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Molecular aggregation in selected crystalline 1:1 complexes of hydrophobic D- and L-amino acids. IV. The L-phenylalanine series

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The amino acid L-phenylalanine has been cocrystallized with D-2-aminobutyric acid, $C_9H_{11}NO_2{\cdot}C_4H_9NO_2$, D-norvaline, $C_9H_{11}NO_2{\cdot}C_5H_{11}NO_2$, and D-methionine, $C_9H_{11}NO_2{\cdot}C_5H_{11}NO_2S$, with linear side chains, as well as with D-leucine, $C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$, D-isoleucine, $C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$, and D-*allo*-isoleucine, $C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$, with branched side chains. The structures of these 1:1 complexes fall into two classes based on the observed hydrogen-bonding pattern. From a comparison with other L:D complexes involving hydrophobic amino acids and regular racemates, it is shown that the structure-directing properties of phenylalanine closely parallel those of valine and isoleucine but not those of leucine, which shares side-chain branching at C^{γ} with phenylalanine and is normally considered to be the most closely related non-aromatic amino acid.

Comment

In three papers, we have presented the structures of various complexes between hydrophobic L- and D-amino acids (Dalhus & Görbitz, 1999*a*,*b*,*c*). All of these crystals are divided into hydrophilic and hydrophobic layers, the former incorporating the same hydrogen-bonding patterns as found in the crystal structures of regular amino acid racemates. The mixed L:D complexes are thus often referred to as pseudo-racemates, the difference from normal racemates being confined to the hydrophobic regions of the crystal structures. A closer look at the hydrophilic layers shows that they are generated from two distinct sheets, shown schematically in Fig. 1. Hydrogen bonding within a sheet engages two of the amine H atoms, while the third serves as a sheet connector. Only two types of sheets have been found for (pseudo)-racemates. The first is called LD and incorporates a mixture of L and D enantiomers, while the second arrangement involves amino acids of one hand only and is called L1 when constructed from L-amino acids and D1 when constructed from D-amino acids (Fig. 2). The sheets give rise to two types of layers, namely LD–LD, characterized by the presence of (pseudo)glide planes, and L1–D1, in which adjacent sheets are related by (pseudo)inversion. Theoretical *ab initio* calculations have indicated that the LD–LD layer, occurring in what has been referred to as class I crystal structures, is inherently preferred over L1–D1 (class II) as far as the hydrogen-bonding energy is concerned (Dalhus & Görbitz, 2004; Görbitz *et al.*, 2009). Steric conflict may nevertheless lead to L1–D1 structures, and Dalhus (2000) gave the following empirical rules for the effect of the side chain: (i) complexes with two linear amino acids crystallize in class I; (ii) complexes with two branched amino acids crystallize in class II; (iii) complexes with one linear and one branched amino acid crystallize in both class I and class II – branching at C^{β}(Ile/Val) gives class I structures, while branching at C^{γ}(Leu) gives class II structures.

Our previous investigations included Ala, 2-aminobutyric acid (Abu), norvaline (Nva), norleucine (Nle) and Met with linear side chains, as well as Val, Ile, *allo*-isoleucine (*a*Ile) and Leu with branched side chains, but not Phe. The only known structure of a 1:1 amino acid complex with this aromatic amino acid is L-Phe:D-Val (Prasad & Vijayan, 1991), which, in accordance with the observations of Dalhus (2000), forms a class II structure. Apart from this, the structure-directing properties of Phe in such complexes are unknown. In the structures of various peptides, Phe can often be replaced by Leu, both with branching at C^{γ}, without major structure modifications, while isostructural peptides with Phe substituted for Ile or Val are less common. We thus anticipated that amino acid complexes with Phe would mimic the equivalent complexes with Leu. In order to verify this hypothesis, attempts were made to crystallize L-Phe with the D enantiomer

