Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A high-pressure polymorph of L-α-leucine

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Received 20 March 2007
Accepted 16 April 2007

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.009 Å
R factor = 0.033
wR factor = 0.104
Data-to-parameter ratio = 10.0

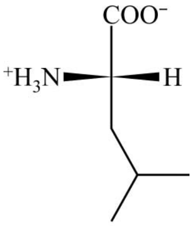
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A new high-pressure phase of the title amino acid (systematic name: 2-ammonio-4-methylpentanoate), $C_6H_{13}NO_2$, is reported, with one molecule per asymmetric unit, in contrast to the atmospheric pressure phase, (I), reported by Harding & Howieson [*Acta Cryst.* (1976). B**32**, 633–634], which has two molecules in the asymmetric unit. The packing consists of a double layer structure, similar to those of (I) and other amino acids with non-polar side chains.

Comment

L-α-Leucine, one of the most common amino acids, has been reported in two different crystal forms, both of them at atmospheric pressure: a room-temperatura one, hereafter (I) (Harding & Howieson, 1976, Coll *et al.*, 1986, Görbitz & Dalhus, 1996) and a higher-temperature one, (II), derived from the former through a phase transition at 353.2 K (Bougeard, 1983).

On measuring the high-pressure solubility of L-α-leucine in water at room temperature (298.2 K), we found a breaking point in the solubility–pressure curve around 200 MPa. (Matsuo *et al.*, 2002) Prismatic crystals 3–4 mm in size were observed as a residue of the process. Such large crystals, which proved to be stable for at least three years at ambient conditions because of hysteresis, could not be obtained by annealing the stable monoclinic form (I) at atmospheric pressure. In addition, its infrared spectrum differed from those of (I) and (II), therefore confirming it as a new phase, [hereafter (III)], the crystal structure of which we report here.



(III)

Fig. 1, the molecular structure of (III), shows the extended conformation adopted, which maximizes the distance of the methyl to the polar groups. Each ammonium group forms hydrogen bonds to three different molecules (Fig. 2 and Table 2), with typical N—H⋯O head-to-tail interactions. The three kinds of hydrogen bonds hold the carboxylate and ammonium groups together in double layers parallel to the *ab* plane, while the nonpolar groups stand alongside each other. The double layer structure is very similar to those of (I) and other amino acids with non-polar side chains such as L-valine

(Torii & Iitaka, 1970), L-methionine (Torii & Iitaka, 1973), L-cystine (Harding & Long, 1968) and L-isoleucine (Torii & Iitaka, 1971). However, bifurcated hydrogen bonds reported in phase (I) are not present in the structure of phase (III). As a result of the packing scheme, some short non-hydrogen-bonded N···O distances arise [2.731 (8) Å for N1···O2 (intramolecular distance), 3.44 (10) Å for N1···O1($x + \frac{1}{2}, y - \frac{1}{2}, z$) and 3.354 (6) Å for O2···N1($-x + \frac{3}{2}, y + \frac{1}{2}, -z + 1$)].

A few further characteristics differentiating (I) and (III) are *e.g.* the Z' values [1 for (III), 2 for (I)] and the X-ray diffraction density [1.173 g cm^{-3} for (III), 1.162 g cm^{-3} for (I)]. The latter difference is a direct consequence of the Le Chatelier principle: at higher pressure, a more compact crystal packing is preferred.

Experimental

L-α-Leucine was produced by Ajinomoto Co. A mixture of the leucine and water (1:1 in weight) was put in a pressure vessel and then pressed at 400 MPa and room temperature for a day. After the pressure was released, crystals were taken out, rinsed with acetone and then dried in a vacuum desiccator.

