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DL-Valine DL-valinium picrate

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The title compound, $C_5H_{12}NO_2^+\cdot C_6H_2N_3O_7^-\cdot C_5H_{11}NO_2$, crystallizes in the monoclinic system with one valinium cation, one valine molecule and one picrate anion in the asymmetric unit. In the crystal structure, the valinium cation is linked to the picrate anion *via* O—H···O hydrogen bonds.

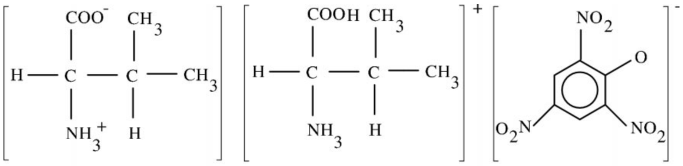
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.181
Data-to-parameter ratio = 12.4

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

Comment

Valine is one of the branched chain amino acids. It plays an important role in tissue repair. The crystal structures of DL-valine (Mallikarjunan & Rao, 1969; Dalhus & Gorbitz, 1996), DL-valine hydrochloride (Di Blasio *et al.*, 1977), 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; Duesler *et al.*, 1978) has also been reported. In the present work, the product, (I), of the reaction of DL-valine with picric acid was investigated in order to study hydrogen bonding between the amino acid and the organic acid.



(I)

The asymmetric unit contains one valine molecule, one valinium cation and one picrate anion (Table 1). For both valine residues, the backbone conformation angle ψ^1 (O1*A*—C1—C2—N1) represents a *cis* form, and ψ^2 (O1*B*—C1—C2—N1) represents a *trans* form. Of the three possible rotamers, only two are observed for the valine residues in the present study (Torii & Iitaka, 1970). Residue I (cation) is *trans* since the amino and carboxyl groups are *trans* to the terminal methyl groups (C4 and C5), while residue II (neutral) has a *gauche*-II conformation since only the amino group is *trans* to C5′, while the carboxyl group is *gauche*-II to C4′ (Torii & Iitaka, 1970).

The picrate anion plays a vital role in hydrogen bonding with the DL-valinium cation. Of the three nitro groups, two are twisted out of the benzene plane. This property is not correlated with the C—N bond distances (Soriano-Garcia *et al.*, 1978). The picrate anion forms an asymmetric O1*B*′—H1′···O11$^{\text{ii}}$ hydrogen bond with valine residue II, since the H atom is closer to that of the O atoms (Olovsson *et al.*, 2001). In residue I, a straight (S2) head-to-tail infinite chain is observed

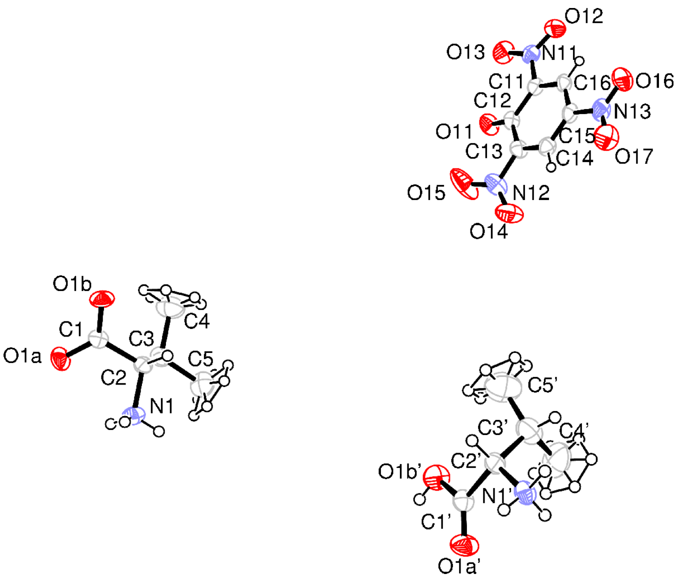


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids. (Johnson, 1976). Both components of the disordered methyl groups are shown.