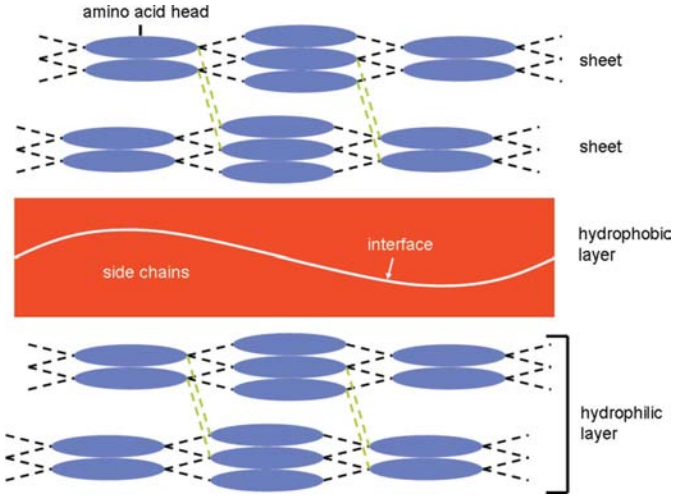

Figure 1
Schematic illustration of the construction of the crystal structures of hydrophobic amino acids (as enantiomers, racemates or L:D complexes). The structures are divided into hydrophobic and hydrophilic layers; the latter are in turn composed of two hydrogen-bonded sheets. At the centre of the hydrophobic layer there is an interface between side chains emanating from adjacent hydrophilic layers.

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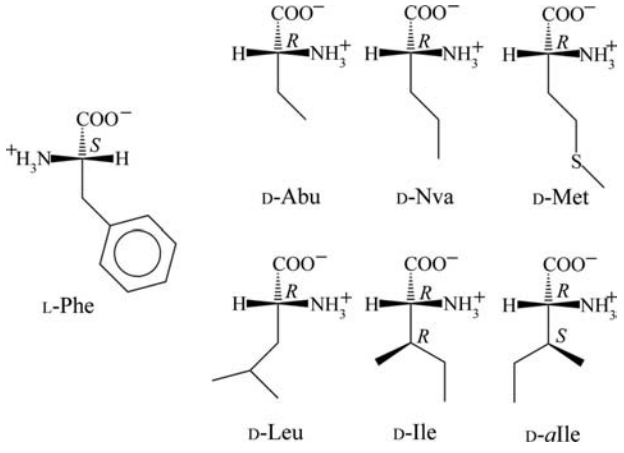
of all other hydrophobic amino acids listed above (except D-Val, but including D-Phe). Three complexes, L-Phe:D-Ala, L-Phe:D-Nle and DL-Phe, failed to give diffraction quality crystals, meaning that the present investigation deals with L-Phe in its complex with the three linear amino acids D-Abu, D-Nva and D-Met, as well as the three branched amino acids D-Leu, D-Ile and D-*a*Ile (see scheme).



The asymmetric units of the complexes between L-Phe and D-amino acids with linear and branched side chains are shown in Figs. 3 and 4, respectively. All structures are well ordered, but extensive thermal vibrations for certain side chains are evident, causing a significant artificial shortening of some covalent bond lengths such as C6*A*—C7*A* [1.318 (6) Å] for L-Phe:D-Leu. Packing diagrams are shown in Figs. 5 and 6. The hydrogen bonds observed in the six structures (Tables 1–6) follow closely the observed patterns for other LD–LD (class I) and L1–D1 (class II) structures. There is always a 'knots-in-holes' fit at the hydrophobic interface (Fig. 1), but this is much more pronounced for class I structures than for class II structures owing to the involvement of two different amino acids in the formation of each hydrogen-bonded sheet, as illustrated for L-Phe:D-Abu in Fig. 5 and L-Phe:D-Leu in Fig. 6.

Dalhus (2000) previously noted that complexes between *a*Ile and other amino acids, if formed at all, invariably yielded crystals of poor quality, in marked contrast to the corresponding complexes with Ile and Leu. A comparison of the unit-cell dimensions of complexes with Nva, Nle and Met (Dalhus & Görbitz, 1999*a*,*b*,*c*; Dalhus, 2000) shows that incorporation of *a*Ile leads to a 6–18 Å^3 increase in the volumes of the asymmetric unit compared with Ile or Leu, clearly indicating a less efficient packing of the hydrophobic side chains. In the present study, *a*Ile shows no such deviating crystallization habit, and the asymmetric unit volume of L-Phe:D-*a*Ile (386.2 Å^3) is midway between the value of 384.8 Å^3 for L-Phe:D-Ile and 391.0 Å^3 for L-Phe:D-Leu. The 6.2 Å^3 range is dwarfed by the 22.7 Å^3 difference between L-Leu:D-Abu (310.5 Å^3) and DL-Val (287.8 Å^3 for the LD pair; Flaig *et al.*, 2002), the more compact hydrophobic layer for the latter being easily recognized in Fig. 6 (note that the total number of side-chain C atoms remains unchanged).

