

DL-Threoninium dihydrogen phosphate

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Key indicators

Single-crystal X-ray study

$T = 293$ K

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

R factor = 0.036

wR factor = 0.091

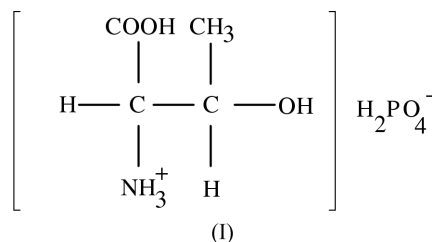
Data-to-parameter ratio = 11.6

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

In the title compound, $\text{C}_4\text{H}_{10}\text{NO}_3^+ \cdot \text{H}_2\text{PO}_4^-$, the threoninium residue forms strong $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds with the phosphate anion. A *gauche* I–*gauche* II conformation with respect to the O^γ and C^γ atoms is observed [the corresponding torsion angles are $59.5(2)$ and $-64.1(3)^\circ$]. The adjacent threoninium cations, related by an *a*-glide plane normal to the *c* axis, are linked *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond involving ammonium and carboxylic acid groups (DL2 head-to-tail sequence). The structure is stabilized by an extensive network of $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, which form a three-dimensional hydrogen-bond system.

Comment

Threonine is an essential amino acid, which helps in maintaining the proper balance of protein in the body. It is found in the heart, skeletal muscles and also in the central nervous system. The crystal structures of DL-threonine and L-threonine (Shoemaker *et al.*, 1950), L-allo-threonine (Swaminathan & Srinivasan, 1975) and bis(L-threoninium) sulfate monohydrate (Sridhar *et al.*, 2001) have been published. In the present paper, the structure of the DL-threoninium salt, (I), of ortho phosphoric acid is reported (Fig. 1).



The backbone conformation angle ψ^1 ($\text{O1A}-\text{C11}-\text{C12}-\text{N11}$) is $-7.8(3)^\circ$. The amino N atom is displaced from the plane of the carboxyl group by $0.053(1)$ Å. This tendency of the C–N bond to twist is found in other amino acid structures (Lakshminarayanan *et al.*, 1967). The branched side chain is in a *gauche* I conformation with respect to the O^γ atom [the $\text{N11}-\text{C12}-\text{C13}-\text{O1C}$ torsion angle is $59.5(2)^\circ$], and in a *gauche* II form with respect to the C^γ atom [the $\text{N11}-\text{C12}-\text{C13}-\text{C14}$ torsion angle is $-64.1(3)^\circ$].

The dihydrogenphosphate anion plays a vital role in the hydrogen bonding (Fig. 2). Three P–O distances agree well with corresponding values expected for single and double P–O bonds. However, the $\text{P1}-\text{O2}$ bond length [$1.517(2)$ Å] is intermediate between the values typical for single and double P–O bonds [1.55 and 1.49 Å, respectively], as found in anhydrous phosphoric acid (Blessing, 1988).

There are seven ‘active’ H atoms in the structure (four hydroxyl groups and the NH_3 group), all of which participate

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in hydrogen bonds of various strengths (Table 2). As a result, both the cation and anion are involved in a complex three-dimensional hydrogen-bonding system. There is, however, only one cation–cation hydrogen bond [N11–H11A···O1B^v; symmetry code: (v) $x - \frac{1}{2}, y, \frac{1}{2} - z$], which links adjacent threoninium cations related by the *a*-glide plane normal to the *c* axis, thus engaging the amino acid residues in the infinite chains along the *a* axis; the hydrogen bonding between the D- and L-amino acids through the amino N atom and the carboxyl O atom *trans* to the amino group is known as the DL2 sequence (Vijayan, 1988).

Experimental

The title compound was crystallized at room temperature from an aqueous solution of DL-threonine and orthophosphoric acid (1:1) by slow evaporation. The solution was prepared from equal volumes (10 ml) of 1 molar concentrations of threonine and phosphoric acid. Crystals were grown over a period of about one month.

