—C(11)—C(16)	118.9 (2)
N(2)—C(4)—N(3)	128.1 (2)	C(12)—C(11)—C(10)	117.8 (2)
N(2)—C(4)—N(1)	117.9 (2)	C(16)—C(11)—C(10)	123.2 (2)
N(3)—C(4)—N(1)	114.0 (2)	C(13)—C(12)—C(11)	120.9 (3)
C(4)—N(2)—C(5)	115.0 (2)	C(14)—C(13)—C(12)	119.8 (3)
N(2)—C(5)—C(6)	121.7 (2)	C(13)—C(14)—C(15)	120.2 (2)
N(2)—C(5)—C(9)	116.3 (3)	C(14)—C(15)—C(16)	120.2 (3)
C(6)—C(5)—C(9)	121.9 (3)	C(11)—C(16)—C(15)	119.9 (3)
C(5)—C(6)—C(7)	118.1 (2)		

Compound (*C*)

Crystal data

$C_{21}H_{23}N_5O_4.H_2O$
M_r = 427.46
Monoclinic
$P2_1$
a = 9.398 (1) Å
b = 18.422 (2) Å
c = 12.663 (1) Å
β = 91.46 (1)°

Mo *K*α radiation
λ = 0.71069 Å
Cell parameters from 75 reflections
θ = 8.07–12.65°
μ = 0.883 mm^{-1}
T = 293 K
Prismatic

V = 2191.8 (7) Å^3
Z = 4
D_x = 1.296 Mg m^{-3}
D_m = 1.289 Mg m^{-3}
D_m measured by flotation

0.76 × 0.32 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
10 173 measured reflections
5049 independent reflections
2404 observed reflections [$I > 2.5\sigma(I)$]

R_{int} = 0.015
θ_{max} = 28°
$h = -12 \rightarrow 12$
$k = -24 \rightarrow 24$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 200 min
intensity variation: 0.92%

Refinement

Refinement on F
R = 0.034
wR = 0.041
S = 0.7469
3617 reflections
558 parameters

All H-atom parameters refined
$(\Delta/\sigma)_{max}$ = 1.70
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: none

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (*C*)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. Atoms of molecules (I) and (II) of the asymmetric unit are indicated by the labels *A* and *B*, respectively.

