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L-Valinium picrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.117
Data-to-parameter ratio = 8.1

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

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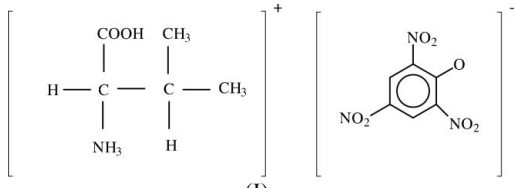
In the title compound, $C_5H_{12}NO_2^+\cdot C_6H_2N_3O_7^-$, the carboxyl group of the valinium residue is engaged in a strong hydrogen bond with the picrate anion. The amino group of the L-valinium cation and the picrate anion are held together by an intermolecular hydrogen bond. The valine residue is involved in a zigzag (Z1) head-to-tail sequence.

Comment

Valine is an essential amino acid. The crystal structures of L-valine (Torii & Iitaka, 1970), DL-valine (Mallikarjunan & Rao, 1969), L-valine hydrochloride monohydrate (Rao, 1969), L-valine hydrochloride (Parthasarathy, 1966; Ando *et al.*, 1967), DL-valine hydrochloride (Di Blasio *et al.*, 1977), L-valinium nitrate (Srinivasan *et al.*, 1997), L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001), DL-valinium nitrate (Srinivasan *et al.*, 2002) and DL-valinium perchlorate (Sridhar *et al.*, 2003) have been reported. The crystal structure of picric acid (Soriano-Garcia *et al.*, 1978; Srikrishnan *et al.*, 1980; Duesler *et al.*, 1978) has also been reported. In the present work, the crystal structure of L-valine with picric acid is reported, *viz*. (I).



(I)

In the valinium ion of (I), the unsymmetrical carboxyl bond distances and angles [1.212 (3)/1.297 (3) Å and 120.9 (2)/

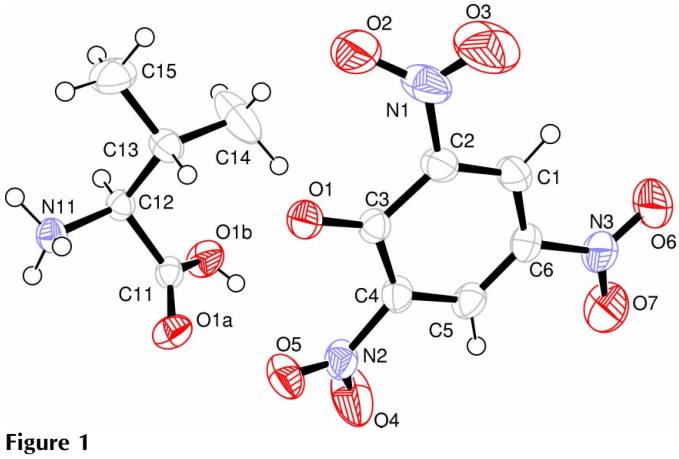


Figure 1
The molecular structure of title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids.

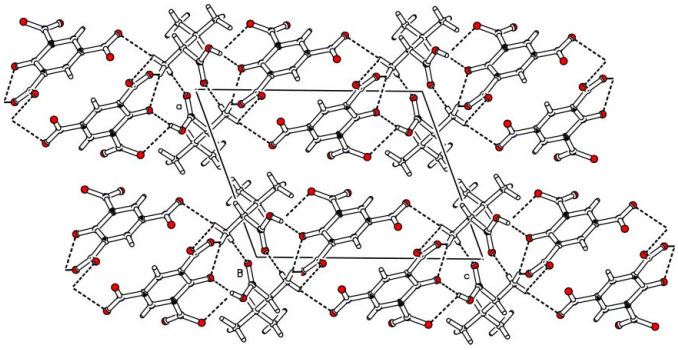


Figure 2
Packing diagram of the title compound, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

112.5 (2)°] clearly indicate protonation of the carboxyl group (Fig. 1). With regard to the backbone conformation angles, ψ^1 is in the *cis* form and ψ^2 is in the *trans* form. All three rotational isomers of the valinium molecule, *viz.* *gauche*-I/*gauche*-II, *gauche*-I/*trans* and *gauche*-II/*trans*, have been found in the crystalline state (Torii & Iitaka, 1970). With regard to the side-chain conformation angles, χ^{11} is in the *trans* form and χ^{12} is in the *gauche*-II form. Atoms C11 and N11 are *trans* to C15 and C14, respectively, indicating a *trans* isomer for the present valinium residue.