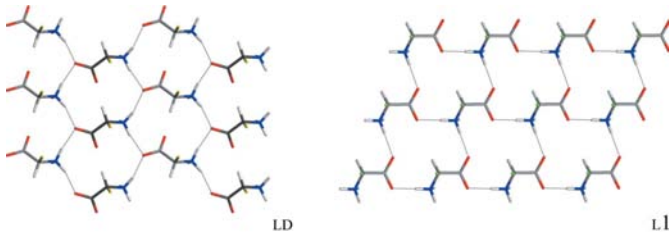


Figure 2
The two types of sheets observed for racemates and pseudo-racemates of hydrophobic amino acids. The D enantiomers in the LD sheet are coloured in a darker grey tone. For clarity, side chains have been replaced by a H atom.

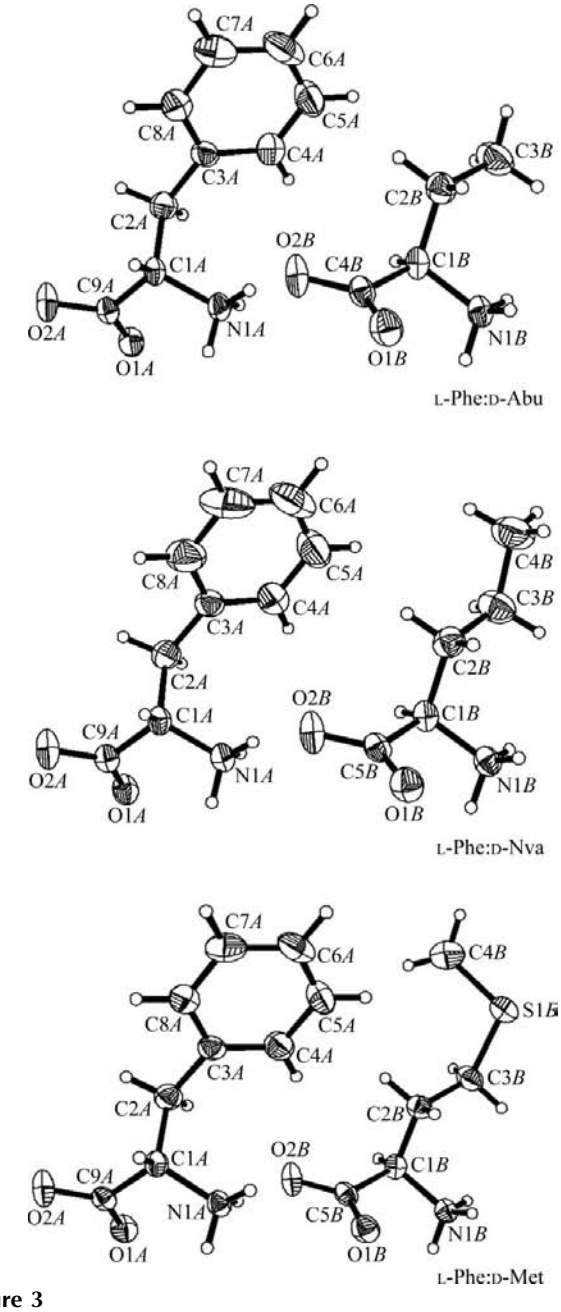


Figure 3
The molecular structures of L-Phe:D-Abu (top), L-Phe:D-Nva (middle) and L-Phe:D-Met (bottom). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

