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L-Leucine L-leucinium picrate

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The asymmetric unit of the title compound, $C_6H_{13}NO_2 \cdot C_6H_{14}NO_2^+ \cdot C_6H_2N_3O_7^-$, contains two unprotonated leucine residues, two protonated leucinium cations and two picrate anions. The leucine residues show a class II hydrogen-bonding scheme and the leucinium residues show a class I hydrogen-bonding scheme. The leucine and leucinium residues form infinite hydrogen-bonded chains running along the *a* axis.

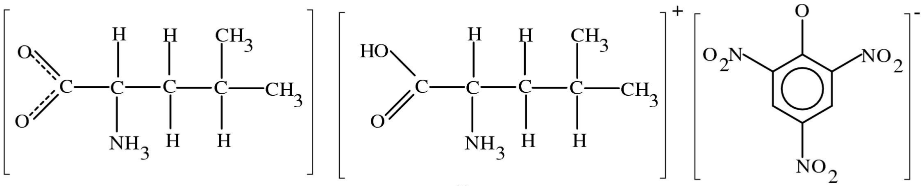
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.051
wR factor = 0.149
Data-to-parameter ratio = 7.2

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

Comment

Leucine is one of the naturally occurring α-amino acids. The crystal structures of L-leucine (Harding & Howieson, 1976; Coll *et al.*, 1986; Görbitz & Dalhus, 1996), DL-leucine (Di Blasio *et al.*, 1975), D-leucine (Moller, 1949) and di-L-leucine hydrochloride (Golič & Hamilton, 1972) have been determined. The crystal structures of amino acids and their complexes have provided interesting information about aggregation, and the effect of other molecules on their interaction and molecular properties (Vijayan, 1988; Prasad & Vijayan 1993). In the present work, L-leucine L-leucinium picrate, (I), is reported.



(I)

The difference between the C—O bond lengths of the carboxyl group clearly indicates the protonation of two of the four leucine residues in the asymmetric unit. The single bond distances of carboxyl O atoms in leucinium cations [1.275 (6) and 1.286 (6) Å] are somewhat shorter than the mean value of 1.303 Å (Nardelli *et al.*, 1962). The most striking feature of this structure is the existence of a hydrogen-bonded assembly of a leucine molecule and a leucinium cation. All the O—H···O hydrogen-bonded assemblies are in an open configuration.

The geometries of all the leucine residues are similar. The backbone conformation angle ψ^1 is in the *cis* form and ψ^2 is in the *trans* form. The side-branched chain conformation angles χ^1 and χ^{21} are in *gauche* II forms, and χ^{22} is in the *trans* form.

The picrate anions play a vital role in hydrogen bonding with all the leucine residues. These two picrate anions in the asymmetric unit have the same geometric parameters and are similar to other picric acid complexes. Of the three nitro groups, two are twisted from the plane of the ring in one of the picrate anions and one nitro group is twisted in the other

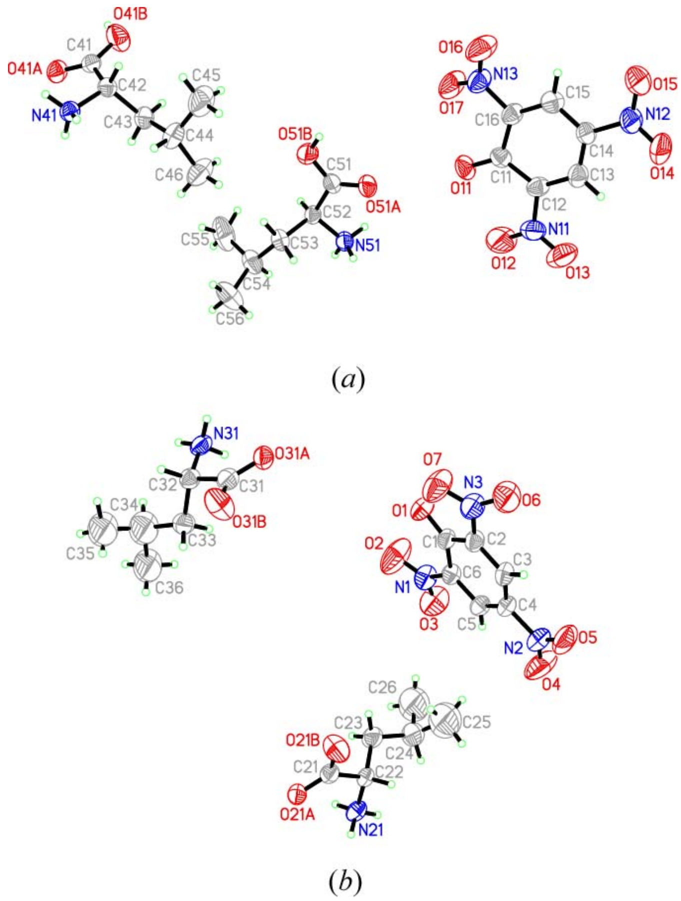


Figure 1
The two halves of the asymmetric unit of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids.

picrate anion (Table 1). This twisting is not correlated with the C—N bond distances (Soriano-Garcia *et al.*, 1978).

