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# Racemic dipeptide glycyl-DL-leucine at 120 K

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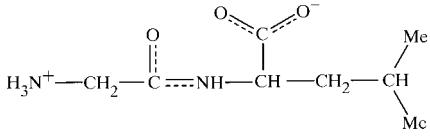
The structure of glycyl-DL-leucine, $C_8H_{16}N_2O_3$, has been determined at 120 K by single-crystal X-ray diffraction. In addition to three N—H···O-type hydrogen bonds of the positively charged $RNH_3^+$ group of the zwitterionic molecule, an intermolecular N—H···O contact exists between the peptide bond and the carboxylate group. Four hydrogen-bond cycles were identified, giving a complex pattern.

## Comment

The study of small peptides has gained interest in the investigation of the geometry of the peptide bond. The structures of over 120 dipeptides can be found in the Cambridge Structural Database (Allen & Kennard, 1993). In most cases, the naturally occurring L-L-forms, less often the racemates and simple derivatives of dipeptides, were investigated. In the course of our ongoing research of comparative charge–density studies of different oligopeptides, we have examined several dipeptides. The structure of the racemic dipeptide glycyl-DL-leucine, (I), was not known until now, but the structure of the resolved L-form was investigated by Pattabhi *et al.* (1974).



(I)

An *ORTEP*III (Burnett & Johnson, 1996) representation of the molecular structure and the atomic numbering scheme is shown in Fig. 1. Although the two C—O bonds of the carboxylate group are chemically equivalent, they have different lengths [1.2468 (10) and 1.2773 (10) Å] (Table 1). The O atom of the shorter bond is an acceptor of two N—H···O hydrogen bonds and of two weak C—H···O bonds, while the oxygen of the longer C—O bond has stronger intractions, namely three N—H···O hydrogen bonds (Table 2).

When fitting the L-enantiomer of the DL-structure to the resolved glycyl-L-leucine, one finds the positions of the short and long C—O bonds [1.240 (5) and 1.263 (5) Å] exchanged. This is not surprising since the hydrogen-bonding scheme of the DL-structure is very different from that of the resolved structure. In the latter, both O atoms of the carboxylate group are acceptors of two N—H···O bonds, and the O atom of the longer C—O bond forms the stronger hydrogen bonds.

A comparison between the torsion angles of the title compound and the corresponding angles of the L-enantiomer (see Table 3) shows that the conformations are basically the same. The placement of the terminal N1 atom differs the most

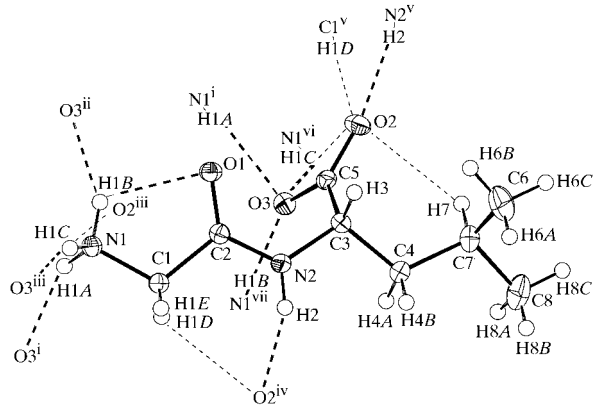



**Figure 1**
The molecular structure and numbering scheme of (I). Displacement ellipsoids are plotted at the 50% probability level [*ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 1990)]. The directions of the intra- and intermolecular hydrogen bonds and short contacts are represented by dashed lines.

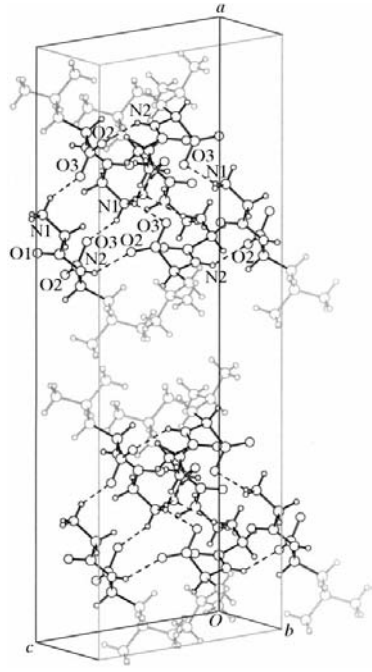



**Figure 2**
Packing of the unit cell of (I) drawn with *SCHAKAL*97 (Keller, 1997). The hydrophilic parts of the cell are drawn in black, while the hydrophobic regions are grey.

