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Molecular aggregation in selected crystalline 1:1 complexes of hydrophobic D- and L-amino acids. II.† The D-norleucine series

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Abstract

The amino acid D-norleucine has been co-crystallized with selected L-amino acids with linear side chains including L-norvaline [D-norleucine–L-norvaline (1/1), $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$, amino-acid side chain R = $CH_2CH_2CH_3$] and L-methionine [D-norleucine–L-methionine, $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2S$ (1/1), $R = CH_2CH_2SCH_3$], as well as amino acids with branched side chains including L-valine [D-norleucine–L-valine (1/1), $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$, R = $CH(CH_3)_2$], L-*allo*-isoleucine [D-norleucine–L-*allo*-isoleucine (1/1), $C_6H_{13}NO_2{\cdot}C_6H_{13}NO_2$, $R = CH(CH_3)CH_2CH_3$] and L-leucine [D-norleucine–L-leucine (1/1), $C_6H_{13}NO_2{\cdot}C_6H_{13}NO_2$, R = $CH_2CH(CH_3)_2$]. The crystal structures are divided into distinct hydrophilic and hydrophobic layers. The polar parts of the D- and L-amino acids are related by pseudo glide-plane symmetry in all complexes except L-Leu:D-Nle, in which parts of the two amino acids are related by pseudo-inversion. Furthermore, the D-Nle molecule is disordered over two positions with nearly equal occupancy. Similarities and differences in both the crystal packing and molecular conformations of D-Nle and the partner molecules are discussed.

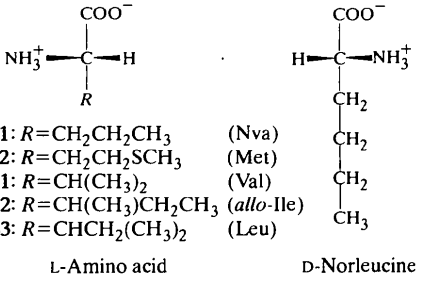
† Part I: Dalhus & Görbitz (1999).

Comment

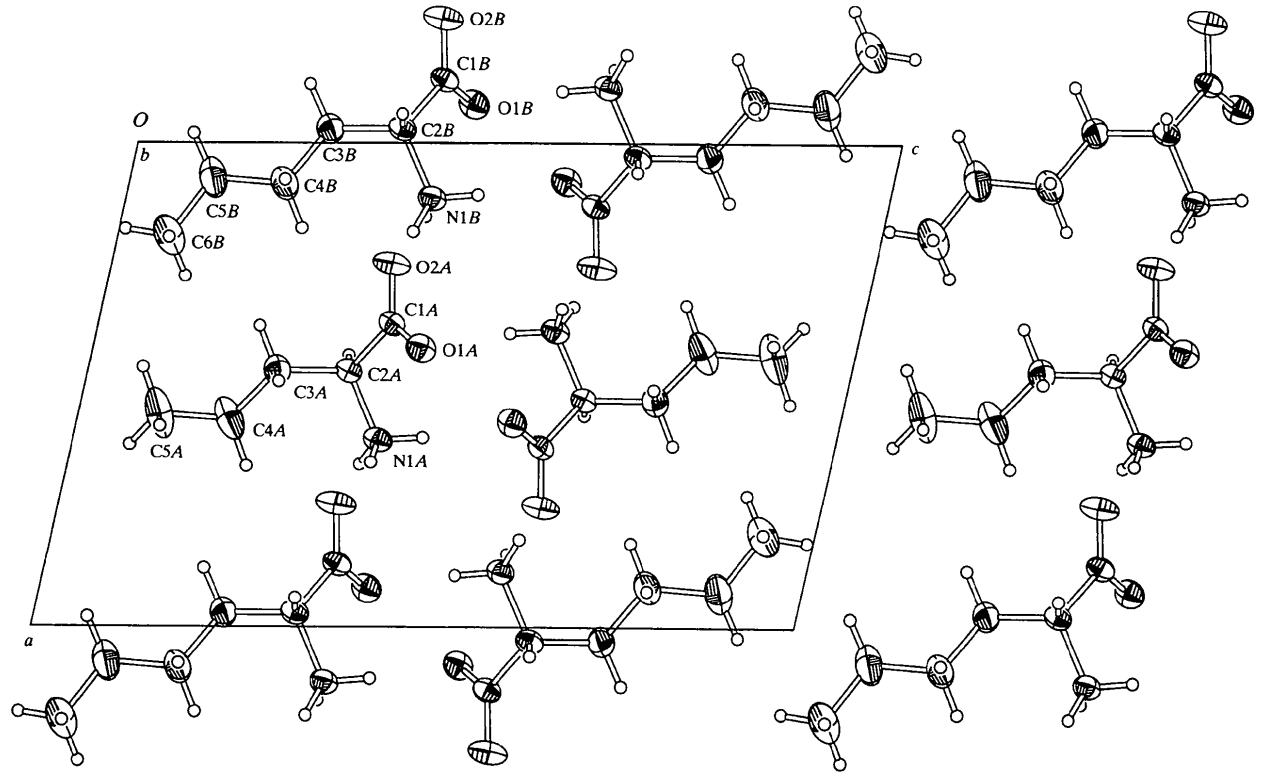
The crystal structures of hydrophobic amino acids fall within three categories; (i) pure enantiomers, (ii) racemates and (iii) complexes of two different hydrophobic amino acids with opposite chirality at C^α. There are no known crystal structures incorporating two different hydrophobic amino acids with the same chirality at C^α.

