

## DL-Valinium dihydrogen phosphate

Bagavath Singh Ravikumar,  
Balasubramanian Sridhar and  
Ramaswamy Karunanandam  
Rajaram\*

Department of Physics, Madurai Kamaraj  
University, Madurai 625 021, India

Correspondence e-mail: sshiya@yahoo.com

## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.028

$wR$  factor = 0.079

Data-to-parameter ratio = 12.6

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

In the title compound,  $\text{C}_5\text{H}_{12}\text{O}_2\text{N}^+\cdot\text{H}_2\text{PO}_4^-$ , the valinium and phosphate ions are held together by a strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond. The valinium residue has *gauche* II conformation. The phosphate anion links the amino acids, extending as a chain running along the  $b$  axis.

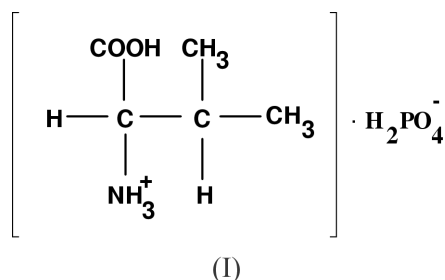
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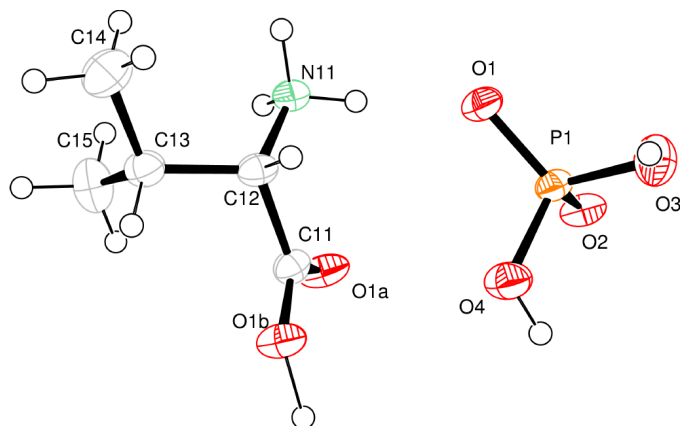
## Comment

Valine is a component of several proteins and functions in contact with other branch-chained amino acids like leucine and isoleucine. It is an aliphatic amino acid and extremely hydrophobic in nature, also seldom useful in routine biochemical reactions, but it is relegated to the duty of determinant in the three-dimensional structure of proteins due to their hydrophobic nature. The crystal structures of L-valine hydrochloride (Parthasarathy, 1966), DL-valine (Mallikarjunan & Rao, 1969), L-valine hydrochloride monohydrate (Rao, 1969), L-valine (Torii & Iitaka, 1970), DL-valine hydrochloride (Di Blasio *et al.*, 1977), L-valine nitrate (Srinivasan *et al.*, 1997), L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001) and DL-valine nitrate (Srinivasan *et al.*, 2002) have been reported. In the present study, the structure of valine reacted with *ortho*-phosphoric acid was undertaken.



In the present investigation of (I), the backbone conformation angles  $\psi_1$  and  $\psi_2$  for the valinium residue are  $-11.5$  (2) and  $169.2$  (2) $^\circ$ , respectively.  $\psi_1$  and  $\psi_2$  deviate from 0 and  $180^\circ$ , respectively, by more than  $10^\circ$  and this is reflected in the structural features, so that the amino N atom is out of the plane of the carboxyl group. This tendency for the C–N bond to twist is found in various amino acids (Lakshminarayanan *et al.*, 1967)

The phosphate ion plays a vital role in forming hydrogen bonds with the valinium ion, thus stabilizing the structure. Three P–O distances in the phosphate anion are in good agreement with single- and double-bond distances. However P–O2 [ $1.521$  (1)  $\text{\AA}$ ] is intermediate in value, as found by Blessing (1988).


**Figure 1**

The molecular structure of the title compound, showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

The valine molecule can have three possible rotational isomers, *viz.* *gauche I*, *trans* and *gauche II* (Torii & Iitaka, 1970). In the present case, the valinium residue adopts a *gauche II* conformation (Table I). The valinium residue is bonded through a strong O—H...O hydrogen bond (Table 2). The phosphate ion forms a strong O—H...O hydrogen bond with its symmetry-related ions. In addition, it also forms a strong O—H...O bond with the carboxyl group of the valinium residue. The amino N atom of the valinium residue forms an N—H...O hydrogen bond with the phosphate ions and the carboxyl group (*DL2* head-to-tail sequence). A three-centered hydrogen bond involves the amino N atom of the valinium residue and the O atoms of the phosphate ion.

