H1*B*	0.355 (2)	0.861 (4)	0.6170 (12)	0.017 (4)
H2*B*	0.505 (3)	0.774 (6)	0.6082 (18)	0.051 (7)
H3*B*	0.407 (2)	0.711 (4)	0.5455 (13)	0.021 (4)

Table 2. *Selected geometric parameters (Å, °)*

O1*A*—C1*A*	1.258 (1)	O1*B*—C1*B*	1.263 (1)
O2*A*—C1*A*	1.255 (1)	O2*B*—C1*B*	1.252 (1)
N1*A*—C2*A*	1.494 (1)	N1*B*—C2*B*	1.491 (2)
N1*A*—H1*A*	0.88 (2)	N1*B*—H1*B*	0.94 (2)
N1*A*—H2*A*	0.82 (2)	N1*B*—H2*B*	0.86 (3)
N1*A*—H3*A*	0.85 (2)	N1*B*—H3*B*	0.80 (2)
C1*A*—C2*A*	1.530 (2)	C1*B*—C2*B*	1.534 (2)
C2*A*—C3*A*	1.535 (1)	C2*B*—C3*B*	1.533 (2)
C3*A*—C4*A*	1.529 (2)	C3*B*—C4*B*	1.531 (2)
C4*A*—C5*A*	1.525 (2)	C4*B*—C6*B*	1.520 (2)
C4*A*—C6*A*	1.530 (2)	C4*B*—C5*B*	1.524 (3)
O2*A*—C1*A*—O1*A*	124.66 (11)	O2*B*—C1*B*—O1*B*	125.45 (11)
O2*A*—C1*A*—C2*A*	118.03 (10)	O2*B*—C1*B*—C2*B*	117.75 (10)
O1*A*—C1*A*—C2*A*	117.27 (9)	O1*B*—C1*B*—C2*B*	116.75 (10)
N1*A*—C2*A*—C1*A*	109.16 (8)	N1*B*—C2*B*—C3*B*	107.77 (10)
N1*A*—C2*A*—C3*A*	107.48 (9)	N1*B*—C2*B*—C1*B*	109.62 (8)
C1*A*—C2*A*—C3*A*	111.96 (9)	C3*B*—C2*B*—C1*B*	111.14 (10)
C4*A*—C3*A*—C2*A*	116.13 (9)	C4*B*—C3*B*—C2*B*	115.07 (11)
C5*A*—C4*A*—C3*A*	111.31 (12)	C6*B*—C4*B*—C5*B*	110.30 (12)
C5*A*—C4*A*—C6*A*	109.56 (11)	C6*B*—C4*B*—C3*B*	109.76 (17)
C3*A*—C4*A*—C6*A*	109.19 (12)	C5*B*—C4*B*—C3*B*	110.87 (13)

O1*A*—C1*A*—C2*A*—N1*A*	−26.75 (13)
N1*A*—C2*A*—C3*A*—C4*A*	−176.81 (10)
C2*A*—C3*A*—C4*A*—C5*A*	64.63 (13)
C2*A*—C3*A*—C4*A*—C6*A*	−174.29 (12)
O1*B*—C1*B*—C2*B*—N1*B*	−32.28 (13)
N1*B*—C2*B*—C3*B*—C4*B*	−170.01 (11)
C2*B*—C3*B*—C4*B*—C5*B*	71.00 (15)
C2*B*—C3*B*—C4*B*—C6*B*	−166.89 (14)

Table 3. *Hydrogen-bond parameters (Å, °)*

D—H···*A*	H···*A*[a]	H···*A*[b]	H···*A*[c]	*D*···*A*	D—H···*A*[a]
N1*A*—H1*A*···O2*A*^{i}	2.01 (2)	1.869	1.932	2.896 (1)	174 (2)
N1*A*—H2*A*···O1*B*^{ii}	1.93 (2)	1.715	1.770	2.744 (1)	176 (2)
N1*A*—H3*A*···O1*B*	2.03 (2)	1.880	1.801	2.808 (1)	151 (2)
N1*B*—H1*B*···O2*B*^{i}	1.94 (2)	1.855	1.815	2.856 (2)	164 (2)
N1*B*—H2*B*···O2*A*^{iii}	2.14 (3)	1.980	2.075	2.983 (2)	165 (3)
N1*B*—H2*B*···O1*A*^{iii}	2.32 (3)	2.201	2.139	2.993 (1)	135 (2)
N1*B*—H3*B*···O1*A*	1.96 (2)	1.724	1.739	2.747 (1)	174 (2)
C2*B*—H4*B*···O1*A*^{iv}	2.39 (2)	2.182		3.255 (2)	166[d]

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

Notes: (*a*) experimental H-atom positions; (*b*) normalized (Taylor & Kennard, 1983) hydrogen bonds with N—H = 1.030 Å and C—H = 1.100 Å; (*c*) Coll *et al.* (1986) (with normalized N—H = 1.030 Å, published with N—H = 1.080 Å); (*d*) e.s.d. meaningless due to constrained refinement of H atom.