Previously, we have determined the crystal structures of seven 1:1 complexes of category (iii) involving L-isoleucine, among them L-isoleucine:D-norleucine (Dalhus & Görbitz, 1999*a*). The seven structures will be referred to as the L-Ile:D-*Xxx* complexes/series. In this paper we present the crystal structures of five additional 1:1 complexes with norleucine as the D-amino acid (D-Nle).

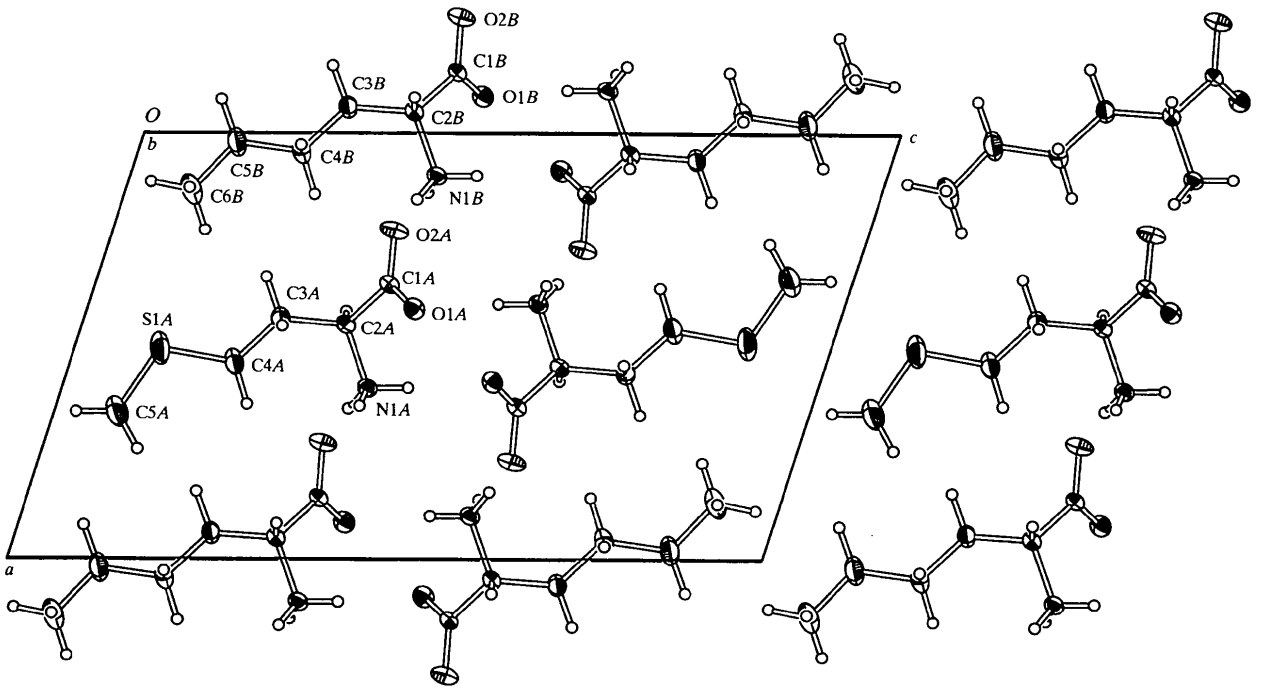
The investigated D-Nle complexes fall into two subcategories depending on the nature of the side chains. In the complexes L-Nva:D-Nle, (**L1**), and L-Met:D-Nle, (**L2**), both amino acids have unbranched side chains, while in L-Val:D-Nle, (**B1**), L-*allo*-Ile:D-Nle, (**B2**), and L-Leu:D-Nle, (**B3**), there is one branched and one unbranched amino-acid side chain. No crystals suitable for diffraction experiments were obtained for D-Nle complexed with L-alanine (L-Ala, $R = CH_3$) or L-α-aminobutyric acid (L-Abu, $R = CH_2CH_3$). Among the L-Ile:D-*Xxx* complexes, alanine gave crystals of low quality compared to the other amino acids in the series.



All crystal structures are divided into distinct hydrophilic and hydrophobic layers (Figs. 1, 2 and 3). This characteristic build-up is due to the dual properties of the hydrophobic amino acids; the charged α-amino and α-carboxylate groups engage in hydrogen bonding with each other, while the side chains, distinctly hydrophobic in nature, are involved in van der Waals interactions only.