The aggregation of the hydrophilic double layers around  $z = 0$  are sandwiched between two hydrophobic zones at  $z = 1/2$  and  $-1/2$  (Fig. 2), as found in *DL*-valinium nitrate (Srinivasan *et al.*, 2002), *L*-phenylalanine nitric acid (Srinivasan *et al.*, 2001) and *DL*-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2001).

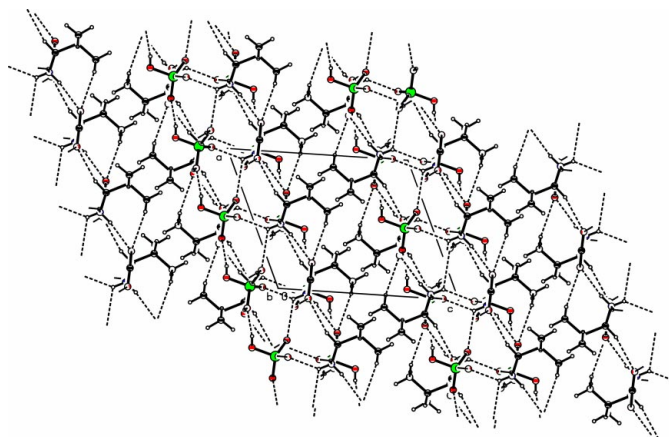
## Experimental

The title compound was crystallized in an aqueous solution from a 1:1 stoichiometric ratio of *DL*-valine and *ortho*-phosphoric acid.

### Crystal data

$C_5H_{12}NO_2^+ \cdot H_2PO_4^-$   
 $M_r = 215.14$   
 Monoclinic,  $P2_1/a$   
 $a = 9.201$  (1) Å  
 $b = 10.0035$  (6) Å  
 $c = 11.195$  (2) Å  
 $\beta = 113.73$  (1)°  
 $V = 943.3$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.515$  Mg m<sup>-3</sup>  
 $D_m = 1.516$  Mg m<sup>-3</sup>

$D_m$  measured by flotation in a mixture of carbon tetrachloride and xylene  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 11.5$ – $14.0$ °  
 $\mu = 0.29$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Needles, colorless  
 $0.5 \times 0.2 \times 0.2$  mm


**Figure 2**

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

### Data collection

Enraf–Nonius sealed-tube diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{min} = 0.905$ ,  $T_{max} = 0.939$   
 1766 measured reflections  
 1652 independent reflections  
 1359 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.008$   
 $\theta_{max} = 25.0$ °  
 $h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 11$   
 $l = -13 \rightarrow 12$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.079$   
 $S = 1.08$   
 1652 reflections  
 131 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.3465P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.28$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0108 (16)

**Table 1**

Selected geometric parameters (Å, °).

P1—O1	1.4822 (14)	O1A—C11	1.224 (2)
P1—O2	1.5205 (13)	O1B—C11	1.289 (2)
P1—O4	1.5710 (14)		
O1A—C11—C12—N11	−11.5 (2)	N11—C12—C13—C14	−66.6 (2)
N11—C12—C13—C15	60.4 (2)	C11—C12—C13—C14	170.86 (18)
C11—C12—C13—C15	−62.1 (2)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H1...O1A <sup>i</sup>	0.88 (3)	1.80 (3)	2.6820 (19)	180 (3)
O3—H2...O2 <sup>ii</sup>	0.75 (3)	1.96 (3)	2.702 (2)	168 (3)
O1B—H1B...O2 <sup>i</sup>	1.17 (4)	1.29 (4)	2.4548 (18)	170 (3)
N11—H11A...O1 <sup>iii</sup>	0.89	1.89	2.738 (2)	160
N11—H11B...O1B <sup>iv</sup>	0.89	2.22	3.087 (2)	164
N11—H11C...O1	0.89	2.07	2.785 (2)	137
N11—H11C...O4 <sup>iv</sup>	0.89	2.59	3.096 (2)	117

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

The H atoms attached of the phosphate ion and the carboxyl group were located and refined isotropically. All other H atoms were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}$  equal to 1.5  $U_{\text{eq}}$  of the carrier atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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