Class I structures usually distribute evenly between the monoclinic space groups $C2$ and $P2_1$, as exemplified in Fig. 5 by L-Ile:D-Nva (Dalhus & Görbitz, 1999*a*) and D-Nle:L-Met (Dalhus & Görbitz, 1999*b*), respectively. L-Phe:D-Met is isostructural with D-Nle:L-Met (disregarding the shifts in chirality) and about five other complexes. The orthorhombic $P2_12_12_1$ structures of L-Phe:D-Abu and L-Phe:D-Nva, on the other hand, have been preceded only by the structure of L-Val:D-Met (Fig. 5; Dalhus & Görbitz, 1999*c*). For the pseudo-symmetric class II complexes there is also an even distribution between two space groups, in this case $P1$ and $P2_1$. The monoclinic system has been chosen for L-Phe:D-Leu and L-Phe:D-*a*Ile, and the triclinic system for L-Phe:D-Ile, which is strikingly similar to the structure of D-Leu:L-Ile (Fig. 6; Dalhus & Görbitz, 1999*a*). This example serves to illustrate that, as long as the partner molecule has a branched side chain, Phe behaves similarly to Leu, or indeed similarly to any other amino acid with a branched side chain, in producing class II structures. Also included in this group are true racemates, such as DL-Val (Fig. 6; Flaig *et al.*, 2002). The difference between Leu and Phe becomes apparent when a comparison is made

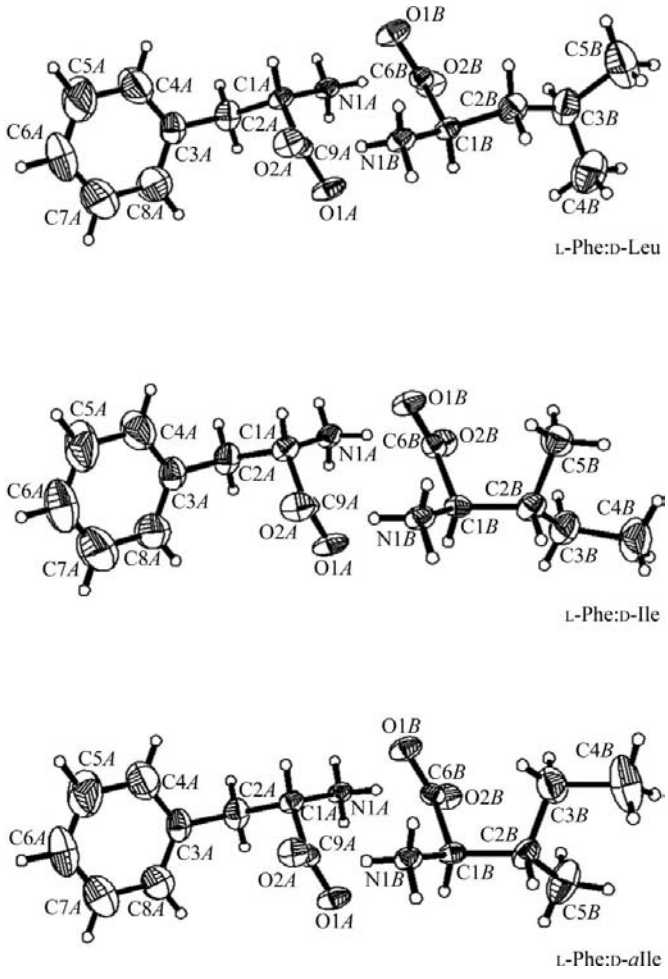


Figure 4
The molecular structures of L-Phe:D-Leu (top), L-Phe:D-Ile (middle) and L-Phe:D-*a*Ile (bottom). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

