Table 3. *Hydrogen-bonds parameters (Å, °)*

D—H···A	H···A^a	D—H^a	D—H···A^a	H···A^b
N1—H1···O2^i	1.96 (1)	0.94 (1)	165 (1)	1.869
N1—H2···O1^{ii}	1.86 (1)	0.88 (1)	178 (1)	1.718
N1—H3···O2^{iii}	2.09 (1)	0.89 (1)	160 (1)	1.963

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y+1, z$; (iii) $1-x, 1-y, 1-z$.

Notes: (*a*) experimental H-atom positions; (*b*) N—H bonds normalized to 1.030 Å (Taylor & Kennard, 1983).

All heavy atoms were refined anisotropically. Amino H atoms were refined isotropically. The remaining H atoms were kept in idealized positions, refining a single C—H distance for all H atoms connected to the same C atom. A common isotropic parameter was refined for the methyl H atoms. U_{iso} values for the tertiary H atoms were fixed at $1.2U_{eq}$ those of their bonded C atoms.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1226). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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DL-Norleucine, β Form at 120 K

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Abstract

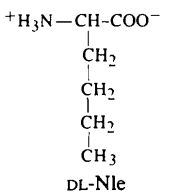
This paper forms part VI in a series of crystal structures of hydrophobic amino acids. The crystal structure of a low-temperature form (120 K) of DL-norleucine (2-aminohexanoic acid, $C_6H_{13}NO_2$) has been solved and refined in the space group $C2/c$. The molecular packing and cell parameters correlate very well with those proposed for the β form of DL-norleucine as deduced by Mathieson [*Acta Cryst.* (1953), **6**, 399–403]. Estimated standard deviations for the bonds between heavy atoms are 0.001–0.002 Å.

Comment

The amino acid norleucine (2-aminohexanoic acid) can be derived from methionine by replacing the S atom with a $-CH_2-$ group. Thus, it is not surprising that the crystal structures of these two compounds display some common properties.

The crystal and molecular structure of DL-methionine (DL-Met) was first presented by Mathieson (1952). From several different crystallization batches he obtained two different monoclinic polymorphs, denoted α-DL-Met and β-DL-Met, with space groups $P2_1/a$ and $I2/a$, respectively. The cell dimensions of β-DL-Met are almost the same as for the α form, except for a doubling of the c axis and a small increase in the β angle (Table 3). The molecular packing arrangement in either structure consists of the stacking of double-layer units along the c axis. The precision of these structures is low by current standards, R = 0.21 (α) and 0.23 (β), with e.s.d.'s in bond lengths of approximately 0.04 Å. This led Taniguchi, Takaki & Sakurai (1980) to carry out a re-examination of both polymorphs. Their DL-Met crystals, grown by slow evaporation from an aqueous solution at room temperature, were all of the β form and various degrees of streaking along c^* were observed, possibly due to disorder in the stacking of the double layers. However, they also found that crystals of the α form could be obtained by heating β-form crystals, suggesting that the β form is a low-temperature form. The crystal of the α form was kept at 333 K during the collection of the X-ray data.

The crystal and molecular structure of the racemate DL-norleucine (DL-Nle) was also first described by Mathieson (1953). The compound crystallizes in the monoclinic space group $P2_1/a$, in accordance with the investigations of Albrecht, Schnakenberg, Dunn & McCullough (1943). Only crystals of this form were obtained, but Mathieson observed that most of the crystals exhibited a superlattice structure with a c axis four times that of the $P2_1/a$ cell. He also found streaking along c^* for reflections $h + k = 2n + 1$; this streaking was interpreted as disorder in the stacking of the double-layer units. In view of the previous findings for DL-Met, Mathieson deduced the existence of a second form for DL-Nle also (β form) with symmetry $I2/a$ and a c axis twice as long as that of the $P2_1/a$ (α form) structure.



DL-Nle

DL-Nle was one of the crystal structures examined in a paper by Mnyukh, Panfilova, Petropavlov & Uchvatova (1975) on polymorphic transitions in molecular crystals. A reversible polymorphic transition in DL-Nle crystals is described at approximately 390 K. Laue diffraction photographs of several DL-Nle crystals at both 378 and 413 K, *i.e.* before and after the transition, are almost identical, showing a single-crystal to single-crystal transition between a low-temperature phase (LTP) and a very similar high-temperature phase (HTP). Further investigations showed that the packing density of the HTP is substantially lower than for the LTP, and Mnyukh *et al.* (1975) concluded that the HTP thus appears not to be the predicted β phase.