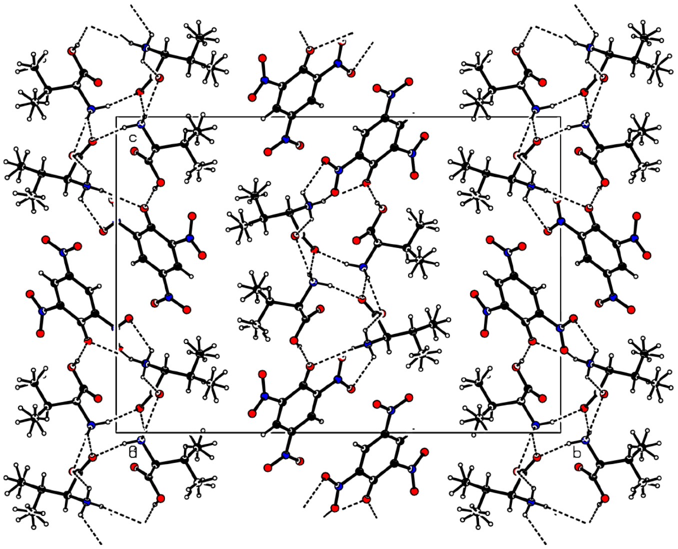


Figure 2
Packing diagram of the crystal structure, viewed down the *b* axis.

along the *a* axis (N1—H1*B*···O1*B*$^{\rm ii}$). Atom O1*B* links two crystallographically independent valine residues (N1—H1*C*···O1*B*$^{\rm ii}$ and N1′—H1*B*′···O1*B*$^{\rm vi}$) and O1*A* links two symmetry-related valine residues (N1′—H1*A*′···O1*A*$^{\rm v}$ and N1′—H1*C*′···O1*A*$^{\rm vii}$). For valine residue I there are two two-centered hydrogen bonds (N1—H1*A*···O12$^{\rm i}$ and N1—H1*B*···O1*B*$^{\rm ii}$) and one chelated three-centered hydrogen bond (N1—H1*C*···O13$^{\rm iii}$ and N1—H1*C*···O11$^{\rm iii}$). This leads to class II hydrogen bonding (Jeffrey & Saenger, 1991). For residue II, three two-centered hydrogen bonds (N1′—H1*A*′···O1*A*$^{\rm v}$, N1′—H1*B*′···O1*B*$^{\rm vi}$ and N1′—H1*C*′···O1*A*$^{\rm vii}$) are observed, leading to class I hydrogen bonding. In the $y = \frac{1}{4}$ planes, there are no hydrogen bonds, leading to a hydrophobic zone, while across the $y = 0$ planes, hydrophilic zones are observed (Fig. 2). In the picrate anion, two O atoms of one nitro group link two valine residues and form an infinite chain along the *a* axis (O12$^{\rm i}$···H1*A*—N1—H1*C*···O13$^{\rm iii}$). (For symmetry codes, see Table 2.)

Experimental

The title compound was crystallized by slow evaporation, at room temperature, of an equimolar solution of DL-valine and picric acid.

