Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A non-planar peptide bond in L-seryl-L-valine

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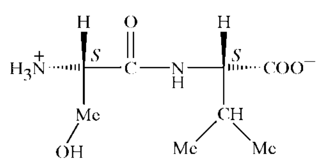
Received 29 April 2004
Accepted 14 June 2004
Online 10 July 2004

The $C^{\alpha}—C'—N—C^{\alpha}$ (ω) torsion angle of the peptide bond in the crystal structure of the title compound, $C_8H_{16}N_2O_4$, is 157.37 (15)°. This is the second-largest deviation from planarity observed for a small linear peptide.

Comment

The structure of L-Ser-L-Val, (I), has been investigated as part of a systematic survey of dipeptides with one hydrophobic residue and one small polar residue. Special attention was focused on the hydrogen-bonding preferences and the aggregation patterns of the hydrophobic groups (Netland *et al.*, 2004, and references therein).



(I)

The molecular structure of (I) is shown in Fig. 1. Bond lengths and angles are normal, but the unusual non-planarity of the peptide bond is quite evident. The associated torsion angle C1—C3—N2—C4 (ω) is 157.37 (15)°, a deviation from 180° that is superceded among small chiral peptides only by the 156.6° ω angle in *N*-(*tert*-butoxycarbonyl)-L-Pro-L-Leu benzyl ester (Sugino *et al.*, 1978).

Fig. 2(*a*) shows the molecular packing arrangement of (I). The crystal structure is divided into hydrophobic and hydrophilic layers in very much the same manner as seen for L-Ser-L-Leu, (II) (Fig. 2*b*; Słowikowska & Lipkowski, 2001), despite a substantial shift in the β angle, which is 98.623 (6)° for (I) but just 84.19° for (II), after transformation of the originally reported unit cell to match the packing observed for (I). The length of the *c* axis increases from 15.588 (10) Å for (I) to 18.1263 (9) Å for (II), as the thickness of the hydrophobic layer increases to accommodate the bulkier Leu side chain. Changes in the other two axes, however, are very modest [for (I), *a* = 5.383 (4) Å and *b* = 6.315 (4) Å, and for (II), *a* = 5.3288 (3) Å and *b* = 6.3696 (6) Å]. The peptide bond twist recurs for (II), which has ω = 157.99 (12)°.

The origin of the low ω values for (I) and (II) is indicated by the detailed view of the hydrogen-bonding interactions of (I) shown in Fig. 3. The C-terminal carboxylate group is clearly rotated away from the planar configuration in order to form good hydrogen bonds with four nearby donors, three amino groups and one Ser hydroxyl group (see also Table 2). The latter is twisted into an unusual eclipsed conformation, with a value of 131 (3)° for the C1—C2—O1—H5 torsion angle (Table 1). Notably, any modification of the main-chain conformation (to bring ω closer to 180°) would break the hydrogen bonds donated by the amide NH group, the side-chain Ser-OH group, or both.

The crystal packing arrangement of L-Ser-L-Ala (Görbitz, 2000), with a three-dimensional hydrogen-bonding pattern, is different from those of (I) and (II). The specific types of intermolecular interactions are nevertheless quite similar. The only modification concerns the amide H atom, which is

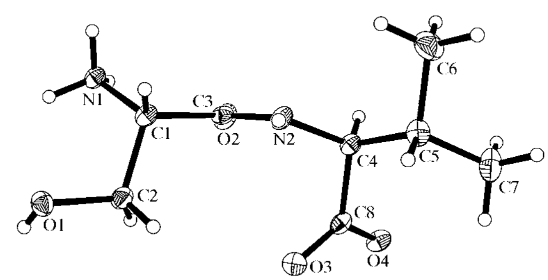


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary size.

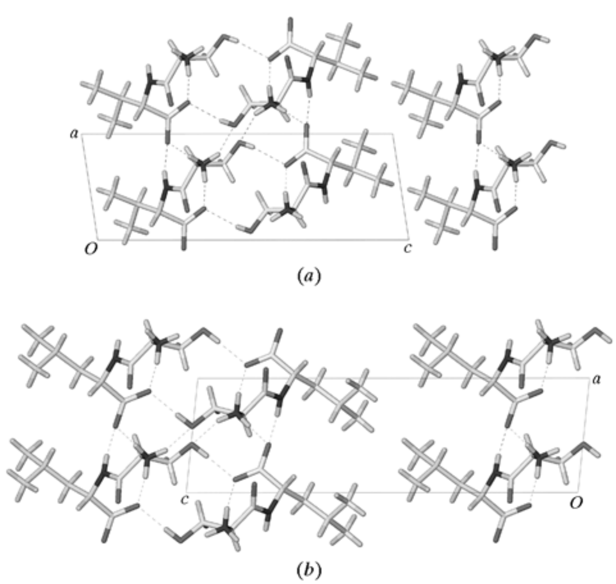


Figure 2
The molecular packing and unit cell of (*a*) L-Ser-L-Val, (I), and (*b*) L-Ser-L-Leu, (II), in the orginally reported unit cell (Słowikowska & Lipkowski, 2001). Both views are along the *b* axis.

