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L-Leucyl-L-leucine 2-methyl-1-propanol solvate

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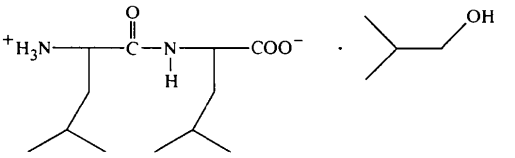
Abstract

The title compound, $C_{12}H_{24}N_2O_3 \cdot C_4H_{10}O$, crystallizes in space group $P2_12_12_1$ with two peptide molecules and two alcohol molecules in the asymmetric unit. The structure has been studied as part of a systematic survey of solvent inclusion for the L-Leu-L-Leu dipeptide, which has previously been crystallized as isomorphous ethanol, 1-propanol and 2-propanol solvates, and also as a dimethyl sulfoxide solvate.

Comment

Dipeptides with two hydrophobic residues (hydrophobic dipeptides) generally crystallize as needles, or occasionally as thin plates. L-Leu-L-Val, on the other hand, forms good quality large crystals in vapour-diffusion experiments with most solvents as precipitating agents, either as a hydrate in a hexagonal space group (Görbitz & Gundersen, 1996*a*) or as an alcohol solvate (Görbitz & Torgersen, 1999). L-Leu-L-Leu can also form good quality crystals, but for this compound, the outcome of crystallization is much more dependent on the choice of solvent. The structure of the dimethyl sulfoxide (DMSO) solvate has been reported previously (space group $P2_1$, $Z = 2$; Mitra & Subramanian, 1994); the 'ill-formed crystals' were obtained 'after a great deal of effort' as extremely thin needles. A survey of numerous other solvents (Görbitz, 1999) revealed that only four produced crystals suitable for diffraction experiments. Three of these, ethanol, 1-propanol and 2-propanol, form isomorphous structures in space group $P2_1$ with $Z = 4$ (Görbitz, 1999*a*). The fourth is 2-methyl-1-propanol (isobutanol), which forms the title complex, LLmp. The use of other solvents during crystallization produces exceedingly thin needles (< 0.01 mm diameter), as does slow cooling of an aqueous solution. We anticipate that the structure of L-Leu-L-Leu in needles devoid of organic solvent is related to the hexagonal structures observed for other hydrophobic dipeptides (Görbitz & Gundersen, 1996*b*; Görbitz, 1999).



LLmp

The asymmetric unit of the L-Leu-L-Leu 2-methyl-1-propanol solvate (LLmp), with two peptide molecules and two alcohol molecules, is depicted in Fig. 1. Bond lengths and angles are normal. The main chains of both peptide molecules are in fairy extended conformations. The side chain of the N-terminal residue of molecule *A* has the common *gauche*$^-$/*trans*,*gauche*$^-$ conformation for $\chi^1/\chi^{2,1},\chi^{2,2}$, while for residue 2, the conformation is *trans*/*trans*,*gauche*$^+$. The side chains of the two residues in molecule *B* have the same two conformations, but in opposite order. There is a significant deviation from planarity for the peptide bond of molecule *B*, easily visible in Fig. 1, with $\omega = 168.4\,(2)°$.

As in numerous other dipeptides, the crystal structure of LLmp is divided into hydrophilic and hydrophobic

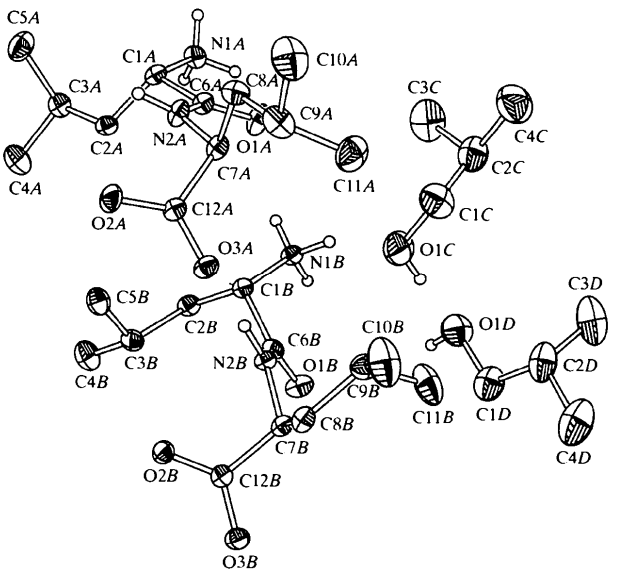


Fig. 1. The asymmetric unit of LLmp with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and selected H atoms are shown as spheres of arbitrary size.

layers. For hydrophobic dipeptides, there is an inherent complication with this crystal packing in that only two of the three amino H atoms can participate in hydrogen bonding within a hydrophilic layer, with no readily available acceptor for the third N—H atom. The solution to this problem is usually cocrystallization of a hydrogen-bond-accepting organic solvent molecule, invariably an alcohol or DMSO.

