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Redetermination of L-Leucine at 120 K

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Abstract

This redetermination of L-leucine, C$_6$H$_{13}$NO$_2$, forms part III in a series of crystal structure determinations of hydrophobic amino acids. The L-leucine crystals were grown from a dilute acetic acid solution. E.s.d.'s for bond lengths between heavy atoms are in the range 0.001–0.002 Å.

Comment

As part of a program aimed at providing high precision X-ray structures of hydrophobic amino acids for multivariate analysis of hydrogen-bond parameters, we have presented previously results for L-valine (L-Val) and L-methionine (L-Met) (Dalhus & Görbitz, 1996), and L-isoleucine (L-Ile) (Görbitz & Dalhus, 1996). The crystal structure of L-leucine (L-Leu) was first determined by Harding & Howieson (1976) with an *R* factor of 0.13 and standard deviations for bond lengths between heavy atoms in the range 0.03–0.05 Å. A redetermi-

nation was carried out by Coll, Solans, Font-Alba & Subirana (1986) with a significantly lower *R* factor of 0.058. This redetermination, however, was based on a rather limited number of observed reflections (686) and bond-length standard deviations were high by current standards, ranging from 0.01 to 0.02 Å. More important for our purpose is the fact that some of the hydrogen bonds in the structure were distributional outliers in our preliminary statistical investigations of hydrogen-bond geometries, suggesting that the published H-atom positions, obtained from refinements with fixed N—H distances of 1.080 Å, are not very accurate. The current low-temperature study yields a further improvement in the *R* factor, with a value of 0.044, and is based on 3546 reflections [3195 observed for *I* > 2σ(*I*)]. E.s.d.'s for the bond lengths are in the range 0.001–0.002 Å. The unit-cell volume is 734.0 (3) Å^3, a 1.9% reduction from the room temperature value of 748 (1) Å^3.
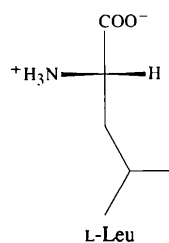
L-Leu

The asymmetric unit of L-Leu, with two crystallographically independent molecules L-Leu(*A*) and L-Leu(*B*), is shown in Fig. 1. There are no unusual bond distances or angles and only small differences between the two molecules. The common hydrophobic amino acids crystallize in monoclinic space groups with two molecules in the asymmetric unit. L-Leu is unique within this group in that both molecules have essentially the same side-chain conformation, with N1—C2—C3—C4 (χ^1) *trans* and C2—C3—C4—C5/C2—C3—C4—C6 ($\chi^{2,1}, \chi^{2,2}$) *gauche$^+$/trans*. In the most closely related structure, that of L-Met (Dalhus & Görbitz, 1996), both molecules have *trans* orientations for χ^1, while χ^2 is *trans* for L-Met(*A*) and *gauche$^+$* for L-Met(*B*).
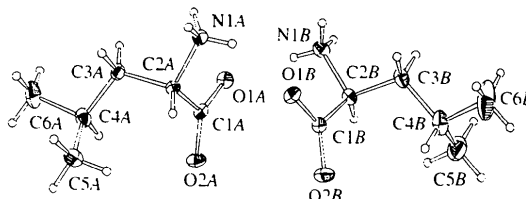

Fig. 1. The asymmetric unit of L-Leu with atomic numbering (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

The crystal packing, with characteristic hydrophilic and hydrophobic layers, is depicted in Fig. 2. The structure and hydrogen-bond pattern are very similar to those