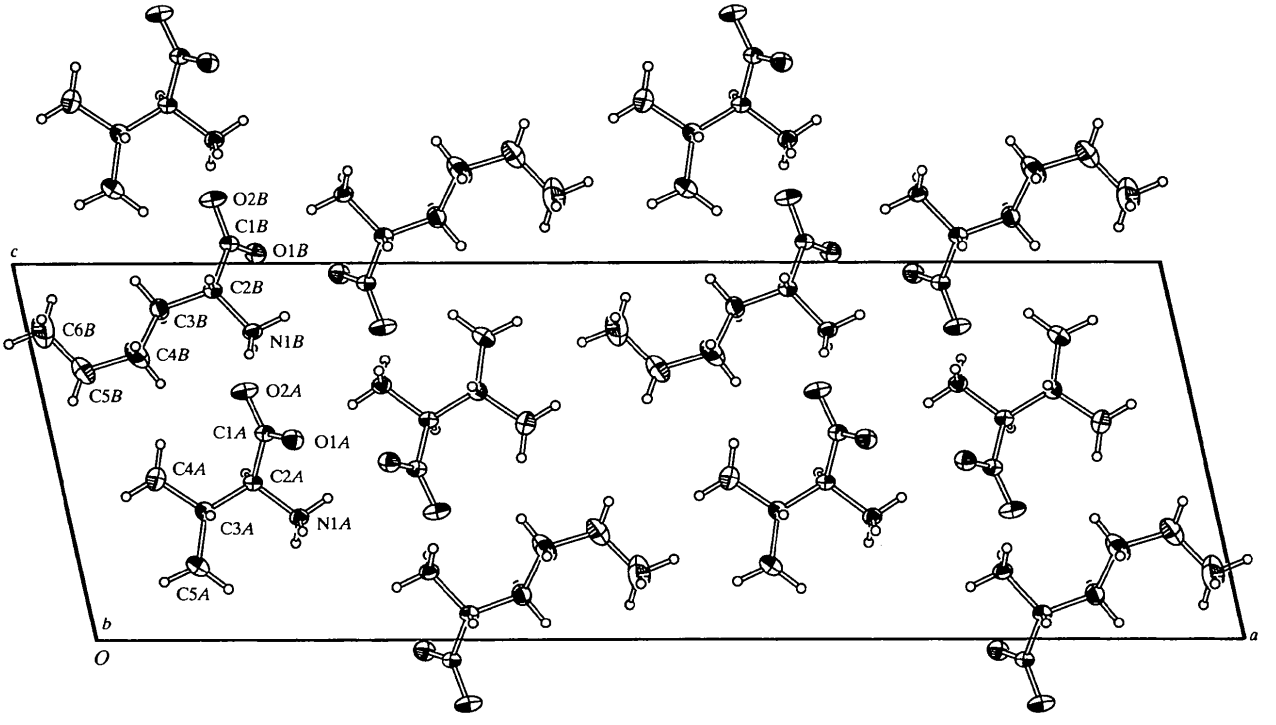


(*a*)

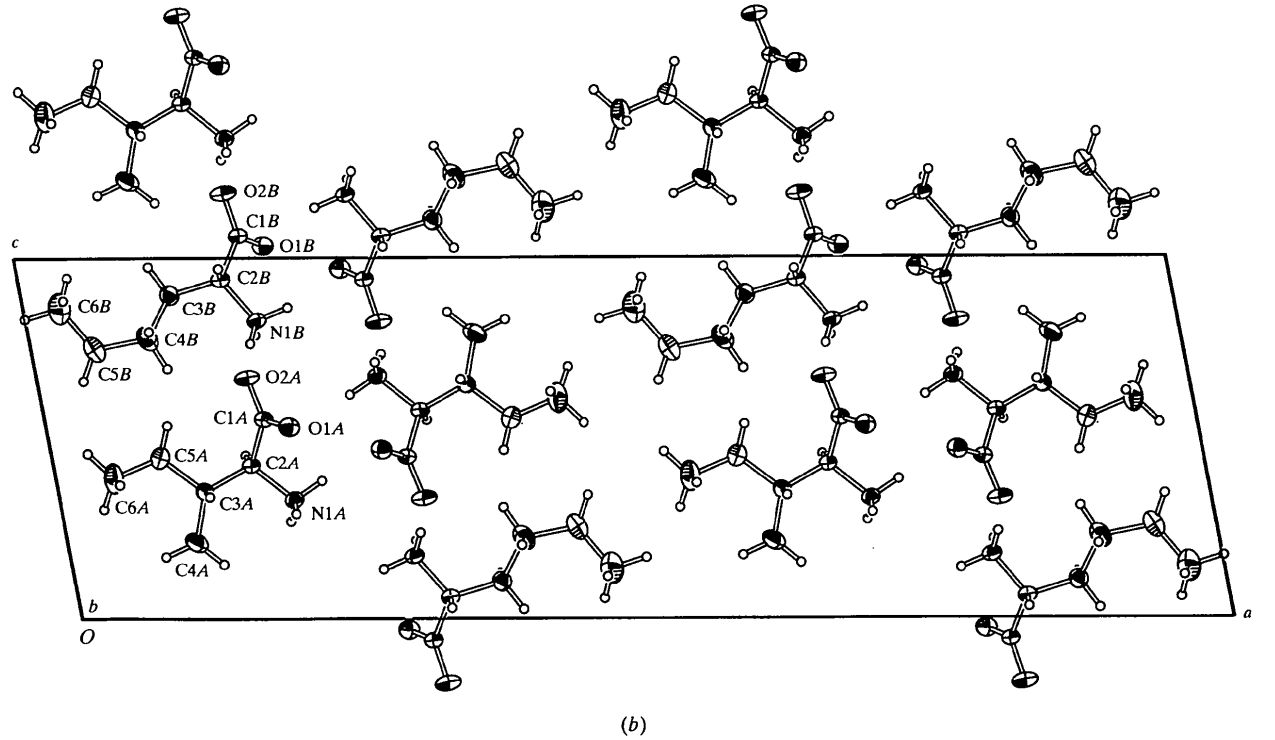


(*b*)

Fig. 1. Molecular packing diagrams for (*a*) L-Nva:D-Nle, **L1**, and (*b*) L-Met:D-Nle, **L2**. Displacement ellipsoids are drawn at the 75% probability level and H atoms are arbitrarily scaled.



(*a*)



(*b*)

Fig. 2. Molecular packing diagrams for (*a*) L-Val:D-Nle, **B1**, and (*b*) L-*allo*-Ile:D-Nle, **B2**. Displacement ellipsoids are drawn at the 75% probability level and H atoms are arbitrarily scaled.