The hydrogen-bonding pattern of LLmp is shown in Fig. 2. It can be seen that for each peptide molecule, two of the amino N—H atoms (H1 and H2) participate in head-to-tail chains (Suresh & Vijayan, 1985), thus generating a two-dimensional hydrogen-bonded sheet. Solvent molecule *C* fulfils its expected role as a hydrogen-bond acceptor of an amino N—H atom (N1*B*—H3*B*). It is surprising, however, that solvent molecule *D* does not have a similar function. Atom O1*D* rather accepts an H atom from solvent molecule *C* and donates an H atom to the carboxylate group of peptide molecule *B*. The third amino N—H atom of molecule *A* is thus not involved in a short intermolecular hydrogen bond [the closest contact is N1*A*—H1*A*···O1*B*($x-1$, y, z) with an H···O distance of 2.76 (3) Å], but is instead donated to O1*A* in an intramolecular hydrogen bond. This kind of interaction is rare, as the atoms in the chain H—N—Cα—C′=O must be almost coplanar, *i.e.* an eclipsed conformation of the amino group with respect to Cα is required. As can be seen from Fig. 1, this is indeed observed for molecule *A*, with H3*A*—N1*A*—C1*A*—C6*A* = 6 (2)° and N1*A*—C1*A*—C6*A*—O1*A* = −15.3 (3)°.

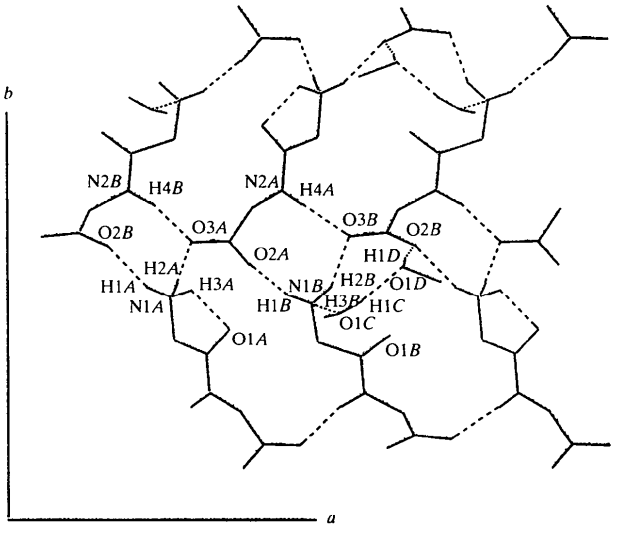


Fig. 2. The hydrogen-bonding pattern in the crystal structure of LLmp, viewed approximately along the *c* axis. For completeness, some isolated peptide C-terminal carboxylate groups have been included. All peptide side chains and Hα atoms have been removed for clarity. For the alcohol molecules, only C—O—H remains. Essential atom labels have been indicated.

Experimental

Diffusion of 2-methyl-1-propanol into 60 µl of an aqueous solution containing about 0.5 mg of the peptide yielded numerous very thin needles and a handful of rather small plate-shaped crystals, the largest of which was used for data collection.

Crystal data

$C_{12}H_{24}N_2O_3 \cdot C_4H_{10}O$
M_r = 318.45
Orthorhombic
$P2_12_12_1$
a = 10.3179 (1) Å
b = 13.6397 (1) Å
c = 27.1830 (5) Å
V = 3825.55 (8) Å^3
Z = 8
D_x = 1.106 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7620 reflections
θ = 1.50–29.06°
μ = 0.078 mm^{-1}
T = 150 (2) K
Plate
0.30 × 0.20 × 0.05 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
Sets of exposures each taken over 0.6°, ω rotation scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.977, T_{max} = 0.996
24 306 measured reflections
9025 independent reflections
7461 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 29.06°
h = −14 → 14
k = −18 → 17
l = −24 → 36
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.145
S = 1.076
9024 reflections
467 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.0595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.046
$\Delta\rho_{max}$ = 0.286 e Å^{-3}
$\Delta\rho_{min}$ = −0.307 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1*A*—C6*A*	1.234 (2)	O2*B*—C12*B*	1.246 (2)
O2*A*—C12*A*	1.248 (2)	O3*B*—C12*B*	1.258 (3)
O3*A*—C12*A*	1.254 (3)	N2*B*—C6*B*	1.345 (2)
N2*A*—C6*A*	1.341 (2)	O1*C*—C1*C*	1.415 (3)
O1*B*—C6*B*	1.228 (3)	O1*D*—C1*D*	1.421 (4)
C6*A*—N2*A*—C7*A*	122.8 (2)	C6*B*—N2*B*—C7*B*	121.8 (2)
N1*A*—C1*A*—C6*A*	105.6 (2)	N1*B*—C1*B*—C6*B*	108.3 (2)
N2*A*—C6*A*—C1*A*	115.1 (2)	N2*B*—C6*B*—C1*B*	115.9 (2)
O2*A*—C12*A*—O3*A*	125.3 (2)	O2*B*—C12*B*—O3*B*	126.1 (2)
N1*A*—C1*A*—C6*A*—N2*A*	168.5 (2)		
C1*A*—C6*A*—N2*A*—C7*A*	174.9 (2)		
C6*A*—N2*A*—C7*A*—C12*A*	−127.0 (2)		
N2*A*—C7*A*—C12*A*—O2*A*	−45.5 (2)		
N1*B*—C1*B*—C6*B*—N2*B*	128.8 (2)		
C1*B*—C6*B*—N2*B*—C7*B*	168.4 (2)		
C6*B*—N2*B*—C7*B*—C12*B*	−86.1 (2)		
N2*B*—C7*B*—C12*B*—O2*B*	−29.7 (2)		
O1*C*—C1*C*—C2*C*—C3*C*	56.3 (4)		