The structure was solved using *SIR*92 (Altomare *et al.*, 1994) and refined with *SHELXL*93 (Sheldrick, 1993). Amino H atoms were refined isotropically, while other H atoms were kept in idealized positions. Only the C—H distances were free to refine, with identical shifts for all H atoms connected to the same C atom. The U_{iso} values were fixed at $1.2U_{eq}$ of the bonded atom, except that a free variable for U_{iso} was refined for each of the four methyl groups.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: PA1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Cysteine, Monoclinic Form, Redetermination at 120 K

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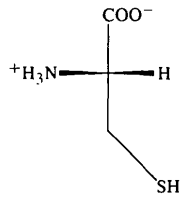
Abstract

This redetermination of the structure of L-cysteine, $C_3H_7NO_2S$, forms part IV in a series of crystal structures of hydrophobic amino acids. The thiol groups of the two molecules in the asymmetric unit are involved in S—H···O and S—H···S interactions. The associated C—S bond lengths are significantly different. The absolute structure could be determined from the X-ray data.

Comment

L-Cysteine crystallizes in two polymorphs: a monoclinic form (Harding & Long, 1968) and an orthorhombic form [Kerr & Ashmore, 1973; Kerr, Ashmore & Koetzle, 1975 (neutron diffraction study)]. Even though side-chain thiol groups may form weak hydrogen bonds, the basic crystal packing and hydrogen-bond pattern of the monoclinic form are shared by a number of hydrophobic amino acids. We intend to use this group of compounds for detailed studies of hydrogen-bonding interactions, and thus require high-precision structure determinations. As part of this programme, the X-ray crystal structures of L-Val and L-Met (Dalhus & Görbitz, 1996), L-Ile (Görbitz & Dalhus, 1996*a*) and L-Leu (Görbitz & Dalhus, 1996*b*) have been redetermined

at low temperature. The current paper describes a similar investigation for monoclinic L-Cys.



L-Cys

The original crystal structure (Harding & Long, 1968) was refined to $R = 0.127$ with estimated standard deviations for bond lengths between heavy atoms in the range 0.012–0.014 Å. The e.s.d.'s have now been reduced to about 0.0015 Å with $R = 0.031$. The new diffraction data permitted determination of the absolute structure by calculating the Flack parameter, $x = -0.01\,(5)$ (Flack, 1983), thus confirming the presence of the L enantiomer.

The asymmetric unit of monoclinic L-Cys, with two crystallographically independent molecules L-Cys(*A*) and L-Cys(*B*), is shown in Fig. 1. Harding & Long (1968) noted a particularly large difference between the C—S bond lengths in the structure, from 1.86 (1) Å for L-Cys(*A*) to 1.77 (1) Å for L-Cys(*B*). In our study, the difference is much smaller, from 1.8189 (14) Å for L-Cys(*A*) to 1.8070 (14) Å for L-Cys(*B*), but may be significant. The thermal motion of S1*B* is larger than for S1*A*, but hardly enough to cause a librational shortening of this magnitude. The two molecules differ in their side-chain orientation at the C^{α}—C^{β} bond, with N1—C2—C3—S1 (χ^1) being *gauche*$^+$ for L-Cys(*A*) and *trans* for L-Cys(*B*). As shown by Görbitz (1990), L-Cys displays a significant preference for the *gauche*$^+$ conformation in the crystal structures of small molecules. A search of the Cambridge Structural Database (October 1995 release, Allen *et al.*, 1991) revealed that L-Cys(*B*) provides the only example of a *trans* conformation, with a total of ten other occurrences all *gauche*$^+$ [including L-Cys(*A*)]. The database entry for *N*-γ-L-glutamyl-L-cysteine ethyl ester (Takimoto-Kamimura, Koyano, Kithara & Fujii, 1990) actually describes the D-enantiomer and thus gives a *gauche*$^-$ orientation for χ^1, which has then been inverted.