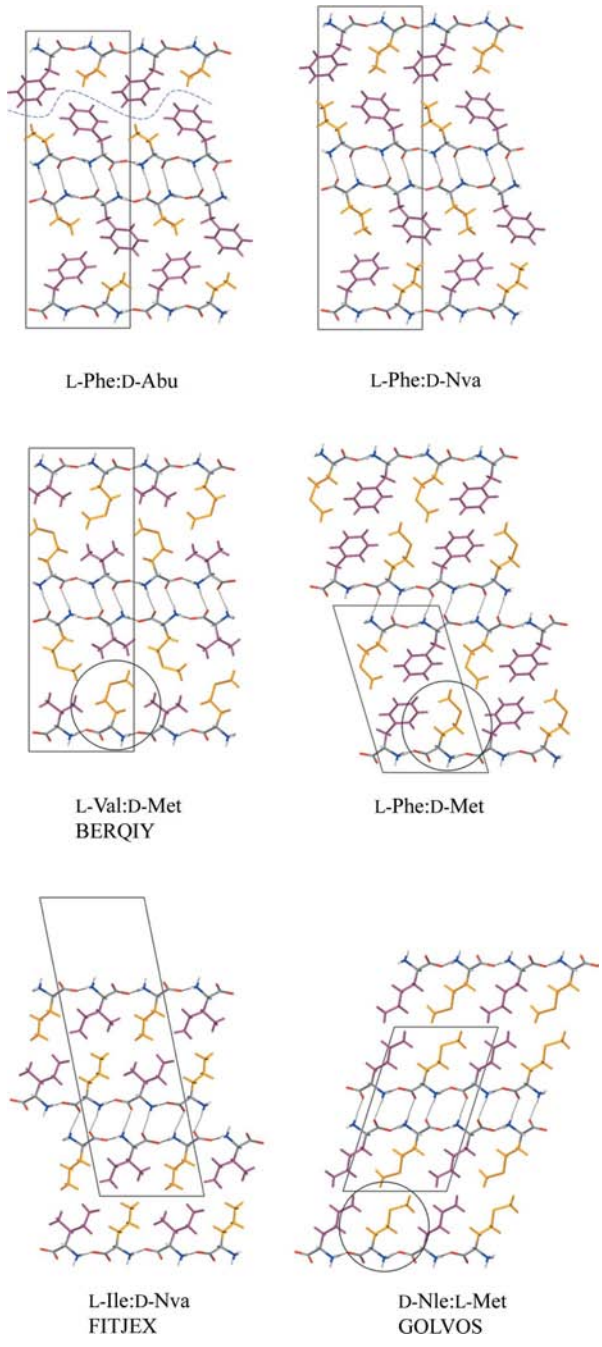


Figure 5
The molecular packing and unit cells of L-Phe:D-Abu (space group $P2_12_12_1$), L-Phe:D-Nva ($P2_12_12_1$) and L-Phe:D-Met ($P2_1$), together with L-Val:D-Met ($P2_12_12_1$; Dalhus & Görbitz, 1999*c*), L-Ile:D-Nva ($C2$; Dalhus & Görbitz, 1999*a*) and D-Nle:L-Met ($P2_1$; Dalhus & Görbitz, 1999*b*), with Cambridge Structural Database refcodes (Allen, 2002). A hydrophobic interface has been indicated for L-Phe:D-Abu; circles highlight different Met conformations. (In the electronic version of the paper, colouring of side chains has been used to emphasize structural similarities and not the chirality of the amino acid.)

between L-Phe:D-Abu (Fig. 5) and L-Leu:D-Abu (Fig. 6). Even when paired with Abu, with a relatively small ethyl side chain, Leu is unable to form a class I complex, while Phe forms class I complexes with any amino acid with a linear side chain. The origin of this important difference between Leu and Phe can