O1C—C1C—C2C—C4C	−179.6 (3)
O1D—C1D—C2D—C4D	173.8 (3)
O1D—C1D—C2D—C3D	−61.2 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···O2*B*^{i}	0.93 (3)	1.98 (3)	2.861 (2)	158 (2)
N1*A*—H2*A*···O3*A*^{i}	0.95 (3)	1.84 (3)	2.763 (2)	163 (2)
N1*A*—H3*A*···O1*A*	0.93 (3)	2.00 (3)	2.610 (2)	122 (2)
N2*A*—H4*A*···O3*B*^{ii}	0.89 (3)	2.00 (3)	2.886 (2)	176 (2)
N1*B*—H1*B*···O2*A*^{i}	0.89 (3)	1.96 (3)	2.762 (2)	148 (2)
N1*B*—H2*B*···O3*B*^{iii}	0.93 (3)	1.88 (3)	2.749 (2)	154 (2)
N1*B*—H3*B*···O1*C*	1.02 (3)	1.74 (3)	2.715 (3)	159 (2)
N2*B*—H4*B*···O3*A*	0.95 (3)	1.94 (3)	2.862 (2)	165 (2)
O1*C*—H1*C*···O1*D*	0.90 (4)	1.81 (4)	2.697 (3)	168 (4)
O1*D*—H1*D*···O2*B*^{iii}	0.88 (4)	1.83 (4)	2.707 (2)	174 (4)

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

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures, with the detector set at $2\theta = 29°$. Each set had a different φ angle for the crystal and each exposure covered 0.6° in ω. The crystal-to-detector distance was 4.99 cm. Coverage of the unique set is over 99% complete to 50° in 2θ. Positional parameters were refined for H atoms bonded to O or N, while other H atoms were placed geometrically and refined with constraints to keep all C—H distances and all C—C—H angles on one C atom the same. U_{iso} values were set at $1.2U_{eq}$ of the carrier atom, or at $1.5U_{eq}$ for amino, methyl and hydroxyl groups. Free rotation about C—C bonds was also permitted for methyl groups.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The purchase of the Siemens SMART diffractometer was made possible through support from The Research Council of Norway (NFR).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1518). Services for accessing these data are described at the back of the journal.

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4,4′-Bipyridyl at 203 K

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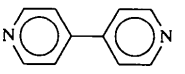
Abstract

The crystal structure of 4,4′-bipyridyl, $C_{10}H_8N_2$, at 203 K contains two independent, non-planar, molecules whose mean planes subtend an angle of 14.1 (8)°. The long axes of the two molecules are oriented at approximately 88° to each other, allowing interaction between the N atoms and phenyl-H atoms on adjacent molecules and thereby giving rise to a sheet structure. The two molecules are primarily differentiated by the dihedral angle between the connected phenyl rings [18.50 (12) and 34.85 (10)°].

Comment

Although the crystal structure of the 4,4′-bipyridyl molecule, (I), has been reported many times in the context of acting as a Lewis base (*e.g.* Blake *et al.*, 1997; Lu *et al.*, 1997), or cocrystallized with hydrogen donors such as alcohols (Coupar *et al.*, 1996; Sharma & Zawarotko, 1996) or transition metal complexes (Blake *et al.*, 1997; Lu *et al.*, 1997) to form macromolecular arrays (Coupar *et al.*, 1996; Sharma & Zawarotko, 1996), the structure of the molecule itself has only been determined by electron diffraction (Almenningen & Bastiansen, 1958), although the structure of 3,3′-dimethyl-4,4′-bipyridyl has been reported (Gourdon, 1993).



(I)

The major difference between the two independent molecules found in the asymmetric unit is the dihedral angle subtended by the phenyl groups across the connecting C—C bond [18.50 (12)° in molecule 1 and 34.85 (10)° in molecule 2]. This angle was determined to be 37.2° in the gas phase and 48.6° from the latest theoretical calculations (Ould-Moussa *et al.*, 1996). In the sterically congested 3,3′-dimethyl-4,4′-bipyridyl the angle is 81.1° (Gourdon, 1993). In all other respects, the two independent molecules are very similar in their bonds lengths and angles. The C—N bonds are some 0.04 Å shorter than the ring C—C bonds and the angle