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in the two crystals. The differences in the torsion angles are 18.2° for N1—C1—C2—N2 and 17.3° for N1—C1—C2—O1. The torsion angles describing the backbone conformation are only slightly different from each other; the torsion angle C2—N2—C3—C4 is −170.49 (7)° in the DL-form and 172.5° in the L-form. However, as already mentioned in the case of the the L-enantiomer, the angle $\omega$ of the peptide bond ($\omega^1$: C1—C2—N2—C3) shows a slight deviation [167.07 (7)°] from planarity. The calculated molecular isometricity index comparing the L-conformer of the racemic crystal and the L-enantiomer of the resolved crystal is 94.4% (Kálmán *et al.*, 1993).

Hydrophobic and hydrophilic layers alternate in the crystal of glycyl-DL-leucine, as shown in a *SCHAKAL* representation (Fig. 2). The zwitterionic functional groups are at $x = \frac{1}{4}$ and $\frac{3}{4}$, while the aliphatic hydrophobic regions are at $x = \frac{1}{2}$ and 1. These layers are parallel to the *bc* crystallographic plane and their thickness is *a*/4. Within each hydrophilic layer, the molecules are connected by a complex system of hydrogen bonds (Table 2).

The three H atoms of the N1 amino group (Fig. 1) take part in four intermolecular interactions to three neighbouring molecules [N1—H1*A*···O3$^{i}$, N1—H1*B*···O3$^{ii}$, N1—H1*C*···O2$^{iii}$ and N1—H1*C*···O3$^{iii}$; symmetry codes: (i) $\frac{3}{2}-x$, $\frac{3}{2}-y$, $2-z$; (ii) $\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (iii) $x$, $1+y$, $z$]. O2 is an acceptor of hydrogen bonds from two neighbouring molecules [O2···H2—N2$^{v}$, O2···H1*D*—C1$^{v}$ and O2···H1*C*—N1$^{vi}$; symmetry codes: (v) $x$, $1-y$, $-\frac{1}{2}+z$; (vi) $x$, $-1+y$, $z$], while O3 accepts from three different neighbours [O3···H1*A*—N1$^{i}$, O3···H1*C*—N1$^{vi}$ and O3···H1*B*—N1$^{vii}$; symmetry code: (vii) $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$]. The N2 atom in the peptide bond participates in an intermolecular interaction with the carboxyl O2 atom [N2—H2···O2$^{iv}$; symmetry code: $x$, $1-y$, $\frac{1}{2}+z$)]. There are two intramolecular hydrogen bonds stabilizing the molecular conformation; these are O1···H1*B*—N1 and O2···H7—C7.

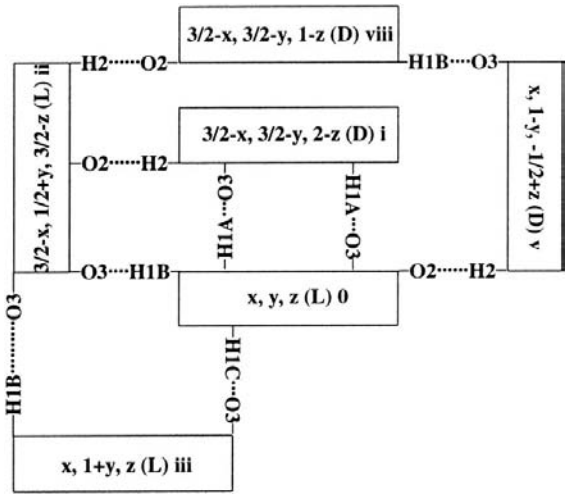


**Figure 3**
Diagram showing the cycles formed by N—H···O-type strong hydrogen bonding. Symmetry operations and chirality are inscribed within the rectangles representing the molecules.

In the crystal lattice, four loops are formed with the participation of hydrogen bonds (Fig. 3). The largest one is a homodromic cycle of four molecules, the hydrogen-bond network graph-set notation (Grell *et al.*, 1999) is $R_4^4(26)$. Two cycles include three molecules, *i.e.* $R_3^2(12)$ and $R_3^3(11)$. One loop consists of two molecules, $R_2^2(16)$, being built up from a D- and an L-form connected through an inversion center (molecules 0 and i in Fig. 3).

## Experimental

Crystals of the title compound were obtained by vapour diffusion of methanol into a saturated aqueous solution of glycyl-DL-leucine.