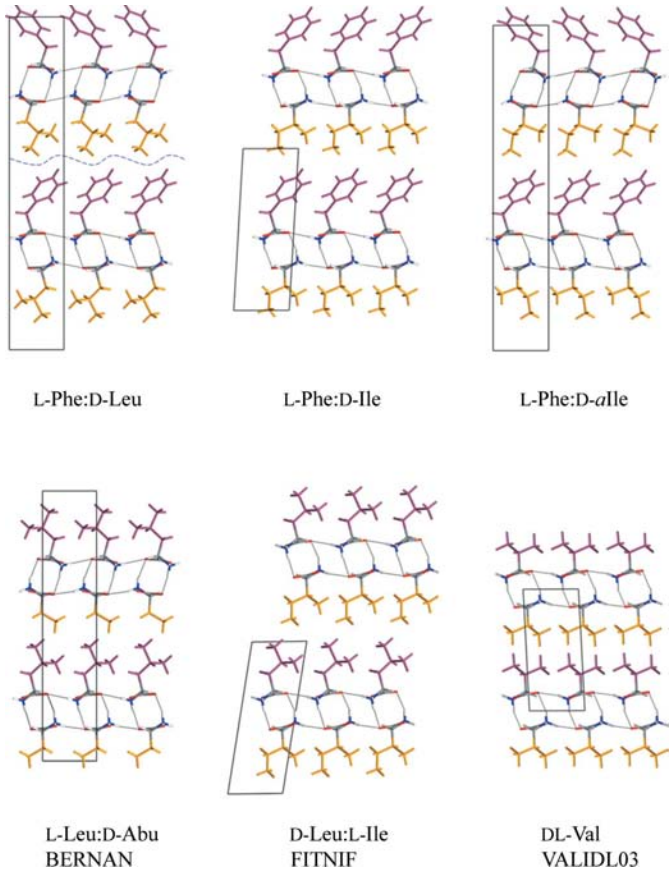


Figure 6
The molecular packing and unit cells of L-Phe:D-Leu ($P2_1$, with hydrophobic interface), L-Phe:D-Ile ($P1$) and L-Phe:D-*a*Ile ($P2_1$), together with L-Leu:D-Abu ($P2_1$; Dalhus & Görbitz, 1999*c*), D-Leu:L-Ile ($P1$; Dalhus & Görbitz, 1999*b*) and DL-Val ($P\overline{1}$; Flaig *et al.*, 2002). (In the electronic version of the paper, colouring of side chains has been used to emphasize structural similarities and not the chirality of the amino acid.)

be derived from an analysis of amino acid side-chain rotamers (Table 7). The table shows that Met is the only amino acid to display any conformational variation within class I. In fact, it occurs with three different side-chain conformations for χ^1,χ^2,χ^3 (L enantiomer), namely *gauche*−,*trans*,*trans*, *gauche*−,*trans*,*gauche*+ and finally *trans*,*trans*,*gauche*−, which is also observed in the class II complex with Leu (Dalhus & Görbitz, 1999*c*). More important is that Table 7 reveals systematic conformational shifts upon change of class, which is evidently a requirement for proper stacking of side chains in the hydrophobic layers. It is then essential that Leu, as the only amino acid, is unable to undergo such a shift as it is restricted to the *trans*,*gauche*+/*trans* conformation for $\chi^1,\chi^{2,1}$/$\chi^{2,2}$ (L enantiomer; Görbitz, 2006).

In summary, in complexes with other hydrophobic amino acids, L-Phe displays the same structure-directing properties as the C^β-branched amino acids Val, Ile and *a*Ile. This means that complexes with linear amino acids form class I (LD–LD) structures, while complexes with branched side chains form class II (L1–D1) structures. The ability of Phe to form the tightly packed LD sheets required for formation of an LD–LD class I layer stems from the availability of more than one possible conformation upon rotation around the $C^\alpha-C^\beta$ bond. In contrast, Leu, which like Phe is branched at C^γ, has only a single viable side-chain conformation and is consequently limited to class II structures with L1–D1 hydrogen-bonded layers.

Experimental

Aqueous solutions of the selected complexes were prepared by dissolving equimolar amounts (typically 1 mg of each) of the two selected amino acids in 90 µl of deionized water. The mixture was distributed into three 30 × 5 mm test tubes and sealed with Parafilm, in which a couple of small holes were then pricked with a needle. Usable crystals emerged for five complexes as acetonitrile diffused into the solutions at room temperature. For the sixth, L-Phe:D-Abu, additional crystallizations had to be carried out. These employed, rather than pure water as the solvent, a mixture of water (80 µl) and tetramethoxysilane (20 µl). After vigorous stirring for about 1 min, the mixture was left to polymerize into a gel (1 h). Equilibration against acetonitrile subsequently proceeded as above, producing in the gel larger crystals of good quality.

L-Phe:D-Abu

Crystal data

$C_9H_{11}NO_2\cdot C_4H_9NO_2$
M_r = 268.31
Orthorhombic, $P2_12_12_1$
a = 4.7869 (7) Å
b = 9.9558 (15) Å
c = 28.423 (4) Å
V = 1354.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.80 × 0.12 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
T_{min} = 0.770, T_{max} = 0.996
10082 measured reflections
1443 independent reflections
1284 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Table 1
Hydrogen-bond geometry (Å, °) for L-Phe:D-Abu.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B	0.92 (2)	1.98 (3)	2.850 (3)	157 (3)
N1A—H2A···O2B^{i}	0.95 (3)	1.95 (3)	2.879 (3)	167 (3)
N1A—H3A···O1A^{ii}	0.92 (2)	1.87 (2)	2.788 (3)	172 (3)
N1B—H1B···O2A^{iii}	0.94 (2)	1.92 (3)	2.817 (3)	159 (3)
N1B—H2B···O1B^{iv}	0.94 (2)	1.83 (2)	2.756 (3)	166 (3)
N1B—H3B···O2A^{v}	0.92 (3)	1.93 (3)	2.835 (3)	168 (3)