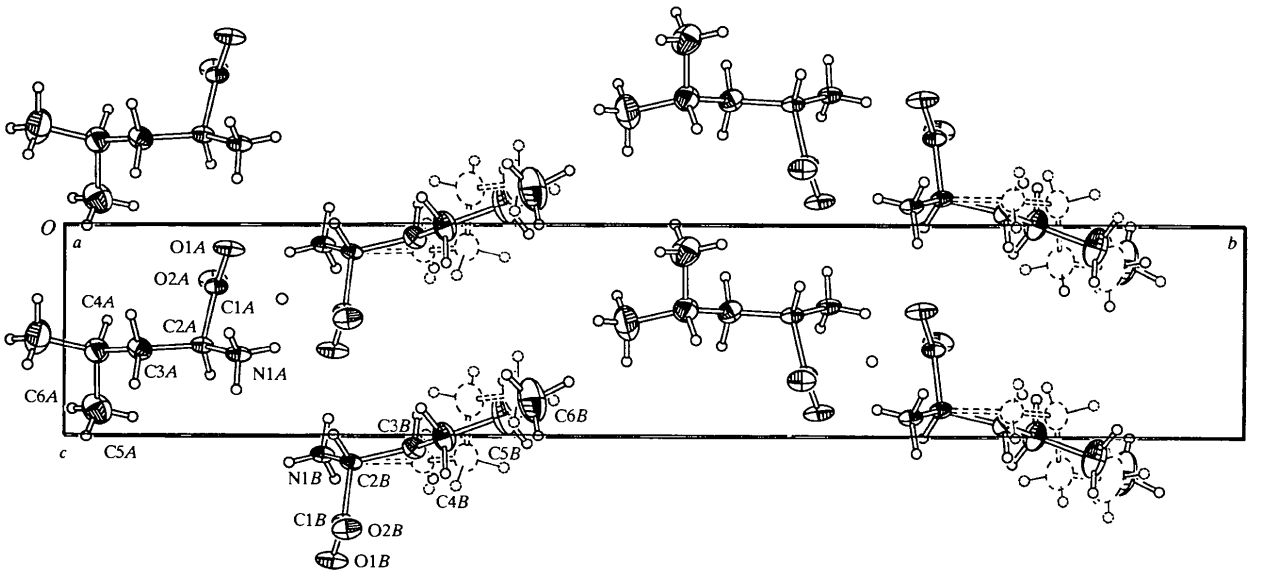
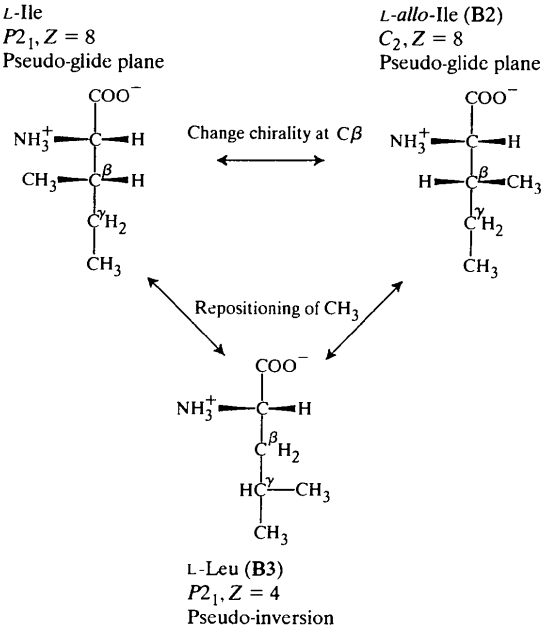


Fig. 3. Molecular packing diagram for L-Leu:D-Nle, **B3**. Displacement ellipsoids are drawn at the 75% probability level. H atoms are arbitrarily scaled. For D-Nle in **B3**, only major sites for N1*B* and C2*B* are displayed and a minor component of the side chain is shown using broken lines and open ellipsoids. Pseudo-inversion centres are indicated with open circles. Atomic numbering for D-Nle is restricted to the major component (full lines).

In the **L1**, **L2**, **B1** and **B2** complexes, the D- and L-amino acids are related by pseudo glide-plane symmetry normal to the unique *b* axes [Figs. 1(*a*)–(*d*) with space groups $P2_1$ for **L1** and **L2**, and *C*2 for **B1** and **B2** (Table 6). Likewise, in the L-Ile:D-*Xxx* series, a pseudo glide plane is present for all complexes involving one linear and one branched amino acid. This molecular packing arrangement is remarkably flexible, also in the present **L1**, **L2**, **B1** and **B2** complexes. Replacement of L-Nva (**L1**) with L-Met (**L2**) gives only minor adjustments in unit-cell parameters [largest shifts: c = 15.3 Å, β = 102.3° (**L1**) → c = 16.4 Å, β = 107.3° (**L2**)] and the molecular conformation of D-Nle remains unchanged: χ^1 = *gauche*$^+$, χ^2 = χ^3 = *trans* (Table 6). Moreover, the molecular conformation of the equivalent parts in L-Nva and L-Met are also identical: χ^1 = *gauche*$^-$ and χ^2 = *trans*. In the same manner, a replacement of L-Val (in **B1**) with L-*allo*-Ile (in **B2**) is also feasible with small shifts in the corresponding unit-cell parameters [largest shifts: a = 29.6 Å, β = 102.7° (**B1**) → a = 31.4 Å, β = 100.8° (**B2**)]. The molecular conformation of D-Nle is χ^1 = *gauche*$^+$, χ^2 = *trans* and χ^3 = *gauche*$^-$ in the two complexes (Table 6) and $\chi^{1,1}$ = *trans* and $\chi^{1,2}$ = *gauche*$^-$ for both L-Val and L-*allo*-Ile.