In a recent paper by Harding, Kariuki & Williams (1995), an X-ray redetermination of the α form of DL-Nle at 296 K is presented. With the aim of obtaining data for the high-temperature form, further diffraction patterns were collected at various temperatures using synchrotron radiation Laue diffraction as crystals were heated through the temperature range 298–398 K. Unfortunately, no high-quality single crystal existed at temperatures above the transition temperature of 390 K. The authors observed marked streaking along c^*, as did Mathieson (1953), but could not find the additional reflections from which Mathieson deduced the superlattice cell.

As part of our programme to provide accurate H-atom positions in crystal structures of hydrophobic amino acids (Dalhus & Görbitz, 1996, and references therein), we decided to redetermine the structure at liquid nitrogen temperature, 120 K. The racemate crystallizes in the monoclinic space group $C2/c$, which is equivalent to $I2/a$ through a transformation of the axes. The cell dimensions are in good agreement with those proposed for the β form by Mathieson (1952) (Table 3). This means that, as for DL-Met, the β form is stable at lower temperatures than the α form. For DL-Met, the transition between the two polymorphic forms occurs somewhere between room temperature and 333 K (Taniguchi *et al.*, 1980), while it occurs at a lower temperature (between 120 K and room temperature) for DL-Nle. The phase transition between the two polymorphic forms is fully reversible; the single crystal used for the low-temperature data collection was heated to room temperature and the subsequent space-group determination confirmed the presence of the $P2_1/a$ form with cell parameters a = 9.875 (3), b = 4.722 (1), c = 16.322 (4) Å and β = 104.68 (2)°. These values are very similar to those given by Harding *et al.* (1995), but our cell axes are slightly shorter, giving a 1% reduction in the cell volume.

It is interesting to note that while the molecular geometries are different in the α and β forms of DL-Met, they are almost identical for DL-Nle, with fully extended side chains. Deviations between corresponding torsion angles in the α form (Harding *et al.*, 1995) and the β form are generally smaller than 1.0°; the maximum difference is 1.8° for C1—C2—C3—C4. Bond lengths and bond angles also agree very well, except that the terminal C—C bonds are significantly shorter in the room-temperature study of the α form, which is clearly a librational effect due to larger thermal motion.

The molecular-packing arrangement in the α and β polymorphs of DL-Nle is depicted in Fig. 2. The α form results from the translation of a double-layer unit, *L*, along the c axis, giving the sequence *L–L–L–L*. In the β form, the corresponding sequence is *L–M–L–M*, where *M* represents a second double-layer unit. The *M* unit is related to the *L* unit by a translation of half a cell length along the b axis. Either packing pattern is completely equivalent to that observed in the corresponding DL-Met structure.

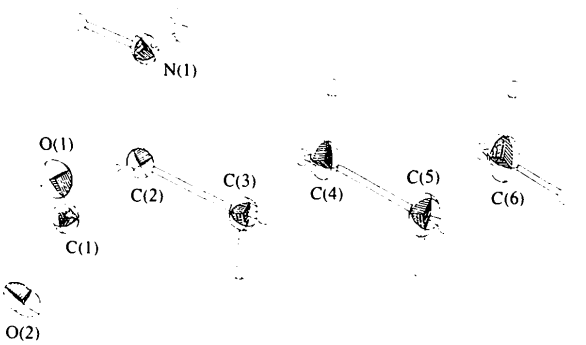


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the L isomer in the racemate DL-norleucine. Displacement ellipsoids are drawn at the 50% probability level. H atoms are arbitrarily scaled.

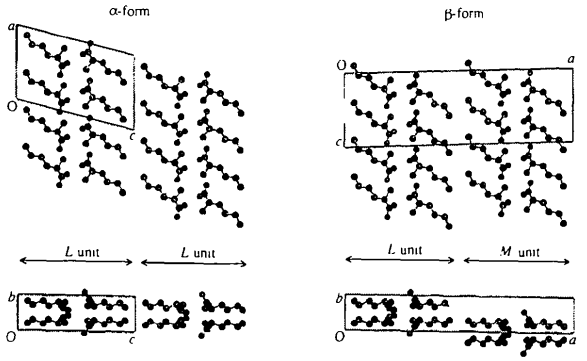


Fig. 2. Molecular-packing diagram of α-DL-norleucine (Harding *et al.*, 1995) (left) and β-DL-norleucine (right). The upper diagrams show projections down the unique *b* axis, the lower diagrams are projections down the *a* and *c* axis for the α and β forms, respectively. *L* and *M* denote the double-layer units.