observed for both L-Met and L-Val (Dalhus & Görbitz, 1996), and L-Ile (Görbitz & Dalhus, 1996); hydrogen-bond parameters are given in Table 3. Deviations from previous hydrogen-bond distances (Coll, Solans, Font-Alba & Subirana, 1986), adjusted for unequal N—H bond lengths, are substantial. The main reasons for these differences are large changes in the C—N—H bond angles involving H1A, H3A, H2B and H3B, and a 10–15° rotation of the L-Leu(A) amino group. In the present low-temperature structure, all C—N—H angles are in the range 108.5 (13) to 110.6 (16)°, while the previous range was 101.5–119.4°.
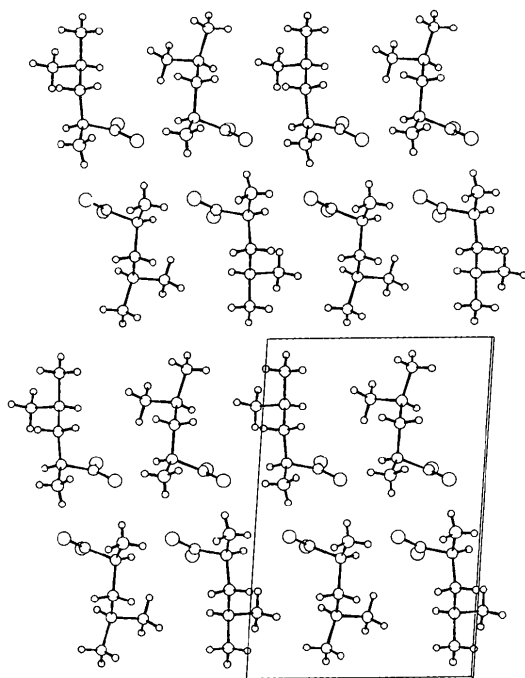

Fig. 2. The unit cell and crystal packing viewed along the b axis.

Experimental

L-Leu is notorious for its low quality crystals, invariably obtained as extremely thin easily bent flakes (Harding & Howieson, 1976). During cocrystallization experiments between amino acids and various carboxylic acids, we accidentally discovered that the presence of acetic acid or propionic acid in the aqueous solution had a positive effect on the thickness of the L-Leu crystals grown by slow evaporation, without inclusion of the carboxylic acid. We thus carried out vapour diffusion experiments, employing diffusion of 2-propanol, acetonitrile or acetone into an acetic acid solution of the amino acid. The crystals obtained by this method were nicely shaped, but small and often twinned. The crystal used for data collection was grown by slow evaporation of a dilute ($\sim$ 0.1 M) acetic acid solution of the amino acid and selected after testing a number of other specimens.

Crystal data

$C_6H_{13}NO_2$
$M_r = 131.17$
Monoclinic
$P2_1$
$a = 9.562 (2)$ Å
$b = 5.301 (1)$ Å
$c = 14.519 (3)$ Å
$\beta = 94.20 (2)°$
$V = 734.0 (3)$ Å^3
$Z = 4$
$D_x = 1.187$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.0–20.0°$
$\mu = 0.088$ mm^{-1}
$T = 120 (2)$ K
Plate
$1.20 \times 0.80 \times 0.07$ mm
Colourless

Data collection

Nicolet $P3$ diffractometer
2θ scans
Absorption correction: none
7081 measured reflections
3546 independent reflections
3195 observed reflections
$[I > 2\sigma(I)]$
$R_{int} = 0.1104$

$\theta_{max} = 35.0°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = -23 \rightarrow 23$
3 standard reflections monitored every 96 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0435$
$wR(F^2) = 0.1044$
$S = 1.086$
3545 reflections
205 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 0.0183P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max} = 0.482$ e Å^{-3}
$\Delta\rho_{min} = -0.214$ 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 isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
O1A	0.36406 (9)	0.6329 (2)	0.41484 (6)	0.0173 (2)
O2A	0.27276 (11)	0.2690 (2)	0.36298 (7)	0.0210 (2)
N1A	0.11318 (10)	0.8489 (2)	0.42780 (6)	0.0143 (2)
C1A	0.26337 (12)	0.4983 (2)	0.38317 (7)	0.0141 (2)
C2A	0.12083 (11)	0.6272 (2)	0.36489 (7)	0.0132 (2)
C3A	0.09863 (13)	0.7250 (2)	0.26535 (7)	0.0173 (2)
C4A	0.09460 (14)	0.5252 (3)	0.18929 (8)	0.0219 (2)
C5A	−0.0311 (2)	0.3500 (3)	0.19462 (11)	0.0297 (3)
C6A	0.0869 (2)	0.6560 (4)	0.09509 (9)	0.0359 (4)
O1B	0.15366 (9)	0.5422 (2)	0.58519 (6)	0.0173 (2)
O2B	0.23254 (11)	0.1529 (2)	0.61759 (7)	0.0232 (2)
N1B	0.41686 (11)	0.7347 (2)	0.59968 (7)	0.0182 (2)
C1B	0.24727 (12)	0.3874 (2)	0.61392 (7)	0.0145 (2)
C2B	0.38848 (12)	0.4986 (2)	0.65091 (7)	0.0155 (2)
C3B	0.38734 (14)	0.5656 (3)	0.75359 (8)	0.0224 (2)
C4B	0.3846 (2)	0.3395 (3)	0.81905 (9)	0.0284 (3)
C5B	0.5249 (2)	0.2016 (4)	0.82503 (11)	0.0378 (4)
C6B	0.3497 (2)	0.4279 (7)	0.91429 (11)	0.0573 (7)
H1A	0.167 (2)	0.970 (4)	0.4078 (12)	0.018 (4)
H2A	0.033 (2)	0.901 (4)	0.4250 (13)	0.018 (4)
H3A	0.138 (2)	0.805 (4)	0.4829 (14)	0.024 (5)