In the **B3** complex on the other hand, the polar parts of L-Leu and D-Nle are related by pseudo-inversion [Fig. 1(*e*)] in space group $P2_1$. The same pseudo-inversion relationship between the D- and L-amino acid is also found in the complexes L-Ile:D-Val and L-Ile:D-Leu (Dalhus & Görbitz, 1999*a*) as well as in L-Ile:D-*allo*-Ile (Dalhus & Görbitz, 1999*b*). The latter three complexes accommodate two amino acids with branched side chains, and in this respect **B3**, with only one branched amino acid, represents an anomalous complex. Furthermore, in **B3**, the D-Nle molecule is disordered over two conformations $\chi^1/\chi^2/\chi^3$ = *trans*/*trans*/*trans* and *trans*/*gauche*$^-$/*trans* (Table 6) with almost similar occupancies. In the 1:1:1:1 complex L-Ile:D-Ile:L-*allo*-Ile:D-*allo*-Ile, an analysis of the distances between alternative sites for disordered C atoms reveals a systematic distribution of the four stereoisomers L-Ile, D-Ile, L-*allo*-Ile and D-*allo*-Ile in the crystal (Dalhus & Görbitz, 1999*b*). Such an analysis of the complex L-Leu:D-Nle (**B3**) on the other hand does not lead to a decisive conclusion as for the distribution of the two D-Nle conformers in **B3**.

It is noteworthy that D-Nle complexed with the three isomers L-Ile, L-*allo*-Ile and L-Leu gives three rather different molecular arrangements. In L-Ile:D-Nle (Dalhus & Görbitz, 1999*a*), there are two L-Ile and two D-Nle molecules in the asymmetric unit, the two D-Nle molecules having different side-chain conformation (Table 6). The D- and L-amino acids are related by pseudo glide planes in $P2_1$. A change in the chirality at C$^\beta$ in L-Ile, transforms L-Ile into L-*allo*-Ile (Scheme 2), and reduces the number of independent molecules in the complex to one D- and one L-amino acid with yet another conformation for D-Nle [(**B2**), Table 6]. Nevertheless, the D- and L-amino acids are still related by pseudo glide planes, now in space group *C*2. A repositioning of the CH_3 group from C$^\beta$ to C$^\gamma$ in L-Ile and (Scheme 2) gives a complex L-Leu:D-Nle (**B3**) which is structurally quite different from L-Ile:D-Nle (Dalhus & Görbitz, 1999*a*) and L-*allo*-Ile:D-Nle (**B2**) as discussed above.



Methionine is a close chemical analogue of norleucine; replacement of the S atom in methionine with a CH_2 group transforms methionine into norleucine. This close relationship is evident in the polymorphism of DL-Met and DL-Nle. Both racemates have a high-temperature (α-form, space group $P2_1/c$) and a low-temperature (β-form, space group $C2/c$) crystalline phase with fully reversible phase transitions (DL-Met; Taniguchi *et al.*, 1980: DL-Nle; Dalhus & Görbitz, 1996). The present study shows that the molecular arrangement in the closely related complex L-Met:D-Nle is, somewhat surprisingly, analogous to the high-temperature forms even at 110 K. The conformation of the amino acids in **L2** is the same as that observed in α-DL-Nle (Table 6) and the crystal packing in the two structures is almost identical.

A survey of all crystal structures of amino acids with hydrophobic side chains has identified three major classes of molecular-packing arrangements, each with a unique hydrogen-bond pattern. Furthermore, it is demonstrated that for complexes of categories (ii) and (iii) the crystal structures belong to either class I or II depending on the side chains in the two amino acids that constitute the complexes (Dalhus & Görbitz, 1999*c*). Class III, on the other hand, includes the structures of enantiomeric amino acids. In class I, H1*A*, H1*B*, H2*A* and H2*B* all have first-level graph set *D* (Etter, 1990; Bernstein *et al.*, 1995) while H3*A* and H3*B* each form a *C*(5) chain along the *b* axis. Crystals in class II, on the other hand, have *C*(5) chains along **a** and **c** for H atoms H1*A*, H2*A*, H1*B* and H2*B*, while the remaining H3*A* and H3*B* each form a first-level dimer *D*. The molecular aggregation in the four complexes **L1**, **L2**, **B1** and **B2** fall within class I, while **B3** is a class II structure. Experimental and normalized (Taylor & Kennard, 1983) hydrogen-bond geometries are listed in Table 7.

Experimental

Aqueous solutions of the title complexes were prepared by dissolving equimolar amounts (typically 5–10 mg, depending on the solubility properties) of the two selected amino acids in deionized water (1 ml). The various solutions were then thoroughly mixed with tetramethoxysilane (0.1 ml), and each resulting mixture was distributed in 10–12 30 × 5 mm test-tubes, sealed with Parafilm, and then left for a couple of minutes to polymerize. Crystals emerged as methanol, ethanol or 2-propanol diffused into the gel at room temperature. Crystals from the ethanol batches were used for data collection.

L-Nva:D-Nle (L1)

Crystal data

$C_6H_{13}NO_2 \cdot C_5H_{11}NO_2$
$M_r = 248.32$
Monoclinic
$P2_1$
$a = 9.9166\ (2)$ Å
$b = 4.7247\ (1)$ Å
$c = 15.3292\ (3)$ Å
$\beta = 102.349\ (1)°$
$V = 701.60\ (2)$ Å^3
$Z = 2$
$D_x = 1.175$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7301 reflections
$\theta = 2.10–40.46°$
$\mu = 0.089$ mm^{-1}
$T = 150\ (2)$ K
Plate
0.65 × 0.45 × 0.10 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.944$, $T_{max} = 0.991$
10 773 measured reflections
6360 independent reflections
5289 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 40.46°$
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 6$
$l = -27 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.127$
$S = 1.049$
6360 reflections
189 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.1367P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.419$ e Å^{-3}
$\Delta\rho_{min} = -0.288$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for* **L1**