The structure is stabilized by an extensive network of O—H···O and N—H···O hydrogen bonds. The structures of many amino acids with non-polar side chains have the arrangement of a double layer of carboxyl and amino groups held together by hydrogen bonds (Torii & Iitaka 1970, 1971, 1973; Harding & Long, 1968). In both leucine residues, two two-centered and one three-centered N—H···O hydrogen bonds lead to a class II hydrogen-bonding scheme. In both leucinium residues, three two-centered hydrogen bonds are observed, leading to a class I hydrogen-bonding scheme (Jeffrey & Saenger, 1991). It is interesting to note that only unprotonated leucine residues have three-centered hydrogen bonds. The carboxyl groups of leucine and the leucinium residues are interconnected through O—H···O hydrogen bonds, forming assemblies of one cation with one neutral molecule. The shortening of the C—O bond distance is consistent with the fact that the charge transfer of the H atom is slightly low and the hydrogen bonding is strong, as observed in bis(L-tyrosinium) sulfate monohydrate (Sridhar *et al.*, 2002).

The carboxyl H atoms (H41*D* and H51*D*) are in a *syn–syn* orientation with respect to the donor and acceptor O atom of the carboxyl group [H41*D*—O41*B*—C41—O41*A* = 7.8°, H41*D*—O21*B*^{i}—C21^{i}—O21*A*^{i} = 2.5°, H51*D*—O51*B*—C51—O51*A* = −2.9° and H51*D*—O31*B*^{i}—C31^{i}—O31*A*^{i} = 2.4°; symmetry code: (i) 1 + *x*, *y*, *z*], as found in betaine betainium oxalate (Rodrigues *et al.*, 2001).

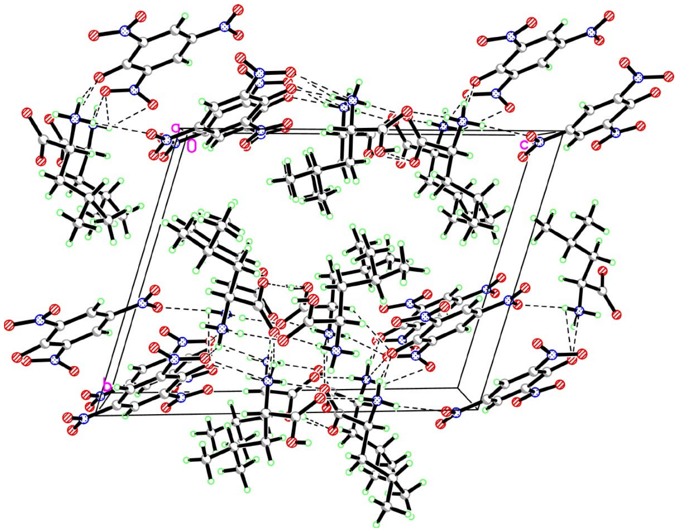


Figure 2
A packing diagram, viewed down the *a* axis.

There is no classical head-to-tail sequence observed in the structure. Both amino groups of the leucinium residues connect to carboxyl O atoms of symmetry-related leucine residues, thus forming infinite chains along the *a* axis. Both leucine residues connect two different picrate anions by N—H···O hydrogen bonds, leading to infinite chains along the *a* axis. In the crystal structure, the hydrophobic layers across $y \simeq \frac{1}{3}$ are sandwiched between hydrophilic layers.

Experimental

The title compound was crystallized by slow evaporation at room temperature, after mixing L-leucine and picric acid in a 2:1 molar ratio in water.