H1B	0.355 (2)	0.861 (4)	0.6170 (12)	0.017 (4)
H2B	0.505 (3)	0.774 (6)	0.6082 (18)	0.051 (7)
H3B	0.407 (2)	0.711 (4)	0.5455 (13)	0.021 (4)

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

O1A—C1A	1.258 (1)	O1B—C1B	1.263 (1)
O2A—C1A	1.255 (1)	O2B—C1B	1.252 (1)
N1A—C2A	1.494 (1)	N1B—C2B	1.491 (2)
N1A—H1A	0.88 (2)	N1B—H1B	0.94 (2)
N1A—H2A	0.82 (2)	N1B—H2B	0.86 (3)
N1A—H3A	0.85 (2)	N1B—H3B	0.80 (2)
C1A—C2A	1.530 (2)	C1B—C2B	1.534 (2)
C2A—C3A	1.535 (1)	C2B—C3B	1.533 (2)
C3A—C4A	1.529 (2)	C3B—C4B	1.531 (2)
C4A—C5A	1.525 (2)	C4B—C6B	1.520 (2)
C4A—C6A	1.530 (2)	C4B—C5B	1.524 (3)
O2A—C1A—O1A	124.66 (11)	O2B—C1B—O1B	125.45 (11)
O2A—C1A—C2A	118.03 (10)	O2B—C1B—C2B	117.75 (10)
O1A—C1A—C2A	117.27 (9)	O1B—C1B—C2B	116.75 (10)
N1A—C2A—C1A	109.16 (8)	N1B—C2B—C3B	107.77 (10)
N1A—C2A—C3A	107.48 (9)	N1B—C2B—C1B	109.62 (8)
C1A—C2A—C3A	111.96 (9)	C3B—C2B—C1B	111.14 (10)
C4A—C3A—C2A	116.13 (9)	C4B—C3B—C2B	115.07 (11)
C5A—C4A—C3A	111.31 (12)	C6B—C4B—C5B	110.30 (12)
C5A—C4A—C6A	109.56 (11)	C6B—C4B—C3B	109.76 (17)
C3A—C4A—C6A	109.19 (12)	C5B—C4B—C3B	110.87 (13)

O1A—C1A—C2A—N1A	−26.75 (13)
N1A—C2A—C3A—C4A	−176.81 (10)
C2A—C3A—C4A—C5A	64.63 (13)
C2A—C3A—C4A—C6A	−174.29 (12)
O1B—C1B—C2B—N1B	−32.28 (13)
N1B—C2B—C3B—C4B	−170.01 (11)
C2B—C3B—C4B—C5B	71.00 (15)
C2B—C3B—C4B—C6B	−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
N1A—H1A···O2A[i]	2.01 (2)	1.869	1.932	2.896 (1)	174 (2)
N1A—H2A···O1B[ii]	1.93 (2)	1.715	1.770	2.744 (1)	176 (2)
N1A—H3A···O1B	2.03 (2)	1.880	1.801	2.808 (1)	151 (2)
N1B—H1B···O2B[i]	1.94 (2)	1.855	1.815	2.856 (2)	164 (2)
N1B—H2B···O2A[iii]	2.14 (3)	1.980	2.075	2.983 (2)	165 (3)
N1B—H2B···O1A[iii]	2.32 (3)	2.201	2.139	2.993 (1)	135 (2)
N1B—H3B···O1A	1.96 (2)	1.724	1.739	2.747 (1)	174 (2)
C2B—H4B···O1A[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, 1996a) and L-Leu (Görbitz & Dalhus, 1996b) have been redetermined