

The structure was solved using *SIR92* (Altomare *et al.*, 1994) and refined with *SHELXL93* (Sheldrick, 1993). Molecular graphics were obtained using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1229). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triclinic Form of DL-Valine

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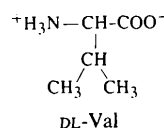
Abstract

The crystal structure of DL-valine, $C_5H_{11}NO_2$, has been refined in the space group $P\bar{1}$ for data collected at 120 K. Estimated standard deviations on bonds between all heavy atoms are less than 0.001 Å. This paper forms

part V in a series on the crystal structures of hydrophobic amino acids.

Comment

The structure of DL-valine (DL-Val) was solved and refined in the monoclinic space group $P2_1/c$ by Mallikarjunan & Thyagaraja Rao (1969). Standard deviations on bond lengths between heavy atoms were in the range 0.006–0.007 Å and the *R* factor was 0.101. As part of our program aimed at providing accurate H-atom positions in crystal structures of hydrophobic amino acids (Dalhus & Görbitz, 1996; Görbitz & Dalhus, 1996a,b,c), we decided to redetermine the structure at liquid-nitrogen temperature, *i.e.* 120 K. Preliminary investigations of cell parameters for the selected crystal, however, indicated a triclinic rather than a monoclinic space group. Cell parameters for a triclinic form have previously been given by Dawson & Mathieson (1951). The crystal structure was solved in the centrosymmetric space group $P\bar{1}$.



The atomic numbering scheme for DL-Val is depicted in Fig. 1. The asymmetric units of both the monoclinic and triclinic forms of DL-Val contain one amino acid zwitterion, compared to two molecules in the asymmetric unit of L-valine (L-Val) (Dalhus & Görbitz, 1996). The L isomer adopts a molecular conformation with $\chi^{1,1} = gauche^+$ in all three structures. In L-Val, the second molecule has $\chi^{1,1} = trans$.

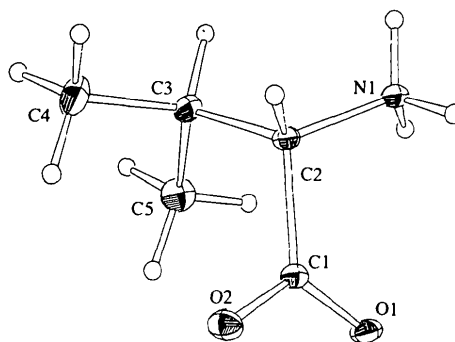


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the L isomer in the DL-Val racemate. Displacement ellipsoids are drawn at the 50% probability level and H atoms are arbitrarily scaled.

It is interesting to note that the carboxylate groups in the two different structures of DL-Val are symmetrical within experimental error. Mean values for the C—O distances are 1.257 and 1.249 Å for the triclinic and monoclinic forms, respectively. In the L-Val crystal,

however, one carboxylate group is clearly asymmetric, with C—O distances of 1.250 (2) and 1.266 (2) Å (Dalhus & Görbitz, 1996).

The crystal is divided into distinct hydrophobic and hydrophilic layers (Fig. 2). In both forms of DL-Val, each amino H atom is engaged in a single hydrogen bond, while in L-Val both amino groups form a three-center hydrogen bond (Dalhus & Görbitz, 1996). The geometric parameters for the hydrogen bonds of DL-Val are listed in Table 3.