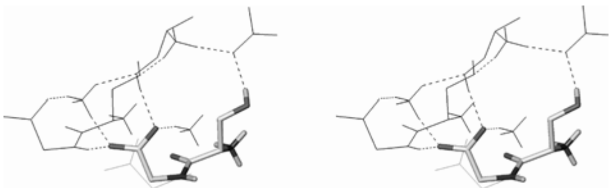


Figure 3
A stereodrawing, showing the hydrogen bonds for the carboxylate group of an individual peptide molecule, depicted as capped sticks. The Val side chain and H atoms not involved in hydrogen bonds have been omitted for clarity. The pale-grey line drawing indicates the position of the carboxylate group with a forced planar peptide bond. The dark-grey line drawing shows a neighbouring peptide molecule along the *a* axis, as well as fragments of several others acting as hydrogen-bond donors or acceptors.

donated to the C-terminal carboxylate group in (I) (Table 2) and (II), while the peptide carbonyl group is the acceptor in L-Ser-L-Ala. The only dipeptide in the Cambridge Structural Database (CSD, Version 5.25 of November 2003; Allen, 2002) with an *N*-terminal Ser residue, other than L-Ser-L-Leu and L-Ser-L-Ala, is L-Ser-Gly (Jones *et al.*, 1978). The crystal structure of L-Ser-Gly contains three $—NH_3^+\cdots{}^-OOC—$ interactions, while the hydroxyl H atom is donated to the peptide carbonyl group. The peptide bonds of L-Ser-L-Ala and L-Ser-Gly are both close to planar.

Experimental

The title compound was obtained from Bachem. Crystals of (I) were prepared by slow diffusion of ethanol into an aqueous solution of the peptide at ambient temperature.

Crystal data

$C_8H_{16}N_2O_4$
M_r = 204.23
Monoclinic, $P2_1$
a = 5.383 (4) Å
b = 6.315 (4) Å
c = 15.588 (10) Å
β = 98.623 (6)°
V = 523.9 (6) Å^3
Z = 2
D_x = 1.295 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3525 reflections
θ = 2.5–27.1°
μ = 0.10 mm^{-1}
T = 105 (2) K
Plate, colourless
0.35 × 0.20 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Sets of exposures each taken over 0.3° ω rotation scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.894, T_{max} = 0.964
4217 measured reflections
1248 independent reflections
1201 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.1°
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.08
1248 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.0968P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C1—C3—N2	152.57 (14)	N1—C1—C2—O1	−52.65 (18)
C1—C3—N2—C4	157.37 (15)	C1—C2—O1—H5	131 (3)
C3—N2—C4—C8	−63.7 (2)	N2—C4—C5—C6	−62.00 (18)
N2—C4—C8—O3	−24.7 (2)	N2—C4—C5—C7	175.09 (16)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3^{i}	0.90 (3)	2.03 (3)	2.871 (2)	156 (2)
N1—H2$\cdots$O1^{ii}	0.91 (2)	2.10 (2)	2.875 (2)	143 (2)
N1—H3$\cdots$O4^{iii}	0.87 (3)	1.88 (3)	2.735 (2)	166 (2)
N2—H4$\cdots$O4^{iv}	0.89 (2)	1.95 (2)	2.824 (2)	166 (2)
O1—H5$\cdots$O3^{v}	0.70 (2)	1.95 (2)	2.637 (2)	170 (3)
C1—H11$\cdots$O2^{iv}	0.97 (2)	2.37 (2)	3.273 (2)	153.9 (19)

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

The absolute structure of (I), which was known for the purchased material, could not be confirmed by the crystallographic experiment due to the absence of significant anomalous dispersion effects. 976 Friedel pairs were thus merged in the final refinement cycles. Positional parameters were refined for H atoms involved in hydrogen bonds. Other H atoms were positioned geometrically and refined with constraints to keep all C—H distances and C—C—H angles on one C atom the same. U_{iso}(H) values were set at $1.2U_{eq}$ of the carrier atom or $1.5U_{eq}$ for amino and methyl groups.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The purchase of the Siemens SMART CCD 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: SX1142). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (1998). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT-Plus*. Version 6.22. Bruker AXS Inc., Madison, Wisconsin, USA.
Görbitz, C. H. (2000). *Acta Cryst.* C**56**, 500–502.
Jones, P. G., Falvello, L. & Kennard, O. (1978). *Acta Cryst.* B**34**, 2379–2381.
Netland, K. A., Andresen, K., Görbitz, C. H. & Dalhus, B. (2004). *Acta Cryst.* E**60**, o951–o953.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Słowikowska, J. & Lipkowski, J. (2001). *Acta Cryst.* C**57**, 187–189.
Sugino, H., Tanaka, I. & Ashida, T. (1978). *Bull. Chem. Soc. Jpn*, **51**, 2855–2861.