The extensive streaking observed along c^* for both DL-Met and DL-Nle indicates that disorder in the stacking sequence of the double-layer units occurs in some crystals. The interaction between the layers is van der Waals type only, and small energy differences between the various stacking arrangements could very well explain the variation in the crystal packing. The superlattice structure, as observed by Mathieson (1953), could possibly be described by the sequences *L–L–M–M* or *L–L–L–M*.

Hydrogen-bond geometries are listed in Table 4. There are three relatively short hydrogen bonds in the crystal with normalized (Taylor & Kennard, 1983) hydrogen-bond lengths of 1.75, 1.80 and 1.80 Å, respectively. The hydrogen-bond connectivity in this structure is different from that observed in other hydrophobic amino acid structures (Dalhus & Görbitz, 1996, and references therein).

Experimental

An aqueous solution of the racemate was mixed with tetramethoxysilane in the ratio 5:1 and left for 2 h to polymerize. Plate-like crystals appeared as ethanol diffused into the gel at room temperature.

Crystal data

$C_6H_{13}NO_2$
M_r = 131.17
Monoclinic
$C2/c$
a = 31.067 (5) Å
b = 4.717 (1) Å
c = 9.851 (2) Å
β = 91.37 (2)°
V = 1443.2 (5) Å^3
Z = 8
D_x = 1.207 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 13.2–20.2°
μ = 0.090 mm^{-1}
T = 120 (2) K
Plate
0.5 × 0.3 × 0.1 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: none
3794 measured reflections
3794 independent reflections
2363 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 37.5°
$h = -52 \rightarrow 52$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 96 reflections
intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0572
$wR(F^2)$ = 0.1210
S = 0.914
3794 reflections
101 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.6573P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.388 e Å^{-3}
$\Delta\rho_{min}$ = −0.269 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.71578 (2)	−0.0773 (2)	0.80067 (8)	0.0186 (2)
O2	0.68537 (3)	0.2043 (2)	0.95401 (7)	0.0215 (2)
N1	0.70227 (3)	0.2976 (2)	0.60017 (8)	0.0163 (2)
C1	0.69415 (3)	0.1333 (2)	0.83429 (9)	0.0146 (2)
C2	0.67399 (3)	0.3110 (2)	0.71972 (9)	0.0147 (2)
C3	0.62927 (3)	0.1939 (2)	0.68403 (10)	0.0185 (2)
C4	0.60724 (3)	0.3240 (3)	0.55874 (11)	0.0222 (2)
C5	0.56239 (4)	0.2063 (3)	0.53200 (13)	0.0286 (2)
C6	0.54177 (4)	0.3139 (4)	0.40024 (14)	0.0354 (3)

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

O1—C1	1.248 (1)	C2—C3	1.529 (1)
O2—C1	1.262 (1)	C3—C4	1.526 (2)
N1—C2	1.487 (1)	C4—C5	1.517 (2)
C1—C2	1.528 (1)	C5—C6	1.521 (2)
O1—C1—O2	126.1 (1)	C1—C2—C3	109.0 (1)
O1—C1—C2	117.0 (1)	C4—C3—C2	115.4 (1)
O2—C1—C2	116.8 (1)	C5—C4—C3	112.7 (1)
N1—C2—C1	108.8 (1)	C4—C5—C6	113.1 (1)
N1—C2—C3	110.7 (1)		
O1—C1—C2—N1	−31.1 (1)	C1—C2—C3—C4	−172.3 (1)
O2—C1—C2—N1	152.7 (1)	C2—C3—C4—C5	−177.9 (1)
N1—C2—C3—C4	−52.7 (1)	C3—C4—C5—C6	−174.6 (1)

Table 3. *Cell parameters (Å, °) for the crystal structures of both polymorphs of* DL-*Met and* DL-*Nle*