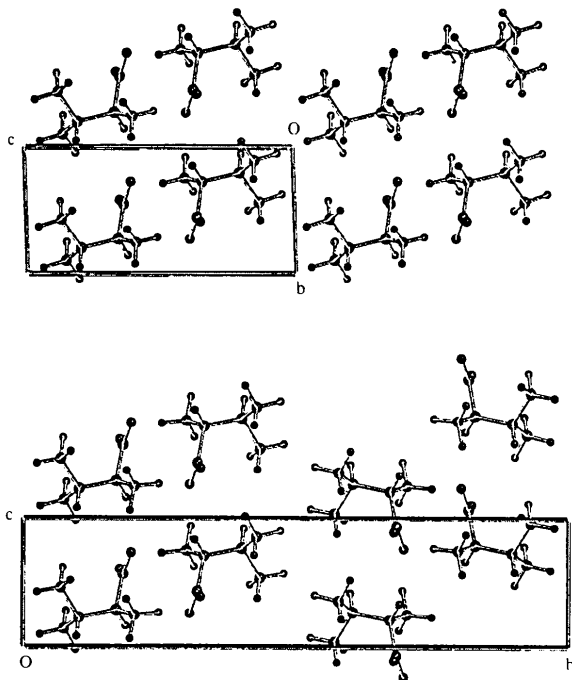


Fig. 2. A molecular-packing diagram of the triclinic (upper) and monoclinic (lower) polymorphs of DL-Val viewed along the *a* axis. Note the different origin definitions in the two unit cells.

The crystal packing of the triclinic and monoclinic forms of DL-Val are illustrated in Fig. 2. The packing arrangement in the monoclinic polymorph can be generated by transforming the 10.838 (2) Å *c* axis in triclinic DL-Val into a twofold screw axis corresponding to the 22.10 (4) Å *b* axis in the monoclinic form.

Experimental

An aqueous solution of the racemate (Sigma) was mixed with tetramethoxysilane in a ratio of 5:1 and left for 2 h to polymerize. Large crystals appeared when methanol diffused into the gel at room temperature.

Crystal data

C₅H₁₁NO₂
M_r = 117.15

Mo *K*α radiation
 $\lambda = 0.71069$ Å

Triclinic
*P*1
a = 5.222 (1) Å
b = 5.406 (1) Å
c = 10.838 (2) Å
 $\alpha = 90.89$ (1)°
 $\beta = 92.34$ (1)°
 $\gamma = 110.02$ (1)°
V = 287.09 (9) Å³
Z = 2
D_x = 1.355 Mg m⁻³

Cell parameters from 25 reflections
 $\theta = 17.5\text{--}21.1^\circ$
 $\mu = 0.104$ mm⁻¹
T = 120 (2) K
 Plate
 0.70 × 0.40 × 0.20 mm
 Colourless

Data collection

Nicolet P3 diffractometer
 2θ scans
 Absorption correction:
 none
 3022 measured reflections
 3022 independent reflections
 2802 observed reflections
 $[I > 2\sigma(I)]$

$\theta_{\max} = 37.50^\circ$
 $h = 0 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -18 \rightarrow 18$
 3 standard reflections
 monitored every 96 reflections
 intensity variation: <1.7%

Refinement

Refinement on *F*²
R(*F*) = 0.0452
 $wR(F^2) = 0.1201$
S = 1.141
 3022 reflections
 93 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 0.04P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.463$ e Å⁻³
 $\Delta\rho_{\min} = -0.628$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

U_{iso} for H atoms: $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$ for others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}/U_{iso}</i>
O1	0.21907 (9)	0.27355 (8)	0.60706 (4)	0.01329 (9)
O2	0.67023 (9)	0.41090 (8)	0.64845 (4)	0.01310 (9)
N1	0.20448 (9)	0.76092 (9)	0.59397 (4)	0.01076 (9)
C1	0.44577 (10)	0.44751 (9)	0.63575 (5)	0.00951 (9)
C2	0.44696 (10)	0.72903 (9)	0.65925 (5)	0.00942 (9)
C3	0.45155 (11)	0.79904 (10)	0.79798 (5)	0.01181 (10)
C4	0.74183 (14)	0.89175 (14)	0.85406 (7)	0.02076 (13)
C5	0.26595 (13)	0.57072 (13)	0.86950 (6)	0.01695 (11)
H1	0.039 (3)	0.657 (3)	0.6259 (12)	0.024 (3)
H2	0.209 (2)	0.926 (3)	0.6001 (11)	0.017 (2)
H3	0.208 (2)	0.720 (2)	0.5142 (11)	0.015 (2)