	x	*y*	*z*	U_{eq}
C(1*A*)	0.2639 (3)	0.3349 (2)	0.3485 (3)	0.044 (1)
C(2*A*)	0.3153 (3)	0.3973 (2)	0.3142 (2)	0.041 (1)
C(3*A*)	0.4686 (3)	0.4164 (2)	0.3329 (3)	0.042 (1)
O(1*A*)	0.5288 (2)	0.40030	0.4174 (2)	0.0617 (9)
N(1*A*)	0.5361 (3)	0.4518 (2)	0.2567 (2)	0.0453 (9)
C(4*A*)	0.6810 (3)	0.4772 (2)	0.2776 (3)	0.055 (1)
C(5*A*)	0.7174 (4)	0.5182 (3)	0.1769 (5)	0.080 (2)
C(6*A*)	0.6289 (5)	0.4812 (3)	0.0926 (4)	0.085 (2)
C(7*A*)	0.4923 (4)	0.4607 (2)	0.1452 (3)	0.057 (1)
C(8*A*)	0.7876 (3)	0.4175 (2)	0.2999 (3)	0.048 (1)
O(2*A*)	0.7491 (3)	0.3521 (2)	0.2694 (2)	0.0593 (9)
O(3*A*)	0.9026 (2)	0.4309 (2)	0.3413 (3)	0.0661 (9)
N(2*A*)	0.2252 (2)	0.4494 (1)	0.2618 (2)	0.0387 (8)
C(9*A*)	0.2021 (3)	0.5144 (2)	0.3058 (3)	0.041 (1)
O(4*A*)	0.2483 (3)	0.5302 (1)	0.3950 (2)	0.0589 (8)
C(10*A*)	0.1198 (3)	0.5689 (2)	0.2419 (3)	0.0408 (9)
C(11*A*)	0.0604 (4)	0.6268 (2)	0.2935 (3)	0.064 (1)
C(12*A*)	−0.0150 (5)	0.6797 (3)	0.2375 (4)	0.072 (1)
C(13*A*)	−0.0301 (4)	0.6748 (2)	0.1295 (3)	0.065 (1)
C(14*A*)	0.0301 (4)	0.6183 (2)	0.0779 (3)	0.064 (1)
C(15*A*)	0.1053 (4)	0.5650 (2)	0.1329 (3)	0.054 (1)
N(3*A*)	0.1197 (3)	0.3186 (2)	0.3409 (2)	0.0498 (9)
C(16*A*)	0.0616 (4)	0.2526 (2)	0.3667 (3)	0.046 (1)
N(5*A*)	0.1465 (3)	0.1997 (2)	0.4021 (2)	0.054 (1)
C(19*A*)	0.0822 (5)	0.1365 (2)	0.4256 (3)	0.064 (1)
C(18*A*)	−0.0627 (5)	0.1290 (2)	0.4157 (3)	0.070 (1)
C(17*A*)	−0.1425 (4)	0.1863 (2)	0.3805 (3)	0.057 (1)
N(4*A*)	−0.0809 (3)	0.2488 (2)	0.3536 (2)	0.0499 (9)
C(21*A*)	0.1788 (7)	0.0775 (3)	0.4666 (5)	0.098 (2)
C(20*A*)	−0.3020 (5)	0.1848 (3)	0.3757 (3)	0.079 (2)
O(10*A*)	0.3496 (4)	0.4490 (2)	0.5783 (2)	0.086 (1)
C(1*B*)	0.1966 (3)	0.5025 (2)	0.8468 (3)	0.047 (1)
C(2*B*)	0.1464 (3)	0.4397 (2)	0.8130 (2)	0.041 (9)
C(3*B*)	−0.0066 (3)	0.4217 (2)	0.8290 (2)	0.042 (1)
O(1*B*)	−0.0645 (2)	0.4347 (2)	0.9134 (2)	0.0600 (8)
N(1*B*)	−0.0796 (3)	0.3907 (2)	0.7488 (2)	0.0432 (8)
C(4*B*)	−0.2286 (3)	0.3682 (2)	0.7645 (3)	0.051 (1)
C(5*B*)	−0.2715 (5)	0.3353 (3)	0.6570 (4)	0.082 (2)
C(6*B*)	−0.1757 (5)	0.3651 (4)	0.5826 (3)	0.087 (2)
C(7*B*)	−0.0388 (3)	0.3843 (2)	0.6376 (3)	0.051 (1)
C(8*B*)	−0.3265 (3)	0.4289 (2)	0.7970 (3)	0.050 (1)
O(2*B*)	−0.2904 (3)	0.4944 (2)	0.7669 (2)	0.0641 (9)
O(3*B*)	−0.4353 (3)	0.4150 (2)	0.8418 (3)	0.068 (1)
N(2*B*)	0.2355 (2)	0.3873 (2)	0.7639 (2)	0.0402 (8)
C(9*B*)	0.2800 (3)	0.3272 (2)	0.8157 (3)	0.043 (1)
O(4*B*)	0.2510 (3)	0.3155 (1)	0.9083 (2)	0.0580 (8)
C(10*B*)	0.3643 (3)	0.2740 (2)	0.7549 (3)	0.0428 (9)
C(11*B*)	0.3494 (3)	0.2657 (2)	0.6464 (3)	0.050 (1)
C(12*B*)	0.4251 (4)	0.2120 (2)	0.5951 (3)	0.059 (1)
C(13*B*)	0.5180 (4)	0.1681 (2)	0.6501 (4)	0.073 (2)
C(14*B*)	0.5348 (5)	0.1765 (3)	0.7586 (4)	0.073 (2)
C(15*B*)	0.4587 (4)	0.2285 (2)	0.8107 (3)	0.062 (1)
N(3*B*)	0.3391 (3)	0.5224 (2)	0.8406 (3)	0.056 (1)
C(16*B*)	0.3907 (4)	0.5899 (2)	0.8633 (3)	0.049 (1)
N(5*B*)	0.3008 (4)	0.6400 (2)	0.8962 (2)	0.059 (1)
C(19*B*)	0.3565 (6)	0.7058 (2)	0.9174 (3)	0.068 (2)
C(18*B*)	0.4978 (6)	0.7196 (3)	0.9044 (3)	0.076 (2)
C(17*B*)	0.5838 (5)	0.6644 (2)	0.8709 (3)	0.063 (1)
N(4*B*)	0.5306 (3)	0.5984 (2)	0.8489 (2)	0.055 (1)
C(21*B*)	0.2547 (8)	0.7617 (3)	0.9573 (4)	0.097 (2)
C(20*B*)	0.7423 (6)	0.6725 (3)	0.8586 (4)	0.091 (2)
O(20*B*)	0.1061 (3)	0.3802 (2)	1.0801 (2)	0.077 (1)