Crystal data

$C_5H_{12}NO_2^+\cdot C_6H_2N_3O_7^-\cdot C_5H_{11}NO_2$
$M_r = 463.41$
Monoclinic, $P2_1/n$
$a = 5.3822$ (4) Å
$b = 23.221$ (2) Å
$c = 16.579$ (2) Å
$\beta = 94.695$ (7)°
$V = 2065.0$ (3) Å^3
$Z = 4$
$D_x = 1.491$ Mg m^{-3}
$D_m = 1.489$ Mg m^{-3}
D_m measured by flotation using mixture of carbon tetracholride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.8$–14.1°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.30 × 0.20 × 0.15 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.970$, $T_{\rm max} = 0.981$
4297 measured reflections
3642 independent reflections
2219 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 6$
$k = -1 \rightarrow 27$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.181$
$S = 1.03$
3642 reflections
293 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 2.0601P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.65$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C1	1.251 (4)	O1*A*′—C1′	1.194 (5)
O1*B*—C1	1.245 (4)	O1*B*′—C1′	1.311 (4)
O1*B*—C1—O1*A*	124.7 (3)	O1*A*′—C1′—O1*B*′	126.2 (3)
O1*B*—C1—C2	118.0 (3)	O1*A*′—C1′—C2′	123.2 (3)
O1*A*—C1—C2	117.2 (3)	O1*B*′—C1′—C2′	110.6 (3)
O1*A*—C1—C2—N1	−32.3 (4)	N1′—C2′—C3′—C5′	−153.4 (4)
O1*B*—C1—C2—N1	148.5 (3)	C1′—C2′—C3′—C5′	84.6 (5)
N1—C2—C3—C4	179.8 (3)	N1′—C2′—C3′—C4′	75.6 (5)
C1—C2—C3—C4	59.0 (4)	C1′—C2′—C3′—C4′	−46.4 (5)
N1—C2—C3—C5	−56.7 (4)	C12—C11—N11—O13	11.2 (5)
C1—C2—C3—C5	−177.5 (3)	C12—C13—N12—O15	−24.9 (6)
O1*A*′—C1′—C2′—N1′	−1.5 (5)	C14—C15—N13—O17	−0.3 (6)
O1*B*′—C1′—C2′—N1′	178.6 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O12$^{\rm i}$	0.89	2.37	3.014 (4)	129
N1—H1*B*···O1*B*$^{\rm ii}$	0.89	2.16	2.887 (4)	138
N1—H1*C*···O13$^{\rm iii}$	0.89	2.20	2.890 (4)	134
N1—H1*C*···O11$^{\rm iii}$	0.89	2.43	3.261 (4)	155
O1*B*′—H1′···O11$^{\rm iv}$	0.83 (5)	1.86 (5)	2.684 (4)	168 (5)
N1′—H1*C*′···O1*A*$^{\rm v}$	0.89	2.00	2.805 (4)	151
N1′—H1*B*′···O1*B*$^{\rm vi}$	0.89	2.13	2.940 (4)	150
N1′—H1*A*′···O1*A*$^{\rm vii}$	0.89	1.93	2.763 (4)	155

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $1+x, y, z$; (iii) $x, 1+y, z$; (iv) $2-x, 1-y, 1-z$; (v) $1-x, 2-y, 1-z$; (vi) $x, y, z-1$; (vii) $x-1, y, z-1$.

The H atom of the carboxyl O atom was refined isotropically and all other H atoms were placed in calculated positions (C—H = 0.93–0.98 Å and N—H = 0.89 Å) and included in the refinement in a riding-model approximation, with $U_{\rm iso}$(H) values of 1.2$U_{\rm eq}$ of the carrier atom. Even after refining the methyl groups with a disordered model, the methyl groups of valine residue II have large $U_{\rm iso}$ values, resulting in the highest peak and deepest hole having relatively large electron density values. An intermolecular short contact between C12 of the valine residue and O3 of the picrate anion is observed, the C12···O3 distance being 2.935 (4) Å and the C—H···O angle being 100°.

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, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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References

Dalhus, B. & Gorbitz, C. H. (1996). *Acta Cryst.* C**52**, 1759–1761.

Di Blasio, B., Napolitano, G. & Pedone, C. (1977). *Acta Cryst.* B**33**, 542–545.

Duesler, E. N., Engelmann, J. H., Curtin, D. Y. & Paul, I. C. (1978). *Cryst. Struct. Commun.* **7**, 449–453.

Enraf–Nonius (1994). *CAD*-4 *Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures.* Berlin/Heidelberg/New York: Springer-Verlag.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mallikarjunan, M. & Rao, S. T. (1969). *Acta Cryst.* B**25**, 296–303.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Olovsson, I., Ptasiewicz-Bak, H., Gustafsson, T. & Majerz, I. (2001). *Acta Cryst.* B**57**, 311–316.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.*. **36**, 7–13.

Sridhar, B., Srinivasan, N., Dalhus, B. & Rajaram. R. K. (2003). *Acta Cryst.* E**59**, o28–o30.

Srinivasan, N., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o95–o897.

Soriano-Garcia, M., Srikrishnan, T. & Parthasarathy, R. (1978). *Acta Cryst.* A**34**, S114.

Torii, K. & Iitaka, Y. (1970). *Acta Cryst.* B**26**, 1317–1326.

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