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

Table 2
Hydrogen-bond geometry (Å, °) for L-Phe:D-Nva.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B	0.92 (2)	1.95 (3)	2.830 (3)	162 (3)
N1A—H3A···O2B^{i}	0.90 (2)	1.97 (3)	2.871 (3)	173 (3)
N1A—H2A···O1A^{ii}	0.93 (2)	1.85 (2)	2.780 (3)	173 (3)
N1B—H1B···O2A^{iii}	0.91 (2)	1.94 (3)	2.809 (3)	159 (3)
N1B—H3B···O1B^{iv}	0.95 (2)	1.80 (2)	2.743 (3)	171 (3)
N1B—H2B···O2A^{v}	0.91 (2)	1.94 (3)	2.835 (3)	168 (3)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.120$
$S = 1.07$
1443 reflections
191 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

L-Phe:D-Nva

Crystal data

$C_9H_{11}NO_2{\cdot}C_5H_{11}NO_2$
$M_r = 282.34$
Orthorhombic, $P2_12_12_1$
$a = 4.7624$ (8) Å
$b = 9.9569$ (17) Å
$c = 30.935$ (6) Å
$V = 1466.9$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 296$ K
$0.48 \times 0.14 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.862$, $T_{max} = 0.995$
14224 measured reflections
1564 independent reflections
1395 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.093$
$S = 1.07$
1564 reflections
200 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

L-Phe:D-Met

Crystal data

$C_9H_{11}NO_2{\cdot}C_5H_{11}NO_2S$
$M_r = 314.40$
Monoclinic, $P2_1$
$a = 10.110$ (2) Å
$b = 4.7064$ (9) Å
$c = 16.686$ (3) Å
$\beta = 106.663$ (2)°
$V = 760.6$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.23$ mm^{-1}
$T = 296$ K
$1.24 \times 0.1 \times 0.02$ mm

Table 3
Hydrogen-bond geometry (Å, °) for L-Phe:D-Met.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B^{i}	0.93 (2)	1.96 (3)	2.863 (3)	162 (3)
N1A—H2A···O2B	0.92 (2)	2.00 (2)	2.887 (3)	163 (3)
N1A—H3A···O1A^{ii}	0.91 (2)	1.86 (2)	2.762 (3)	172 (3)
N1B—H1B···O1B^{iii}	0.90 (2)	1.85 (2)	2.752 (3)	176 (3)
N1B—H2B···O2A^{iv}	0.88 (2)	1.98 (2)	2.838 (3)	168 (3)
N1B—H3B···O2A^{v}	0.89 (2)	1.95 (2)	2.817 (3)	163 (3)

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

Table 4
Hydrogen-bond geometry (Å, °) for L-Phe:D-Leu.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B	0.93 (3)	1.98 (3)	2.875 (4)	161 (3)
N1A—H2A···O1A^{i}	0.91 (2)	1.82 (2)	2.735 (3)	176 (3)
N1A—H3A···O2A^{ii}	0.90 (2)	2.03 (3)	2.921 (3)	174 (3)
N1B—H1B···O2A	0.90 (3)	2.02 (3)	2.896 (4)	163 (3)
N1B—H2B···O2B^{iii}	0.91 (2)	1.98 (3)	2.887 (3)	174 (3)
N1B—H3B···O1B^{iv}	0.94 (2)	1.79 (2)	2.729 (3)	178 (3)

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

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.800$, $T_{max} = 0.995$
5312 measured reflections
2580 independent reflections
2406 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.18$
2580 reflections
208 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 1082 Friedel pairs
Flack parameter: 0.00 (10)

L-Phe:D-Leu

Crystal data

$C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$
$M_r = 296.36$
Monoclinic, $P2_1$
$a = 5.1861$ (5) Å
$b = 29.698$ (3) Å
$c = 5.4158$ (5) Å
$\beta = 110.372$ (1)°
$V = 781.95$ (13) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 296$ K
$0.3 \times 0.2 \times 0.06$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.909$, $T_{max} = 0.995$
7778 measured reflections
1411 independent reflections
1269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.089$
$S = 1.10$
1411 reflections
208 parameters
12 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