Crystal data

$C_6H_{13}NO_2$
$M_r = 131.17$
Monoclinic, $C2$
$a = 8.807$ (3) Å
$b = 5.975$ (1) Å
$c = 14.193$ (3) Å
$\beta = 96.17$ (2)°
$V = 742.5$ (3) Å^3
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 0.72$ mm^{-1}
$T = 296$ (2) K
0.40 × 0.40 × 0.20 mm

Data collection

Rigaku AFC-5S diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.738$, $T_{\max} = 0.868$
1570 measured reflections
834 independent reflections
756 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.024$
3 standard reflections every 150 reflections intensity decay: 2.9%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.104$
$S = 1.50$
834 reflections
83 parameters
H-atom parameters not refined
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected bond lengths (Å).

O1—C2	1.248 (8)	C1—C3	1.528 (3)
O2—C2	1.250 (17)	C3—C4	1.526 (4)
N1—C1	1.493 (3)	C4—C5	1.525 (17)
C1—C2	1.530 (9)	C4—C6	1.526 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H13···O1$^{\rm i}$	0.94	1.97	2.890 (10)	165
N1—H12···O1$^{\rm ii}$	0.95	1.99	2.884 (2)	156
N1—H11···O2$^{\rm iii}$	0.96	1.73	2.680 (8)	179

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

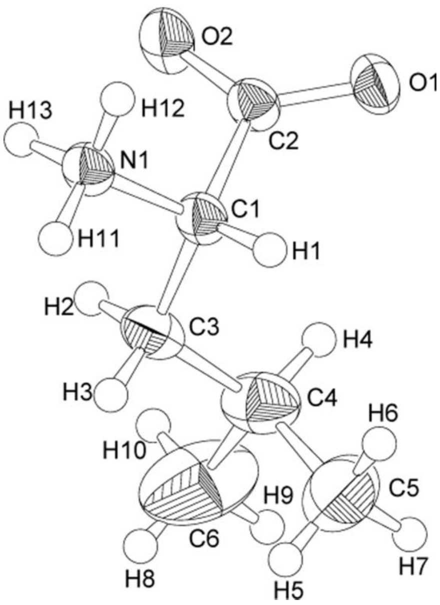


Figure 1
The molecular structure of L-α-leucine. Displacement ellipsoids are drawn at the 50% probability level.

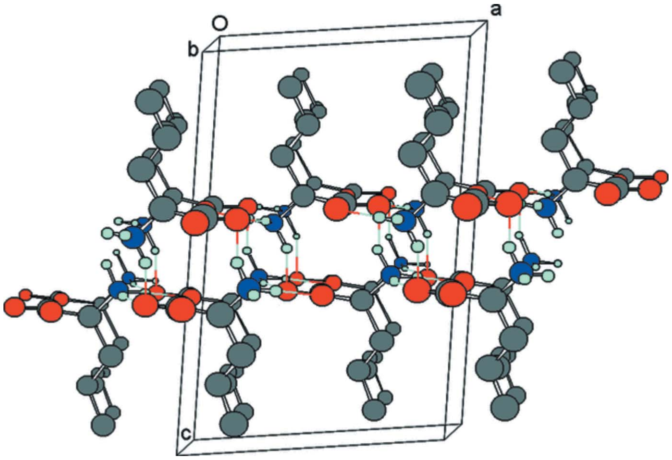


Figure 2
A crystal packing diagram of (III), viewed approximately along the *b* axis. Hydrogen bonds are shown by lines in combined colors of red and light blue. H atoms not involved in hydrogen bonds have been omitted.

H atoms were placed at idealized positions (and kept fixed during refinement), at 0.95 Å from the host atom and completing a tetrahedral arrangement around it; in the case of CH_3 and NH_3 groups, H atoms were set in a *gauche* position to the host's next-nearest neighbors. In all cases, $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(host). Since anomalous scattering effects were too small to provide a reliable indication of the absolute configuration, which is known for this compound, Friedel pairs were averaged.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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This work was partially supported by the 'Academic Frontier' Project from MEXT, 2004–2008. MY expresses his sincere thanks to Professor N. Nakamura of Ritsumeikan University for valuable advice and encouragement.

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