*Crystal data*

$C_8H_{16}N_2O_3$
$M_r = 188.23$
Monoclinic, *C*2/*c*
$a = 29.038$ (6) Å
$b = 7.233$ (1) Å
$c = 9.629$ (2) Å
$\beta = 95.45$ (3)°
$V = 2013.3$ (7) Å$^3$
$Z = 8$
$D_x = 1.242$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 9661 reflections
$\theta = 1.41$–$30.83$°
$\mu = 0.095$ mm$^{-1}$
$T = 120$ (2) K
Column, colourless
0.82 × 0.32 × 0.30 mm

*Data collection*

Bruker AXS SMART CCD diffractometer
$\omega$ and $\varphi$ scans
Absorption correction: empirical (*SADABS*; Blessing, 1995; Sheldrick, 1996)
$T_{min} = 0.926$, $T_{max} = 0.972$
13963 measured reflections
3108 independent reflections
2782 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 30.83$°
$h = -40 \rightarrow 41$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.115$
$S = 1.073$
3108 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.7749P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å$^{-3}$
$\Delta\rho_{min} = -0.26$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0043 (8)

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

| | | | |
|---|---|---|---|
| O1—C2 | 1.2286 (10) | C1—C2 | 1.5274 (12) |
| O2—C5 | 1.2468 (10) | C3—C4 | 1.5387 (12) |
| O3—C5 | 1.2773 (10) | C3—C5 | 1.5442 (12) |
| N1—C1 | 1.4872 (11) | C4—C7 | 1.5395 (13) |
| N2—C2 | 1.3452 (11) | C6—C7 | 1.5266 (18) |
| N2—C3 | 1.4670 (11) | C7—C8 | 1.5317 (17) |
| | | | |
| N1—C1—C2 | 110.88 (7) | C3—C4—C7 | 116.16 (7) |
| O1—C2—N2 | 124.30 (8) | O2—C5—O3 | 123.52 (8) |
| O1—C2—C1 | 120.91 (7) | O3—C5—C3 | 118.15 (7) |

All H atoms were found in difference Fourier maps. Five types of H atoms were refined [C—H 0.94 (2)–1.05 (2) Å] with a free variable of the displacement parameters.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure:

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O3$^{i}$ | 0.89 (2) | 2.00 (2) | 2.765 (1) | 143.7 (1) |
| N1—H1$B$···O1 | 0.87 (2) | 2.29 (2) | 2.716 (1) | 110.2 (1) |
| N1—H1$B$···O3$^{ii}$ | 0.87 (2) | 2.20 (2) | 3.017 (1) | 155.9 (1) |
| N1—H1$C$···O2$^{iii}$ | 0.86 (1) | 2.58 (1) | 3.218 (1) | 132.1 (1) |
| N1—H1$C$···O3$^{iii}$ | 0.86 (1) | 1.96 (1) | 2.786 (1) | 158.7 (1) |
| N2—H2···O2$^{iv}$ | 0.85 (1) | 1.97 (1) | 2.786 (1) | 162.9 (1) |
| C1—H1$D$···O2$^{iv}$ | 0.97 (1) | 2.60 (1) | 3.258 (1) | 125.4 (1) |
| C7—H7···O2 | 1.00 (1) | 2.54 (1) | 3.217 (1) | 125.5 (1) |

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

**Table 3**
Comparison of torsional angles of the DL- and L-forms.

| | Glycyl-DL-leucine | Glycyl-L-leucine | |
|---|---|---|---|
| N1—C1—C2—N2 | −170.25 (7) | 171.6 | $\psi_1$ |
| N1—C1—C2—O1 | 9.0 (1) | −8.2 | $\psi_2$ |
| C1—C2—N2—C3 | 167.07 (7) | 168.7 | $\omega_1$ |
| C2—N2—C3—C4 | −170.49 (7) | 172.5 | $\varphi_1$ |
| C2—N2—C3—C5 | −51.3 (1) | −64.9 | $\varphi_2$ |
| N2—C3—C5—O3 | −31.8 (1) | −30.2 | $\psi_2'$ |
| N2—C3—C5—O2 | 151.25 (7) | 151.9 | $\psi_2''$ |
| N2—C3—C4—C7 | −176.25 (8) | −175.8 | $\chi_1$ |
| C3—C4—C7—C6 | 68.0 (1) | 62.9 | $\chi_2'$ |
| C3—C4—C7—C8 | −167.2 (1) | −173.0 | $\chi_2''$ |

*SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996), *PLATON* (Spek, 1990) and *SCHAKAL* (Keller, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1407). Services for accessing these data are described at the back of the journal.

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