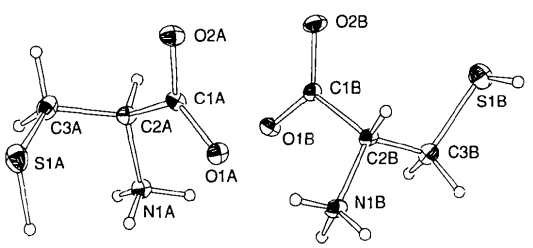


Fig. 1. The asymmetric unit with atomic numbering (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as spheres of arbitrary size.

The unit cell and crystal packing are shown in Fig. 2. The main chains generate a double-sheet structure with N—H···O hydrogen bonds (Table 3) similar to those observed for hydrophobic amino acids. The side chains, on the other hand, form pseudo-hydrophobic layers which include additional hydrogen bonds involving the thiol groups (Fig. 3). In the orthorhombic form of L-Cys (Kerr, Ashmore & Koetzle, 1975), the thiol H atom is disordered over two sites, forming alternate interactions with either a carboxylate O atom or the S atom of another thiol group. Two refinement models, with an ordered or disordered S atom, yield hydrogen-bond lengths d(H···O) = 2.40 (2)/d(H···S) = 2.75 (2) Å and d(H···O) = 2.40 (2)/d(H···S) = 2.63 (2) Å, respectively. In the monoclinic form there is a reasonably strong S1*A*—H···O2*A*^{i} [(i) = x, $y-1$, z] hydrogen bond with d(H···O) = 2.183 Å (normalized length, Table 3). This value compares favourably with S—H···O hydrogen bonds in glutathione (Görbitz, 1987), *N*-γ-L-glutamyl-L-cysteine ethyl ester (Takimoto-Kamimura, Koyano, Kithara & Fujii, 1990) and *N*-acetyl-L-cysteine (neutron diffraction study at 16 K; Takusagawa, Koetzle, Kou & Parthasarathy, 1981) (Table 3). S1*A* also acts as acceptor in a weak S1*B*—H···S1*A* interaction with d(H···S) = 2.801 Å. This is the first direct observation of such a hydrogen bond in crystal structures with fully ordered L-cysteine residues. d(S···S) for S1*B*—

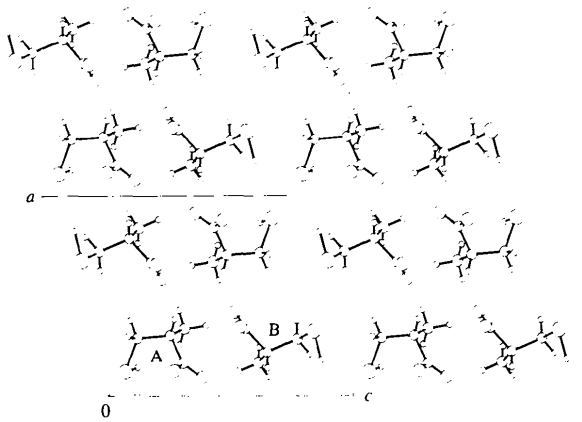


Fig. 2. The unit cell and crystal packing viewed along the *b* axis.

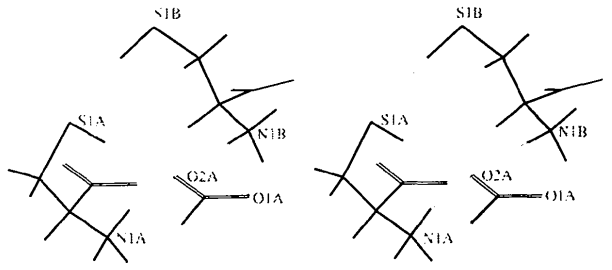


Fig. 3. Stereodiagram illustrating hydrogen bonds for the thiol group. Only the carboxylate group is shown for the third amino acid involved.

H···S1*A* is 4.080 (1) Å, which is not the shortest intermolecular S···S distance in the crystal. L-Cys(*A*) molecules related by the twofold screw axis have *d*(S1*A*···S1*A*) = 3.589 (1) Å and a second S1*B*···S1*A* distance of 3.839 (1) Å is also found. As is evident from Fig. 2, however, neither contact is a hydrogen bond.

Experimental

The crystals were grown by slow cooling of a warm saturated aqueous solution.