Table 6. *Selected geometric parameters* (Å, °) *for* (*C*)

C(1*A*)—C(2*A*)	1.325 (5)	C(1*B*)—C(2*B*)	1.317 (5)
C(1*A*)—N(3*A*)	1.389 (4)	C(1*B*)—N(3*B*)	1.392 (4)
C(2*A*)—N(2*A*)	1.431 (4)	C(2*B*)—N(2*B*)	1.431 (4)
C(2*A*)—C(3*A*)	1.496 (4)	C(2*B*)—C(3*B*)	1.494 (4)
C(3*A*)—O(1*A*)	1.233 (4)	C(3*B*)—O(1*B*)	1.235 (4)
C(3*A*)—N(1*A*)	1.337 (4)	C(3*B*)—N(1*B*)	1.338 (4)
N(1*A*)—C(4*A*)	1.459 (4)	N(1*B*)—C(7*B*)	1.474 (4)
N(1*A*)—C(7*A*)	1.470 (4)	N(1*B*)—C(4*B*)	1.479 (4)
C(4*A*)—C(8*A*)	1.509 (5)	C(4*B*)—C(8*B*)	1.511 (5)
C(4*A*)—C(5*A*)	1.529 (7)	C(4*B*)—C(5*B*)	1.535 (6)
C(5*A*)—C(6*A*)	1.501 (7)	C(5*B*)—C(6*B*)	1.430 (7)
C(6*A*)—C(7*A*)	1.509 (6)	C(6*B*)—C(7*B*)	1.490 (6)
C(8*A*)—O(3*A*)	1.214 (4)	C(8*B*)—O(3*B*)	1.209 (4)
C(8*A*)—O(2*A*)	1.314 (5)	C(8*B*)—O(2*B*)	1.312 (5)
N(2*A*)—C(9*A*)	1.341 (4)	N(2*B*)—C(9*B*)	1.346 (4)
C(9*A*)—O(4*A*)	1.235 (4)	C(9*B*)—O(4*B*)	1.230 (4)
C(9*A*)—C(10*A*)	1.493 (4)	C(9*B*)—C(10*B*)	1.488 (5)
C(10*A*)—C(11*A*)	1.378 (5)	C(10*B*)—C(11*B*)	1.385 (5)
C(10*A*)—C(15*A*)	1.384 (5)	C(10*B*)—C(15*B*)	1.399 (5)
C(11*A*)—C(12*A*)	1.388 (6)	C(11*B*)—C(12*B*)	1.389 (5)
C(12*A*)—C(13*A*)	1.374 (7)	C(12*B*)—C(13*B*)	1.386 (6)
C(13*A*)—C(14*A*)	1.360 (6)	C(13*B*)—C(14*B*)	1.388 (7)
C(14*A*)—C(15*A*)	1.387 (6)	C(14*B*)—C(15*B*)	1.375 (6)
N(3*A*)—C(16*A*)	1.376 (4)	N(3*B*)—C(16*B*)	1.363 (5)
C(16*A*)—N(5*A*)	1.330 (4)	C(16*B*)—N(5*B*)	1.326 (5)
C(16*A*)—N(4*A*)	1.347 (4)	C(16*B*)—N(4*B*)	1.342 (4)
N(5*A*)—C(19*A*)	1.349 (5)	N(5*B*)—C(19*B*)	1.344 (6)
C(19*A*)—C(18*A*)	1.371 (7)	C(19*B*)—C(18*B*)	1.366 (8)
C(19*A*)—C(21*A*)	1.501 (7)	C(19*B*)—C(21*B*)	1.501 (8)
C(18*A*)—C(17*A*)	1.362 (6)	C(18*B*)—C(17*B*)	1.374 (7)
C(17*A*)—N(4*A*)	1.337 (5)	C(17*B*)—N(4*B*)	1.340 (5)
C(17*A*)—C(20*A*)	1.499 (6)	C(17*B*)—C(20*B*)	1.509 (7)
C(2*A*)—C(1*A*)—N(3*A*)	121.9 (3)	C(2*B*)—C(1*B*)—N(3*B*)	123.4 (3)
C(1*A*)—C(2*A*)—N(2*A*)	121.1 (3)	C(1*B*)—C(2*B*)—N(2*B*)	121.7 (3)
C(1*A*)—C(2*A*)—C(3*A*)	120.7 (3)	C(1*B*)—C(2*B*)—C(3*B*)	119.0 (3)
N(2*A*)—C(2*A*)—C(3*A*)	118.2 (3)	N(2*B*)—C(2*B*)—C(3*B*)	119.0 (3)
O(1*A*)—C(3*A*)—N(1*A*)	121.8 (3)	O(1*B*)—C(3*B*)—N(1*B*)	120.8 (3)
O(1*A*)—C(3*A*)—C(2*A*)	120.0 (3)	O(1*B*)—C(3*B*)—C(2*B*)	121.3 (3)
N(1*A*)—C(3*A*)—C(2*A*)	118.2 (3)	N(1*B*)—C(3*B*)—C(2*B*)	117.9 (3)
C(3*A*)—N(1*A*)—C(4*A*)	118.9 (3)	C(3*B*)—N(1*B*)—C(7*B*)	128.2 (3)
C(3*A*)—N(1*A*)—C(7*A*)	128.4 (3)	C(3*B*)—N(1*B*)—C(4*B*)	119.1 (3)
C(4*A*)—N(1*A*)—C(7*A*)	112.1 (3)	C(7*B*)—N(1*B*)—C(4*B*)	112.1 (2)
N(1*A*)—C(4*A*)—C(8*A*)	114.4 (3)	N(1*B*)—C(4*B*)—C(8*B*)	114.5 (3)
N(1*A*)—C(4*A*)—C(5*A*)	103.6 (3)	N(1*B*)—C(4*B*)—C(5*B*)	102.7 (3)
C(8*A*)—C(4*A*)—C(5*A*)	110.8 (3)	C(8*B*)—C(4*B*)—C(5*B*)	112.7 (3)
C(6*A*)—C(5*A*)—C(4*A*)	103.7 (4)	C(6*B*)—C(5*B*)—C(4*B*)	106.1 (4)
C(5*A*)—C(6*A*)—C(7*A*)	105.2 (4)	C(5*B*)—C(6*B*)—C(7*B*)	109.5 (4)
N(1*A*)—C(7*A*)—C(6*A*)	103.4 (3)	N(1*B*)—C(7*B*)—C(6*B*)	102.9 (3)
O(3*A*)—C(8*A*)—O(2*A*)	123.3 (3)	O(3*B*)—C(8*B*)—O(2*B*)	124.0 (3)
O(3*A*)—C(8*A*)—C(4*A*)	120.8 (3)	O(3*B*)—C(8*B*)—C(4*B*)	119.9 (3)
O(2*A*)—C(8*A*)—C(4*A*)	115.9 (3)	O(2*B*)—C(8*B*)—C(4*B*)	115.9 (3)
C(9*A*)—N(2*A*)—C(2*A*)	120.4 (3)	C(9*B*)—N(2*B*)—C(2*B*)	121.4 (3)