O1*A*—C1*A*	1.249 (2)	O2*B*—C1*B*	1.2649 (13)
O2*A*—C1*A*	1.2658 (14)	N1*B*—C2*B*	1.4904 (13)
N1*A*—C2*A*	1.4937 (13)	C1*B*—C2*B*	1.535 (2)
C1*A*—C2*A*	1.537 (2)	C2*B*—C3*B*	1.535 (2)
C2*A*—C3*A*	1.532 (2)	C3*B*—C4*B*	1.532 (2)
C3*A*—C4*A*	1.528 (2)	C4*B*—C5*B*	1.520 (2)

C4A—C5A	1.524 (2)	C5B—C6B	1.529 (2)
O1B—C1B	1.253 (2)		
N1A—C2A—C3A—C4A	−56.6 (2)	C2B—C3B—C4B—C5B	175.9 (2)
C2A—C3A—C4A—C5A	−177.8 (2)	C3B—C4B—C5B—C6B	174.1 (2)
N1B—C2B—C3B—C4B	50.9 (2)		

L-Met:D-Nle (L2)

Crystal data

$C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2S$
M_r = 280.38
Monoclinic
$P2_1$
a = 9.8756 (2) Å
b = 4.7029 (1) Å
c = 16.4192 (3) Å
β = 107.3283 (7)°
V = 727.96 (3) Å^3
Z = 2
D_x = 1.279 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6770 reflections
θ = 2.16–49.77°
μ = 0.232 mm^{-1}
T = 110 (2) K
Plate
0.75 × 0.45 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.840, T_{max} = 0.955
17 402 measured reflections
11 604 independent reflections

10 891 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 49.77°
$h = -20 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -33 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.070
S = 1.059
11 604 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.0136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.003
$\Delta\rho_{max}$ = 0.421 e Å^{-3}
$\Delta\rho_{min}$ = −0.315 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for* ***L2***

S1A—C5A	1.8006 (6)	O1B—C1B	1.2543 (5)
S1A—C4A	1.8101 (4)	O2B—C1B	1.2653 (4)
O1A—C1A	1.2536 (5)	N1B—C2B	1.4911 (4)
O2A—C1A	1.2651 (4)	C1B—C2B	1.5339 (5)
N1A—C2A	1.4901 (5)	C2B—C3B	1.5351 (5)
C1A—C2A	1.5353 (5)	C3B—C4B	1.5310 (5)
C2A—C3A	1.5355 (5)	C4B—C5B	1.5270 (6)
C3A—C4A	1.5293 (5)	C5B—C6B	1.5284 (7)
N1A—C2A—C3A—C4A	−53.09 (5)	N1B—C2B—C3B—C4B	52.77 (4)
C2A—C3A—C4A—S1A	−179.42 (3)	C2B—C3B—C4B—C5B	177.03 (4)
C3A—C4A—S1A—C5A	−170.78 (4)	C3B—C4B—C5B—C6B	174.30 (4)

L-Val:D-Nle (B1)

Crystal data

$C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$
M_r = 248.32
Monoclinic
$C2$
a = 29.5751 (4) Å
b = 4.7386 (1) Å
c = 9.9402 (1) Å
β = 102.7111 (8)°
V = 1358.92 (4) Å^3
Z = 4
D_x = 1.214 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8088 reflections
θ = 1.41–49.79°
μ = 0.091 mm^{-1}
T = 150 (2) K
Plate
0.60 × 0.45 × 0.15 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.947, T_{max} = 0.986
17 095 measured reflections
11 130 independent reflections

9640 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 49.79°
$h = -61 \rightarrow 60$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.106
S = 1.052
11 129 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.0342P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.357 e Å^{-3}
$\Delta\rho_{min}$ = −0.422 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for* ***B1***

O1A—C1A	1.2553 (6)	O2B—C1B	1.2635 (6)
O2A—C1A	1.2627 (6)	N1B—C2B	1.4923 (6)
N1A—C2A	1.4939 (6)	C1B—C2B	1.5324 (6)
C1A—C2A	1.5395 (6)	C2B—C3B	1.5314 (7)
C2A—C3A	1.5436 (7)	C3B—C4B	1.5210 (8)
C3A—C4A	1.5318 (8)	C4B—C5B	1.5299 (9)
C3A—C5A	1.5342 (8)	C5B—C6B	1.5080 (13)
O1B—C1B	1.2540 (6)		
N1A—C2A—C3A—C4A	−171.99 (6)	C2B—C3B—C4B—C5B	176.99 (6)
N1A—C2A—C3A—C5A	−49.00 (6)	C3B—C4B—C5B—C6B	−62.2 (1)
N1B—C2B—C3B—C4B	60.04 (7)		

L-*allo*-Ile:D-Nle (B2)

Crystal data

$C_6H_{13}NO_2{\cdot}C_6H_{13}NO_2$
M_r = 262.35
Monoclinic
$C2$
a = 31.4433 (4) Å
b = 4.7622 (1) Å
c = 9.9363 (2) Å
β = 100.8378 (4)°
V = 1461.32 (5) Å^3
Z = 4
D_x = 1.192 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6199 reflections
θ = 2.25–49.57°
μ = 0.089 mm^{-1}
T = 150 (2) K
Plate
0.65 × 0.40 × 0.10 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.944, T_{max} = 0.991
18 157 measured reflections
10 942 independent reflections

9640 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 49.57°
$h = -65 \rightarrow 66$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.105
S = 1.075
10 942 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.0971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.379 e Å^{-3}
$\Delta\rho_{min}$ = −0.299 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for* **B2**