L-Phe:D-Ile

Crystal data

$C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$
$M_r = 296.36$
Triclinic, $P1$
$a = 5.2317$ (12) Å
$b = 5.4232$ (12) Å
$c = 14.459$ (3) Å
$\alpha = 85.936$ (3)°
$\beta = 85.343$ (3)°
$\gamma = 70.424$ (2)°
$V = 384.83$ (15) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 296$ K
$0.32 \times 0.18 \times 0.03$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.762$, $T_{max} = 0.997$
2821 measured reflections
1359 independent reflections
1054 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.099$
$S = 1.06$
1359 reflections
210 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 5
Hydrogen-bond geometry (Å, °) for L-Phe:D-Ile.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B	0.91 (3)	2.01 (3)	2.896 (5)	163 (4)
N1A—H2A···O1A^{i}	0.91 (3)	1.83 (3)	2.740 (5)	177 (5)
N1A—H3A···O2A^{ii}	0.94 (3)	2.01 (3)	2.949 (5)	177 (4)
N1B—H1B···O2A	0.94 (3)	2.04 (3)	2.933 (5)	157 (4)
N1B—H2B···O2B^{iii}	0.93 (3)	1.98 (3)	2.895 (5)	169 (4)
N1B—H3B···O1B^{iv}	0.92 (3)	1.84 (3)	2.758 (5)	174 (5)

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

L-Phe:D-*a*Ile

Crystal data

$C_9H_{11}NO_2{\cdot}C_6H_{13}NO_2$
M_r = 296.36
Monoclinic, $P2_1$
a = 5.2436 (5) Å
b = 28.949 (3) Å
c = 5.4069 (5) Å
β = 109.747 (1)°
V = 772.49 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.58 × 0.16 × 0.1 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*b*)
T_{min} = 0.903, T_{max} = 0.991
8740 measured reflections
1668 independent reflections
1605 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
S = 1.07
1668 reflections
210 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 6
Hydrogen-bond geometry (Å, °) for L-Phe:D-*a*Ile.

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O2B	0.91 (2)	2.00 (2)	2.887 (3)	162 (3)
N1A—H2A···O1A^{i}	0.90 (2)	1.82 (2)	2.722 (2)	176 (3)
N1A—H3A···O2A^{ii}	0.90 (2)	2.06 (2)	2.959 (3)	177 (3)
N1B—H1B···O1B^{iii}	0.91 (2)	1.84 (2)	2.750 (2)	177 (3)
N1B—H2B···O2A	0.88 (2)	2.10 (2)	2.937 (3)	157 (3)
N1B—H3B···O2B^{iv}	0.88 (2)	2.02 (2)	2.890 (2)	166 (3)

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

H atoms bonded to C atoms were positioned with idealized geometry and C—H distances were fixed in the range 0.93–0.98 Å. Positional parameters were refined for H atoms bonded to N atoms, but with a mild *SHELXTL* (Sheldrick, 2008*a*) restraint for the N—H distances, which accordingly varied between 0.88 (2) and 0.95 (3) Å. U_{iso}(H) values were set at 1.2U_{eq} of the carrier atom, or 1.5U_{eq} for ammonium and methyl groups. Friedel pairs were merged for all data sets except L-Phe:D-Met, for which the anomalous scattering effects of 1082 Friedel pairs were used to confirm the known absolute configurations of the complex components.

For all compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008*a*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 7
Observed N—C^{α}—C^{β}—C^{γ} rotamers (χ^1) in amino acid complexes (after inversion to the L enantiomer if the D enantiomer was crystallized in the complex).

Amino acid	Class I (LD–LD)	Class II (L1–D1)
L-Abu/L-Nva/L-Phe	*gauche*−	*trans*
L-Met	*gauche*−, *trans*	*trans*
L-Val/L-Ile/L-*a*Ile	*trans*/*gauche*−[a]	*gauche*+/*trans*[a]

Note: (*a*) $\chi^{1,1}/\chi^{1,2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3316). Services for accessing these data are described at the back of the journal.

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