	Space group	a	b	c	β
α-DL-Met[a]	$P2_1/a$	9.89 (2)	4.70 (2)	16.74 (3)	102.3 (7)
β-DL-Met[a]	$I2/a$	9.912 (5)	4.700 (7)	33.13 (2)	106.3 (3)
β-DL-Met[b]	$C2/c$	31.80	4.70	9.91	91.1
α-DL-Nle[c]	$P2_1/a$	9.907 (1)	4.737 (2)	16.382 (2)	104.68 (1)
β-DL-Nle[d]	$I2/a$	9.84	4.74	33.12	104.5
β-DL-Nle[b]	$C2/c$	32.10	4.74	9.84	92.8
β-DL-Nle[e]	$C2/c$	31.067 (5)	4.717 (1)	9.851 (2)	91.37 (2)

Notes: (*a*) Taniguchi *et al.* (1980); (*b*) *I2/a* transformed to *C2/c*; (*c*) Harding *et al.* (1995); (*d*) deduced by Mathieson (1953); (*e*) this work.

Table 4. *Hydrogen bonds (Å, °) in β-DL-norleucine*

D—H···A	H···A[a]	D—H[a]	D—H···A[a]	D···A	H···A[b]
N1—H1···O1^{i}	1.83 (2)	0.95 (2)	171 (2)	2.769 (1)	1.746
N1—H2···O2^{ii}	1.89 (2)	0.94 (2)	165 (1)	2.799 (1)	1.795
N1—H3···O2^{iii}	1.90 (2)	0.93 (2)	169 (1)	2.814 (1)	1.797

Symmetry codes: (i) $\frac{3}{2}-x, y+\frac{1}{2}, \frac{3}{2}-z$; (ii) $x, 1-y, z-\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$.

Notes: (*a*) experimental H-atom positions; (*b*) N—H bonds normalized to 1.030 Å (Taylor & Kennard, 1983).

Diffraction intensities, measured at 120 K, were corrected for Lorentz and polarizing effects. The structure was solved by direct methods using *SIR*92 (Altomare *et al.*, 1994) and refined with *SHELXL*93 (Sheldrick, 1993). All heavy atoms were refined anisotropically. Amino H atoms were refined isotropically. Remaining H atoms were kept in idealized positions, refining a single C—H distance for all H atoms connected to the same C atom. A common isotropic displacement parameter for the methyl H atoms was refined. U_{iso} values for tertiary and secondary H atoms were fixed at 1.2 × U_{eq} of the bonded C atom.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1228). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Valyl-L-alanine

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Abstract

L-Valyl-L-alanine, $C_8H_{16}N_2O_3$, crystallizes in space group $P6_1$. The side chains aggregate into large hydrophobic columns parallel to the hexagonal axis, with conspicuous empty central channels. The three-dimensional hydrogen-bond pattern is unique among dipeptide structures.

Comment

Dipeptide crystals are often divided into distinct hydrophilic and hydrophobic layers (Görbitz & Etter, 1992). In a hydrophilic layer, two of the three amino H atoms usually form hydrogen bonds to the C-terminal carboxylate group, generating two separate head-to-tail chains in two-dimensional hydrogen-bonded sheets (Suresh & Vijayan, 1985). Alternatively, one of the two chains may be interrupted by a solvent water molecule. In the case of glycine residues, the important third amino H atom can be accepted by a main-chain carboxylate or carbonyl group in a molecule of an adjacent sheet, but more generally, when the inter-sheet distances are larger, the H atom is accepted by a group in one of the two peptide side chains (Görbitz & Backe, 1996). Dipeptides with two hydrophobic residues represent a problem in this respect since there are no hydrogen-bond acceptors (or donors) in the side chains. In the crystal structure of L-Met-L-Met (Stenkamp & Jensen, 1975), the last amino H atom is not used for hydrogen bonding. Such a failure to use all active H atoms may clearly be regarded as an exception (Görbitz & Etter, 1992). In L-Leu-L-Leu.DMSO (Mitra & Subramanian, 1994) and L-Leu-L-Val.2-propanol (Görbitz & Gundersen, 1996*b*), the cocrystallized solvent molecule accepts the third amino H atom, preserving a layered structural build-up. L-Leu-L-Val can also be crystallized as a hydrate in the hexagonal space group $P6_2$, with four dipeptide molecules in the asymmetric unit (Görbitz & Gundersen, 1996*a*) and the water molecules acting as both hydrogen-bond acceptors and hydrogen-bond donors. In L-Ala-L-Ala (Fletterick, Tsai & Hughes, 1971), however, the demand for maximum hydrogen bonding has been satisfied through the formation of a chessboard-like pattern with fourfold symmetry (tetragonal, $I4$). The crystal structure of the title compound, L-Val-L-Ala,