O(4A)—C(9A)—N(2A)	122.3 (3)	O(4B)—C(9B)—N(2B)	122.3 (3)
O(4A)—C(9A)—C(10A)	120.1 (3)	O(4B)—C(9B)—C(10B)	120.8 (3)
N(2A)—C(9A)—C(10A)	117.5 (3)	N(2B)—C(9B)—C(10B)	116.9 (3)
C(11A)—C(10A)—C(15A)	118.8 (3)	C(11B)—C(10B)—C(15B)	118.8 (3)
C(11A)—C(10A)—C(9A)	118.3 (3)	C(11B)—C(10B)—C(9B)	122.9 (3)
C(15A)—C(10A)—C(9A)	122.9 (3)	C(15B)—C(10B)—C(9B)	118.2 (3)
C(10A)—C(11A)—C(12A)	120.5 (4)	C(10B)—C(11B)—C(12B)	120.1 (3)
C(13A)—C(12A)—C(11A)	120.1 (4)	C(13B)—C(12B)—C(11B)	120.7 (4)
C(14A)—C(13A)—C(12A)	119.7 (4)	C(12B)—C(13B)—C(14B)	119.6 (4)
C(13A)—C(14A)—C(15A)	120.8 (4)	C(15B)—C(14B)—C(13B)	120.3 (4)
C(10A)—C(15A)—C(14A)	120.1 (3)	C(14B)—C(15B)—C(10B)	120.4 (4)
C(16A)—N(3A)—C(1A)	124.6 (3)	C(16B)—N(3B)—C(1B)	124.4 (3)
N(5A)—C(16A)—N(4A)	126.1 (3)	N(5B)—C(16B)—N(4B)	126.6 (3)
N(5A)—C(16A)—N(3A)	119.3 (3)	N(5B)—C(16B)—N(3B)	118.4 (3)
N(4A)—C(16A)—N(3A)	114.6 (3)	N(4B)—C(16B)—N(3B)	115.0 (3)
C(16A)—N(5A)—C(19A)	116.0 (3)	C(16B)—N(5B)—C(19B)	116.3 (4)
N(5A)—C(19A)—C(18A)	121.1 (4)	N(5B)—C(19B)—C(18B)	121.2 (4)
N(5A)—C(19A)—C(21A)	115.6 (4)	N(5B)—C(19B)—C(21B)	115.9 (5)
C(18A)—C(19A)—C(21A)	123.3 (4)	C(18B)—C(19B)—C(21B)	122.9 (4)
C(17A)—C(18A)—C(19A)	119.3 (4)	C(19B)—C(18B)—C(17B)	118.8 (4)
N(4A)—C(17A)—C(18A)	120.8 (4)	N(4B)—C(17B)—C(18B)	121.1 (4)
N(4A)—C(17A)—C(20A)	116.4 (4)	N(4B)—C(17B)—C(20B)	115.6 (4)
C(18A)—C(17A)—C(20A)	122.7 (4)	C(18B)—C(17B)—C(20B)	123.3 (5)
C(17A)—N(4A)—C(16A)	116.7 (3)	C(17B)—N(4B)—C(16B)	116.1 (3)