O1*A*—C1*A*	1.2558 (7)	O1*B*—C1*B*	1.2534 (7)
O2*A*—C1*A*	1.2636 (6)	O2*B*—C1*B*	1.2646 (6)
N1*A*—C2*A*	1.4948 (7)	N1*B*—C2*B*	1.4917 (6)
C1*A*—C2*A*	1.5390 (7)	C1*B*—C2*B*	1.5327 (7)
C2*A*—C3*A*	1.5466 (7)	C2*B*—C3*B*	1.5327 (7)
C3*A*—C4*A*	1.5340 (8)	C3*B*—C4*B*	1.5283 (8)
C3*A*—C5*A*	1.5354 (9)	C4*B*—C5*B*	1.5344 (10)
C5*A*—C6*A*	1.5311 (12)	C5*B*—C6*B*	1.5158 (14)
N1*A*—C2*A*—C3*A*—C4*A*	−50.34 (6)	N1*B*—C2*B*—C3*B*—C4*B*	58.81 (7)
N1*A*—C2*A*—C3*A*—C5*A*	−174.35 (6)	C2*B*—C3*B*—C4*B*—C5*B*	173.07 (6)
C2*A*—C3*A*—C5*A*—C6*A*	−173.69 (8)	C3*B*—C4*B*—C5*B*—C6*B*	−65.5 (1)

L-Leu:D-Nle (B3)

Crystal data

$C_6H_{13}NO_2 \cdot C_6H_{13}NO_2$
M_r = 262.35
Monoclinic
$P2_1$
a = 5.1778 (1) Å
b = 27.8078 (5) Å
c = 5.3995 (1) Å
β = 112.303 (1)°
V = 719.28 (2) Å^3
Z = 2
D_x = 1.211 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6268 reflections
θ = 2.93–49.52°
μ = 0.090 mm^{-1}
T = 150 (2) K
Plate
0.55 × 0.50 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.952, T_{max} = 0.993
17 963 measured reflections
11 326 independent reflections

10 090 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 49.52°
$h = -9 \rightarrow 10$
$k = -52 \rightarrow 57$
$l = -11 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.135
S = 1.192
11 326 reflections
249 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 0.1433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.363 e Å^{-3}
$\Delta\rho_{min}$ = −0.471 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Selected geometric parameters (Å, °) for* **B3**

O1*A*—C1*A*	1.2592 (9)	C1*B*—C2′*B*	1.541 (11)
O2*A*—C1*A*	1.2610 (9)	N1*B*—C2*B*	1.495 (5)
N1*A*—C2*A*	1.4929 (10)	C2*B*—C3*B*	1.532 (4)
C1*A*—C2*A*	1.5392 (10)	C3*B*—C4*B*	1.534 (2)
C2*A*—C3*A*	1.5333 (13)	C4*B*—C5*B*	1.520 (3)
C3*A*—C4*A*	1.5337 (14)	C5*B*—C6*B*	1.528 (5)
C4*A*—C5*A*	1.534 (2)	N1′*B*—C2′*B*	1.497 (5)
C4*A*—C6*A*	1.532 (2)	C2′*B*—C3′*B*	1.541 (5)
O1*B*—C1*B*	1.2604 (10)	C3′*B*—C4′*B*	1.535 (3)
O2*B*—C1*B*	1.2587 (10)	C4′*B*—C5′*B*	1.511 (4)
C1*B*—C2*B*	1.540 (10)	C5′*B*—C6′*B*	1.529 (5)
N1*A*—C2*A*—C3*A*—C4*A*	−169.96 (7)		
C2*A*—C3*A*—C4*A*—C5*A*	73.80 (11)		
C2*A*—C3*A*—C4*A*—C6*A*	−164.04 (10)		
N1*B*—C2*B*—C3*B*—C4*B*	162.6 (9)		
C2*B*—C3*B*—C4*B*—C5*B*	−172.2 (5)		
C3*B*—C4*B*—C5*B*—C6*B*	176.0 (4)		
N1′*B*—C2′*B*—C3′*B*—C4′*B*	169.0 (10)		
C2′*B*—C3′*B*—C4′*B*—C5′*B*	−75.5 (6)		
C3′*B*—C4′*B*—C5′*B*—C6′*B*	−171.9 (5)		

Table 6. *Side-chain conformation of* D*-norleucine/*D*-methionine in related structures*

χ^1 = N1—C2—C3—C4, χ^2 = C2—C3—C4—C5 and χ^3 = C3—C4—C5—C6 in D-norleucine, and χ^1 = N1—C2—C3—C4, χ^2 = C2—C3—C4—S1 and χ^3 = C3—C4—S1—C5 in D-methionine.

Structure	Space group	χ^1	χ^2	χ^3	Reference
L-Nva:D-Nle (**L1**)	$P2_1$	g^+	t	t	(1)
L-Met:D-Nle (**L2**)	$P2_1$	g^+	t	t	(1)
L-Val:D-Nle (**B1**)	$C2$	g^+	t	g^-	(1)
L-*allo*-Ile:D-Nle (**B2**)	$C2$	g^+	t	g^-	(1)
L-Leu:D-Nle (**B3**)[a]	$P2_1$	t	t	t	(1)
L-Leu:D-Nle (**B3**)[b]	$P2_1$	t	g^-	t	(1)
L-Ile:D-Nle[c]	$P2_1$	g^+	t	t	(2)
L-Ile:D-Nle[c]	$P2_1$	t	t	g^+	(2)
DL-Nle (α-form)	$P2_1/c$	g^+	t	t	(3)
DL-Nle (β-form)	$C2/c$	g^+	t	t	(4)
DL-Met (α-form)	$P2_1/c$	g^+	t	g^-	(5)
DL-Met (β-form)	$C2/c$	g^+	t	t	(5)

Notes: (*a*) major component; (*b*) minor component; (*c*) two D-Nle molecules in the asymmetric unit.

References: (1) present work; (2) Dalhus & Görbitz (1999*a*); (3) Harding *et al.* (1995); (4) Dalhus & Görbitz (1996); (5) Taniguchi *et al.* (1980).