In the picrate anion, the nitro groups play a vital role in forming hydrogen bonds. There is no relationship between the C—N bond distances and the amount of twisting of the nitro groups from the mean benzene plane (Soriano-Garcia *et al.*, 1978). In the picrate anion, one nitro group [C5—C6—N3—O7 = 2.6 (5)°] is almost coplanar with the plane of the benzene ring, while the other two nitro groups [C1—C2—N1—O3 = −34.0 (5)° and C3—C4—N2—O5 = −23.8 (4)°] are twisted away from the ring.

The valinium cation and picrate anion are linked by strong O—H···O hydrogen bonding. The amino N atom of the L-valinium cation forms N—H···O hydrogen bonds with the O atoms of the picrate anion. In addition, an intermolecular N—H···O hydrogen bond with the carbonyl O atom is observed. Two three-centred hydrogen bonds and one two-centred hydrogen bond are observed, leading to a class III hydrogen-bonding pattern (Jeffery & Saenger, 1991). A zigzag (Z1) head-to-tail sequence is observed (Vijayan, 1988), leading to the formation of a helix along the *b* axis. The amino group links three different picrate anions into an infinite chain along the *b* axis [N11—H11*A*···O4^{iii} and N11—H11*C*···O1/O5^{iv}; symmetry code: (iii) $-x, \frac{1}{2}+y, -z$; (iv) $-x, y-\frac{1}{2}, -z$]. Across the $x = \frac{1}{2}$ and $z = \frac{1}{2}$ planes, no hydrogen bonding is observed, leading to some of the O atoms of the picrate anion not being involved in hydrogen bonding (O2, O3 and O7) (Fig. 2). These O atoms are also found to have large U_{eq} values.

Experimental

The title compound was crystallized by slow evaporation, under ambient conditions, of an equimolar solution of L-valine and picric acid.

Crystal data

$C_5H_{12}NO_2^+\cdot C_6H_2N_3O_7^-$
$M_r = 346.26$
Monoclinic, $P2_1$
$a = 9.9714$ (13) Å
$b = 6.2930$ (5) Å
$c = 12.6480$ (9) Å
$\beta = 110.50$ (1)°
$V = 743.40$ (13) Å^3
$Z = 2$
$D_x = 1.547$ Mg m^{-3}
$D_m = 1.540$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–14.0°
$\mu = 0.14$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.35 × 0.20 × 0.12 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.942$, $T_{max} = 0.999$
2454 measured reflections
1766 independent reflections
1564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.0°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 8$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.117$
$S = 1.16$
1766 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1203P)^2 + 0.2829P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.212 (3)	O1*B*—C11	1.297 (3)
O1*A*—C11—O1*B*	126.6 (2)	O1*B*—C11—C12	112.5 (2)
O1*A*—C11—C12	120.9 (2)		
C1—C2—N1—O3	−34.0 (5)	O1*A*—C11—C12—N11	−28.3 (3)
C1—C6—N3—O6	4.3 (5)	O1*B*—C11—C12—N11	153.1 (2)
C3—C2—N1—O2	−41.8 (4)	N11—C12—C13—C15	−59.9 (3)
C3—C4—N2—O5	−23.8 (4)	N11—C12—C13—C14	175.7 (3)
C5—C4—N2—O4	−23.8 (4)	C11—C12—C13—C15	−178.8 (2)
C5—C6—N3—O7	2.6 (5)	C11—C12—C13—C14	56.9 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O1^{i}	0.82	1.87	2.678 (3)	167
N11—H11*A*···O6^{ii}	0.89	2.46	3.233 (3)	146
N11—H11*A*···O4^{iii}	0.89	2.40	2.898 (4)	115
N11—H11*B*···O1*A*^{iii}	0.89	1.96	2.825 (3)	164
N11—H11*C*···O1^{iv}	0.89	2.20	2.807 (3)	125
N11—H11*C*···O5^{iv}	0.89	2.06	2.872 (4)	150

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

The carboxyl H atom was fixed in the position found in a difference map, and all other H atoms were placed in calculated positions and included in the refinement in the riding-model approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl and ammonium H atoms). 649 Friedel pairs were merged in the final cycle of refinement, and the absolute configuration was assumed from that of L-valine.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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