Crystal data

$C_6H_{13}NO_2 \cdot C_6H_{14}NO_2^+ \cdot C_6H_2N_3O_7^-$
M_r = 491.46
Triclinic, $P1$
a = 7.1470 (5) Å
b = 11.8540 (8) Å
c = 15.456 (1) Å
α = 106.45 (2)°
β = 95.17 (1)°
γ = 91.02 (2)°
V = 1249.5 (2) Å^3
Z = 2
D_x = 1.306 Mg m^{-3}
D_m = 1.297 Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetracholride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.4–13.9°
μ = 0.11 mm^{-1}
T = 293 (2) K
Block, yellow
0.25 × 0.15 × 0.12 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.981, T_{max} = 0.987
5538 measured reflections
4392 independent reflections
3495 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 25.0°
$h = -1 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 1%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.150$
$S = 1.03$
4392 reflections
609 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 0.3632P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C21—O21*A*	1.249 (6)	C41—O41*A*	1.223 (6)
C21—O21*B*	1.253 (6)	C41—O41*B*	1.275 (6)
C31—O31*A*	1.247 (6)	C51—O51*A*	1.212 (6)
C31—O31*B*	1.253 (6)	C51—O51*B*	1.286 (6)
O21*A*—C21—O21*B*	126.4 (4)	O41*A*—C41—O41*B*	126.4 (5)
O21*A*—C21—C22	119.3 (4)	O41*A*—C41—C42	121.5 (4)
O21*B*—C21—C22	114.2 (4)	O41*B*—C41—C42	112.1 (4)
O31*A*—C31—O31*B*	126.4 (4)	O51*A*—C51—O51*B*	125.5 (4)
O31*A*—C31—C32	119.8 (4)	O51*A*—C51—C52	121.8 (4)
O31*B*—C31—C32	113.7 (4)	O51*B*—C51—C52	112.7 (4)
C3—C2—N3—O6	28.3 (8)	O31*A*—C31—C32—N31	−9.5 (6)
C1—C2—N3—O6	−152.3 (5)	O31*B*—C31—C32—N31	172.3 (4)
C5—C6—N1—O2	166.1 (6)	N31—C32—C33—C34	−71.0 (8)
C1—C6—N1—O2	−12.8 (8)	C32—C33—C34—C35	−69.7 (11)
C5—C4—N2—O4	2.2 (9)	C32—C33—C34—C36	163.9 (8)
C3—C4—N2—O4	−176.8 (6)	O41*A*—C41—C42—N41	−14.8 (6)
C13—C12—N11—O12	−173.6 (6)	O41*B*—C41—C42—N41	168.3 (4)
C11—C12—N11—O12	5.3 (9)	N41—C42—C43—C44	−75.3 (5)
C13—C14—N12—O14	−1.6 (9)	C42—C43—C44—C45	−67.9 (6)
C15—C14—N12—O14	175.4 (6)	C42—C43—C44—C46	166.7 (5)
C15—C16—N13—O16	−23.1 (8)	O51*A*—C51—C52—N51	−11.3 (6)
C11—C16—N13—O16	154.3 (6)	O51*B*—C51—C52—N51	167.2 (4)
O21*A*—C21—C22—N21	−9.5 (6)	N51—C52—C53—C54	−76.2 (5)
O21*B*—C21—C22—N21	170.4 (4)	C52—C53—C54—C55	−74.6 (6)
N21—C22—C23—C24	−78.6 (6)	C52—C53—C54—C56	162.9 (5)
C22—C23—C24—C26	163.5 (8)	H41*D*—O21*B*^{i}—C21^{i}—O21*A*^{i}	2.5
C22—C23—C24—C25	−79.2 (7)	H51*D*—O31*B*^{i}—C31^{i}—O31*A*^{i}	2.4

Symmetry code: (i) $x + 1, y, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O51*B*—H51*D*···O31*B*^{i}	0.82	1.65	2.454 (5)	166
N51—H51*C*···O31*A*	0.89	2.12	2.999 (5)	168
N51—H51*B*···O7	0.89	2.23	3.098 (6)	164
N51—H51*A*···O21*A*^{ii}	0.89	1.93	2.798 (5)	166
O41*B*—H41*D*···O21*B*^{i}	0.82	1.68	2.471 (5)	161
N41—H41*C*···O21*A*	0.89	2.07	2.942 (5)	166
N41—H41*B*···O11^{iii}	0.89	2.02	2.907 (5)	173
N41—H41*A*···O31*A*^{iv}	0.89	2.05	2.913 (5)	162
N31—H31*C*···O5^{v}	0.89	2.16	2.977 (6)	153
N31—H31*B*···O17^{vi}	0.89	2.25	2.998 (6)	142
N31—H31*B*···O12	0.89	2.62	3.364 (9)	142
N31—H31*A*···O51*A*	0.89	1.97	2.861 (5)	176
N21—H21*C*···O41*A*	0.89	2.10	2.983 (5)	174
N21—H21*B*···O6^{iv}	0.89	2.57	3.355 (6)	147
N21—H21*B*···O15^{vii}	0.89	2.56	3.084 (6)	118
N21—H21*A*···O1^{iii}	0.89	1.91	2.753 (6)	157

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

All H atoms were placed in geometrically calculated positions (C—H = 0.93–0.98 Å, N—H = 0.89 Å and O—H = 0.82 Å) and included in the refinement in the riding-model approximation, with U_{iso}(H) equal to $1.2U_{eq}$ or $1.5U_{eq}$ of the carrier atom for C and N/O atoms, respectively. In addition to the 4392 unique reflections, 982 Friedel pairs were measured. However, owing to the absence of atoms with significant anomalous dispersion effects, these data were merged. The absolute configuration was assigned on the basis of the starting material.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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