Crystal data

C₄H₁₀NO₃⁺·H₂PO₄⁻
M_r = 217.12
 Orthorhombic, *Pbca*
a = 9.0590 (6) Å
b = 19.507 (3) Å
c = 10.1015 (9) Å
V = 1785.1 (3) Å³
Z = 8
D_x = 1.616 Mg m⁻³
D_m = 1.612 Mg m⁻³

D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
 Mo *Kα* radiation
 Cell parameters from 25 reflections
 $\theta = 11.4\text{--}14.0^\circ$
 $\mu = 0.32\text{ mm}^{-1}$
T = 293 (2) K
 Needle, colorless
 0.5 × 0.5 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.889, *T_{max}* = 0.968
 2103 measured reflections
 1570 independent reflections
 1262 reflections with *I* > 2σ(*I*)

R_{int} = 0.016
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -1 \rightarrow 10$
 $k = -23 \rightarrow 1$
 $l = -1 \rightarrow 12$
 25 standard reflections every 3 reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.091
S = 1.23
 1570 reflections
 135 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.4021P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24\text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0234 (14)

Table 1

Selected geometric parameters (Å, °).

P1–O1	1.4774 (16)	P1–O4	1.5722 (16)
P1–O2	1.5172 (16)	O1A–C11	1.219 (3)
P1–O3	1.5667 (18)	O1B–C11	1.295 (3)
O1A–C11–C12–N11	−7.8 (3)	C11–C12–C13–O1C	−60.8 (2)
N11–C12–C13–O1C	59.5 (2)	N11–C12–C13–C14	−64.1 (3)

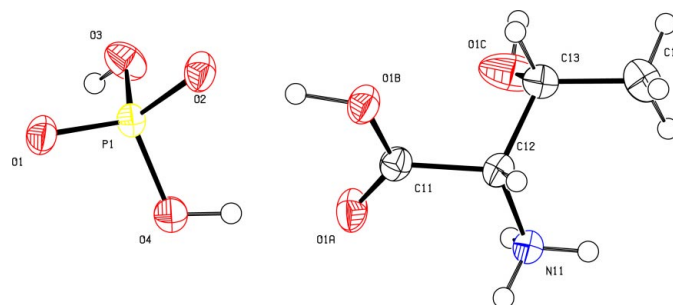


Figure 1

The threoninium cation and dihydrogenphosphate anion in the structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

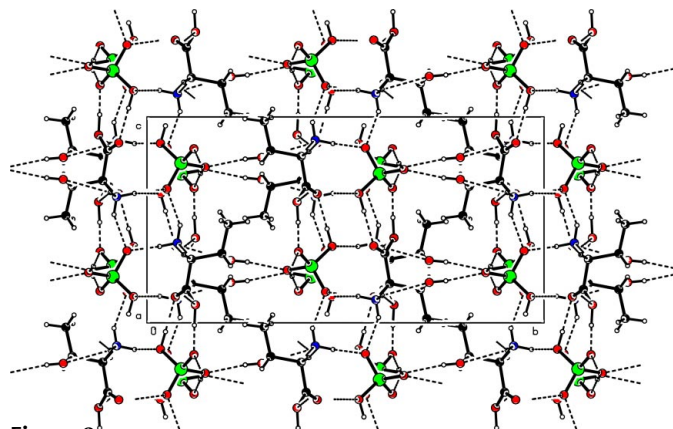


Figure 2

Packing diagram of the crystal structure of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

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>
O3–H3P···O2 ⁱ	0.78 (3)	1.84 (3)	2.617 (2)	172 (4)
O4–H4P···O1A ⁱⁱ	0.90 (3)	1.79 (4)	2.685 (2)	179 (3)
O1B–H1B···O2 ⁱⁱ	1.02 (5)	1.45 (5)	2.470 (2)	173 (4)
O1C–H1C···O3 ⁱⁱⁱ	0.82 (4)	2.08 (4)	2.886 (3)	165 (3)
N11–H11A···O1 ^{iv}	0.89	1.91	2.730 (2)	152
N11–H11B···O1B ^v	0.89	2.16	2.986 (3)	153
N11–H11C···O1	0.89	2.08	2.837 (2)	142

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

The H atoms belonging to the dihydrogenphosphate anion, the carboxyl and the hydroxyl groups (H3P, H4P, H1B, and H1C) were located and refined (O–H 0.78–1.02 Å). All other H atoms were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with *U_{iso}* equal to 1.2*U_{eq}* of the carrier atom (1.5*U_{eq}* for methyl and NH₃ H atoms).

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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