Crystal data

$C_3H_7NO_2S$
M_r = 121.16
Monoclinic
$P2_1$
a = 9.441 (2) Å
b = 5.222 (1) Å
c = 11.337 (4) Å
β = 109.00 (2)°
V = 528.5 (2) Å^3
Z = 4
D_x = 1.523 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.0–20.0°
μ = 0.496 mm^{-1}
T = 120 (2) K
Block
0.95 × 0.50 × 0.35 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.954, T_{max} = 0.983
3094 measured reflections
3000 independent reflections
2896 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0249
θ_{max} = 37.5°
$h = -16 \rightarrow 15$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 19$
3 standard reflections monitored every 96 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0311
$wR(F^2)$ = 0.0836
S = 1.066
3000 reflections
161 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.0609P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.061
$\Delta\rho_{max}$ = 0.365 e Å^{-3}
$\Delta\rho_{min}$ = −0.717 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)
Absolute configuration: Flack (1983) parameter = −0.01 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1*A*	0.11263 (4)	0.82302 (8)	0.09326 (3)	0.02145 (7)
O1*A*	0.08519 (9)	0.9939 (2)	0.39891 (8)	0.01471 (14)
O2*A*	0.12029 (10)	1.3406 (2)	0.29716 (9)	0.01687 (15)
N1*A*	0.33018 (10)	0.7544 (2)	0.39478 (9)	0.01266 (14)
C1*A*	0.15624 (10)	1.1219 (2)	0.34317 (10)	0.01158 (15)
C2*A*	0.29769 (11)	1.0033 (2)	0.32817 (10)	0.01188 (15)
C3*A*	0.28458 (13)	0.9734 (3)	0.19096 (11)	0.0174 (2)
S1*B*	0.32276 (5)	1.41241 (8)	0.92329 (4)	0.02765 (9)
O1*B*	0.41579 (10)	1.0490 (2)	0.62518 (9)	0.01519 (14)
O2*B*	0.34280 (11)	1.4559 (2)	0.62690 (10)	0.0181 (2)
N1*B*	0.15813 (11)	0.8770 (2)	0.64868 (10)	0.0142 (2)
C1*B*	0.33335 (11)	1.2229 (2)	0.64556 (10)	0.01153 (15)
C2*B*	0.21423 (11)	1.1327 (2)	0.70159 (10)	0.01188 (15)
C3*B*	0.27882 (14)	1.1084 (3)	0.84356 (11)	0.0171 (2)

Table 2. *Selected geometric parameters (Å, °)*

S1*A*—C3*A*	1.8189 (14)	S1*B*—C3*B*	1.8070 (14)
S1*A*—H7*A*	1.34 (4)	S1*B*—H7*B*	1.35 (3)
O1*A*—C1*A*	1.2539 (14)	O1*B*—C1*B*	1.2650 (14)
O2*A*—C1*A*	1.2551 (15)	O2*B*—C1*B*	1.2435 (15)
N1*A*—C2*A*	1.4839 (15)	N1*B*—C2*B*	1.489 (2)
C1*A*—C2*A*	1.5312 (14)	C1*B*—C2*B*	1.5345 (14)
C2*A*—C3*A*	1.528 (2)	C2*B*—C3*B*	1.530 (2)
C3*A*—S1*A*—H7*A*	98.1 (14)	C3*B*—S1*B*—H7*B*	90.6 (20)
O1*A*—C1*A*—O2*A*	125.30 (10)	O2*B*—C1*B*—O1*B*	126.06 (10)
O1*A*—C1*A*—C2*A*	117.98 (10)	O2*B*—C1*B*—C2*B*	118.26 (10)
O2*A*—C1*A*—C2*A*	116.72 (10)	O1*B*—C1*B*—C2*B*	115.66 (10)
N1*A*—C2*A*—C3*A*	111.32 (9)	N1*B*—C2*B*—C3*B*	108.49 (9)
N1*A*—C2*A*—C1*A*	109.94 (8)	N1*B*—C2*B*—C1*B*	108.72 (9)
C3*A*—C2*A*—C1*A*	111.71 (9)	C3*B*—C2*B*—C1*B*	111.48 (9)
C2*A*—C3*A*—S1*A*	115.12 (8)	C2*B*—C3*B*—S1*B*	113.66 (9)
O1*A*—C1*A*—C2*A*—N1*A*	−4.47 (14)		
N1*A*—C2*A*—C3*A*—S1*A*	74.39 (10)		
C2*A*—C3*A*—S1*A*—H7*A*	−64.6 (14)		
O1*B*—C1*B*—C2*B*—N1*B*	−35.30 (13)		
N1*B*—C2*B*—C3*B*—S1*B*	−170.15 (7)		
C2*B*—C3*B*—S1*B*—H7*B*	80.8 (16)		