Table 7. *Hydrogen-bond distances* (Å) *between water molecules and molecules* (I) *and* (II) *of the asymmetric unit of compound* (*C*)

O(10)···O(1A)	2.822 (4)	O(20)···O(1B)	2.804 (4)
O(10)···N(2B)	2.846 (4)	O(20)···O(2A^{i})	2.835 (4)
O(10)···O(4A)	2.902 (4)	O(20)···O(4A)	2.856 (4)

Symmetry code: (i) $x, y, z-1$.

For compound (*A*): $w = W_fW_s$, where $W_f(|F_o| < 25) = (|F_o|/25)^{1.5}$, $W_f(|F_o| > 33) = (33/|F_o|)^{0.5}$, $W_f(25 < |F_o| < 33) = 1.0$, $W_s(\sin\theta < 0.30) = (\sin\theta/0.30)^{3.0}$, $W_s(\sin\theta > 0.32) = (0.32/\sin\theta)^{3.0}$, $W_s(0.30 < \sin\theta < 0.30) = 1.0$.

For compound (*B*): $w = 2W_fW_s$, where $W_f(|F_o| < 19) = (|F_o|/19)^{1.0}$, $W_f(|F_o| > 26) = (33/|F_o|)^{1.5}$, $W_f(19 < |F_o| < 26) = 1.0$, $W_s(\sin\theta < 0.36) = (\sin\theta/0.36)^{1.5}$, $W_s(\sin\theta > 0.39) = (0.39/\sin\theta)^{5.0}$, $W_s(0.36 < \sin\theta < 0.39) = 1.0$.

For compound (*C*): $w = 4W_fW_s$, where $W_f(|F_o| < 8) = (|F_o|/8)^{1.0}$, $W_f(|F_o| > 14) = (14/|F_o|/25)^{1.0}$, $W_f(8 < |F_o| < 14) = 1.0$, $W_s(\sin\theta < 0.33) = (\sin\theta/0.33)^{2.0}$, $W_s(\sin\theta > 0.37) = (0.37/\sin\theta)^{6.0}$, $W_s(0.33 < \sin\theta < 0.37) = 1.0$; the positions of H atoms were calculated and included in structure-factor calculations as fixed-atom contributions.

For all compounds, data collection: Enraf-Nonius CAD-4 software. Cell refinement: *XRAY*76 *PARAM* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Data reduction: *XRAY*76 *DATCOR*, *DATRDN*. Program(s) used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (*A*), (*B*); *SHELXS*86 (Sheldrick, 1985) for (*C*). Program(s) used to refine structure: *XRAY*76 *CRYSLQ*. Software used to prepare material for publication: *XRAY*76 *BONDLA*, *LISTFC*; *Xtal*3.0 *BONDLA* (Hall & Stewart, 1990). Scattering factors for neutral atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71458 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1033]

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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

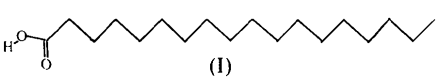
Two bimolecular layers forming a double-layered polytypic structure exist in a repeating unit along the stacking direction. One bimolecular layer has essentially the same structure as that of the ordinary single-layered type of the B form.

Comment

The structure determination of the orthorhombic modification of the B form of stearic acid (I) (octadecanoic acid) has been undertaken to confirm its 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 [0$\bar{1}$0] 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



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