Table 7. *Hydrogen-bond geometry (Å,°) in L1, L2, B1 and B2*

N—H···O	N—H	H···O[a]	H···O[b]	N···O	N—H···O[a]
L-Nva:D-Nle (**L1**)					
N1*A*—H1*A*···O2*B*^{i}	0.95 (3)	1.90 (3)	1.817	2.829 (2)	167 (2)
N1*A*—H2*A*···O2*B*^{ii}	0.89 (2)	1.95 (2)	1.810	2.810 (2)	164 (2)
N1*A*—H3*A*···O1*A*^{iii}	0.92 (2)	1.86 (2)	1.749	2.775 (1)	173 (2)
N1*B*—H1*B*···O2*A*^{iv}	0.88 (2)	1.95 (2)	1.808	2.819 (2)	167 (2)
N1*B*—H2*B*···O2*A*	1.04 (2)	1.81 (2)	1.824	2.808 (2)	158 (2)
N1*B*—H3*B*···O1*B*^{v}	0.93 (2)	1.85 (2)	1.751	2.775 (1)	173 (2)
L-Met:D-Nle (**L2**)					
N1*A*—H1*A*···O2*B*^{i}	0.92 (1)	1.91 (1)	1.807	2.817 (1)	166 (1)
N1*A*—H2*A*···O2*B*^{ii}	0.88 (1)	1.94 (1)	1.791	2.792 (1)	164 (1)
N1*A*—H3*A*···O1*A*^{iii}	0.89 (1)	1.88 (1)	1.742	2.769 (1)	175 (1)
N1*B*—H1*B*···O2*A*^{iv}	0.92 (1)	1.90 (1)	1.797	2.813 (1)	169 (1)
N1*B*—H2*B*···O2*A*	0.93 (1)	1.90 (1)	1.803	2.789 (1)	160 (1)
N1*B*—H3*B*···O1*B*^{v}	0.88 (1)	1.91 (1)	1.755	2.783 (1)	175 (1)
L-Val:D-Nle (**B1**)					
N1*A*—H1*A*···O2*B*^{vi}	0.85 (1)	1.98 (1)	1.807	2.820 (1)	168 (1)
N1*A*—H2*A*···O2*B*^{vii}	0.95 (1)	1.87 (1)	1.798	2.789 (1)	161 (1)
N1*A*—H3*A*···O1*A*^{viii}	0.91 (1)	1.89 (1)	1.761	2.789 (1)	175 (1)
N1*B*—H1*B*···O2*A*^{iv}	0.95 (1)	1.92 (1)	1.834	2.846 (1)	168 (1)
N1*B*—H2*B*···O2*A*	0.87 (2)	1.99 (2)	1.836	2.841 (1)	166 (1)
N1*B*—H3*B*···O1*B*^{ix}	0.92 (1)	1.86 (1)	1.753	2.753 (1)	166 (1)
L-*allo*-Ile:D-Nle (**B2**)					
N1*A*—H1*A*···O2*B*^{vi}	0.89 (2)	1.95 (2)	1.813	2.827 (1)	168 (1)
N1*A*—H2*A*···O2*B*^{vii}	0.84 (1)	1.99 (2)	1.811	2.796 (1)	161 (1)
N1*A*—H3*A*···O1*A*^{viii}	0.92 (2)	1.87 (2)	1.762	2.787 (1)	173 (1)
N1*B*—H1*B*···O2*A*^{iv}	0.93 (2)	1.93 (2)	1.832	2.848 (1)	169 (1)
N1*B*—H2*B*···O2*A*	0.91 (2)	1.96 (2)	1.851	2.843 (1)	162 (1)
N1*B*—H3*B*···O1*B*^{ix}	0.93 (1)	1.85 (1)	1.744	2.753 (1)	166 (1)

Notes: (*a*) experimental N—H distance; (*b*) N—H distance normalized to 1.03 Å (Taylor & Kennard, 1983).
Symmetry codes: (i) $x+1, y-1, z$; (ii) $x+1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$; (v) $-x, y-\frac{1}{2}, -z+1$; (vi) $x, y-1, z-1$; (vii) $x, y, z-1$; (viii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$; (ix) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+2$.

Data collections covered a hemisphere of reciprocal space by a combination of five–eight sets of exposures. All structures were solved using direct methods (*SHELXTL*; Sheldrick, 1994), followed by full-matrix least-squares refinement. In **L1**, **L2**, **B1** and **B2**, all non-H atoms were refined anisotropically. Amino-H atoms were refined isotropically, while all 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 rotating-group refinement was utilized for all methyl-H atoms using the *AFIX*138 of *SHELXTL*. Isotropic displacement parameters for the H atoms were fixed at $1.5U_{eq}$ (for CH_3) and $1.2U_{eq}$ (for CH_2 and CH) of the bonded C atom. In L-Leu:D-Nle (**B3**), the D-Nle molecule is disordered over two conformations. Except for the carboxylate group (O1, O2 and C1), all non-H atoms in D-Nle were refined over two positions. The two components, with occupancy factors 0.538 (4) and 0.462 (4), where restrained to have the same 1–2 and 1–3 distances within an effective standard deviation of 0.01 Å using the *SAME* command of *SHELXTL*. Amino-H atoms were refined isotropically, while all other H atoms were kept in idealized positions; *AFIX*138 and $U_{iso} = 1.5U_{eq}$ of the bonded C atom for CH_3, *AFIX*24 and *AFIX*14, both with $U_{iso} = 1.2U_{eq}$ of the bonding atom for CH_2 and CH, respectively.

For all compounds, data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1053). Services for accessing these data are described at the back of the journal.

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