Table 3. *Hydrogen-bond parameters (Å, °) and comparison with other* L-*Cys structures*

D—H···*A*	*D*—H	H···*A*[a]	H···*A*[b]	*D*···*A*	*D*—H···*A*[a]
N1*A*—H1*A*···O2*A*^{i}	0.93 (3)	2.00 (3)	1.899	2.897 (2)	163 (2)
N1*A*—H2*A*···O1*B*^{ii}	0.95 (3)	1.77 (3)	1.685	2.703 (1)	169 (2)
N1*A*—H3*A*···O1*B*	0.99 (3)	2.12 (3)	2.089	2.910 (2)	136 (3)
N1*A*—H3*A*···O2*B*^{i}	0.99 (3)	2.28 (3)	2.251	3.027 (2)	132 (3)
N1*B*—H1*B*···O2*B*^{i}	0.97 (3)	2.00 (3)	1.943	2.866 (2)	149 (2)
N1*B*—H2*B*···O2*A*^{iii}	0.84 (3)	2.09 (3)	1.914	2.894 (1)	160 (3)
N1*B*—H2*B*···O1*A*^{iii}	0.84 (3)	2.35 (3)	2.225	2.960 (1)	131 (3)
N1*B*—H3*B*···O1*A*	0.98 (3)	1.82 (3)	1.767	2.756 (2)	160 (4)
C2*B*—H4*B*···O1*A*^{iv}	0.94[c]	2.35	2.210	3.279 (1)	170
S1*A*—H7*A*···O2*A*^{i}	1.34 (4)	2.18 (3)	2.183	3.404 (1)	149 (2)
S1*B*—H7*B*···S1*A*^{iv}	1.35 (3)	2.79 (3)	2.801	4.080 (1)	159 (3)
S—H···O[d]	1.338 (2)	2.216 (2)	2.216	3.404 (2)	149.2 (2)
S—H···O[e]	1.21 (5)	2.33 (5)	2.217	3.499 (5)	161 (4)
S—H···O[f]	1.26	2.20 (6)	2.153	3.479 (5)	171

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

Notes: (*a*) experimental H-atom positions; (*b*) normalized (Taylor & Kennard, 1983) hydrogen bonds with N—H = 1.030, C—H = 1.100 Å (Allen *et al.*, 1987) and S—H = 1.338 Å (Takusagawa, Koetzle, Kou & Parthasarathy, 1981); (*c*) e.s.d. meaningless due to constrained refinement of H atom; (*d*) *N*-acetyl-L-cysteine (Takusagawa, Koetzle, Kou & Parthasarathy, 1981); (*e*) glutathione (Görbitz, 1987); (*f*) *N*-γ-L-glutamyl-L-cysteine ethyl ester (Takimoto-Kamimura, Koyano, Kithara & Fujii, 1990).

Amino-group H atoms were refined isotropically. Only positional parameters were refined for the thiol H atoms, with fixed $U_{iso} = 2.0U_{eq}$ of the bonded atom. Other H atoms were kept in idealized positions, but with the C—H distance free to refine. All H atoms connected to the same C atom were given the same shifts. The U_{iso} values were fixed at $1.2U_{eq}$ of the bonded atom.

The structure was solved using *SIR*92 (Altomare *et al.*, 1994) and refined with *SHELXL*93 (Sheldrick, 1993). Molecular graphics were obtained using *ORTEP*II (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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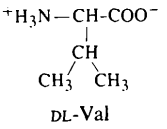
Abstract

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, 1996*a*,*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 $P\bar{1}$.



DL-Val

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*.

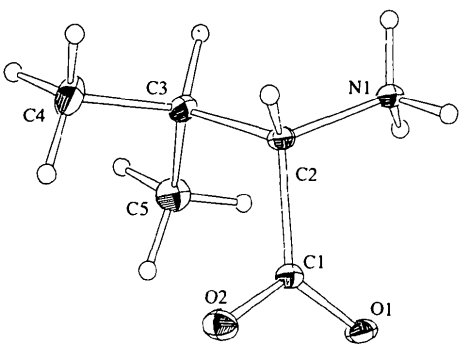


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the L isomer in the DL-Val racemate. Displacement ellipsoids are drawn at the 50% probability level and H atoms are arbitrarily scaled.

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,

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