Table 2. Selected geometric parameters (Å, °)

O1—C1	1.2574 (7)	C2—C3	1.5419 (8)
O2—C1	1.2564 (7)	C3—C4	1.5210 (9)
N1—C2	1.4879 (7)	C3—C5	1.5283 (9)
C1—C2	1.5370 (7)		
O2—C1—O1	125.82 (5)	C1—C2—C3	112.53 (4)
O2—C1—C2	117.24 (5)	C4—C3—C5	110.87 (5)
O1—C1—C2	116.94 (4)	C4—C3—C2	110.74 (5)
N1—C2—C1	109.49 (4)	C5—C3—C2	112.29 (5)
N1—C2—C3	110.08 (4)		
O1—C1—C2—N1	-23.48 (6)	N1—C2—C3—C5	81.84 (5)
N1—C2—C3—C4	-153.63 (5)		

Table 3. *Hydrogen-bonds parameters* (\AA , $^\circ$)

$D-H \cdots A$	$H \cdots A^a$	$D-H^a$	$D-H \cdots A^a$	$H \cdots A^b$
$N1-H1 \cdots O2'$	1.96 (1)	0.94 (1)	165 (1)	1.869
$N1-H2 \cdots O1''$	1.86 (1)	0.88 (1)	178 (1)	1.718
$N1-H3 \cdots O2'''$	2.09 (1)	0.89 (1)	160 (1)	1.963

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

Notes: (a) experimental H-atom positions; (b) N—H bonds normalized to 1.030 \AA (Taylor & Kennard, 1983).

All heavy atoms were refined anisotropically. Amino H atoms were refined isotropically. 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 common isotropic parameter was refined for the methyl H atoms. U_{iso} values for the tertiary H atoms were fixed at $1.2U_{eq}$ those of their bonded C atoms.

Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1226). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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DL-Norleucine, β Form at 120 K

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Abstract

This paper forms part VI in a series of crystal structures of hydrophobic amino acids. The crystal structure of a low-temperature form (120 K) of DL-norleucine (2-amino-hexanoic acid, $C_6H_{13}NO_2$) has been solved and refined in the space group $C2/c$. The molecular packing and cell parameters correlate very well with those proposed for the β form of DL-norleucine as deduced by Mathieson [*Acta Cryst.* (1953), **6**, 399–403]. Estimated standard deviations for the bonds between heavy atoms are 0.001–0.002 \AA .

Comment

The amino acid norleucine (2-amino-hexanoic acid) can be derived from methionine by replacing the S atom with a $-CH_2-$ group. Thus, it is not surprising that the crystal structures of these two compounds display some common properties.

The crystal and molecular structure of DL-methionine (DL-Met) was first presented by Mathieson (1952). From several different crystallization batches he obtained two different monoclinic polymorphs, denoted α -DL-Met and β -DL-Met, with space groups $P2_1/a$ and $I2/a$, respectively. The cell dimensions of β -DL-Met are almost the same as for the α form, except for a doubling of the c axis and a small increase in the β angle (Table 3). The molecular packing arrangement in either structure consists of the stacking of double-layer units along the c axis. The precision of these structures is low by current standards, $R = 0.21$ (α) and 0.23 (β), with e.s.d.'s in bond lengths of approximately 0.04 \AA . This led Taniguchi, Takaki & Sakurai (1980) to carry out a re-examination of both polymorphs. Their DL-Met crystals, grown by slow evaporation from an aqueous solution at room temperature, were all of the β form and various degrees of streaking along c^* were observed, possibly due to disorder in the stacking of the double layers. However, they also found that crystals of the α form could be obtained by heating β -form crystals, suggesting that the β form is a low-temperature form. The crystal of the α form was kept at 333 K during the collection of the X-ray data.