

Triethanolammonium dihydrogenphosphite

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{P}-\text{O}) = 0.002 \text{ \AA}$

Disorder in main residue

R factor = 0.039

wR factor = 0.086

Data-to-parameter ratio = 16.9

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

The title compound, $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3](\text{H}_2\text{PO}_3)$ or $\text{C}_6\text{H}_{16}\text{NO}_3^+\cdot\text{H}_2\text{PO}_3^-$, is isostructural with its hydrogenselenite congener and contains a network of partially disordered triethanolammonium cations and dihydrogenphosphite anions [for the latter species: $d_{\text{av}}(\text{P}-\text{O}) = 1.514(2) \text{ \AA}$ and $\theta_{\text{av}}(\text{O}-\text{P}-\text{O}) = 111.9(2)^\circ$]. The $[\text{H}_2\text{PO}_3]^-$ units are linked into a polymeric chain by $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonds along the polar [010] direction, with the chains crosslinked into (001) sheets by way of $\text{O}-\text{H}\cdots\text{O}$ bonds involving the organic species. Some $\text{C}-\text{H}\cdots\text{O}$ interactions may also be present [$d_{\text{av}}(\text{H}\cdots\text{O}) = 2.45 \text{ \AA}$, $\theta_{\text{av}}(\text{C}-\text{H}\cdots\text{O}) = 158^\circ$ and $d_{\text{av}}(\text{C}\cdots\text{O}) = 3.364(4) \text{ \AA}$]. The $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ cation contains a typical trifurcated intramolecular $\text{N}-\text{H}\cdots(\text{O},\text{O},\text{O})$ hydrogen bond [$d_{\text{av}}(\text{H}\cdots\text{O}) = 2.31 \text{ \AA}$ and $\theta_{\text{av}}(\text{N}-\text{H}\cdots\text{O}) = 112.7^\circ$].

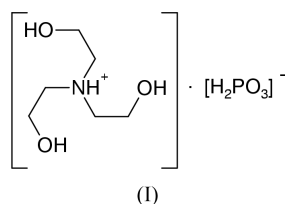
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Comment

Triethanolammonium dihydrogenphosphite, $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3](\text{H}_2\text{PO}_3)$, (I), is isostructural with the recently reported triethanolammonium hydrogenselenite, $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3](\text{HSeO}_3)$, which shows cytotoxic activity (Lukevics *et al.*, 2002).



The structure of (I) consists of triethanolammonium cations and dihydrogenphosphate anions (Fig. 1). The triethanolammonium cation is partially disordered over two positions [major component: atoms C1, C3, and C5 with an occupancy of 0.866(5) and $d_{\text{av}}(\text{N}-\text{C}) = 1.503(4) \text{ \AA}$; minor component: atoms C11, C13, and C15 with an occupancy of 0.134(5) and $d_{\text{av}}(\text{N}-\text{C}) = 1.50(2) \text{ \AA}$]. Otherwise, it exhibits a typical (Yilmaz *et al.*, 1996; Demir *et al.*, 2003) tripodal conformation [for the major component; $d_{\text{av}}(\text{C}-\text{C}) = 1.474(4) \text{ \AA}$ and $d_{\text{av}}(\text{C}-\text{O}) = 1.408(4) \text{ \AA}$], in which the ammonium H atom forms an intramolecular trifurcated hydrogen bond with the O atoms of the three ethanol groups [$d_{\text{av}}(\text{H}\cdots\text{O}) = 2.31 \text{ \AA}$ and $\theta_{\text{av}}(\text{N}-\text{H}\cdots\text{O}) = 112.7^\circ$]. The dihydrogenphosphite group shows its usual (Gordon & Harrison, 2003) pseudo-pyramidal geometry [$d_{\text{av}}(\text{P}-\text{O}) = 1.514(2) \text{ \AA}$ and $\theta_{\text{av}}(\text{O}-\text{P}-\text{O}) = 111.9(2)^\circ$], with the protonated P—O3 vertex showing its expected lengthening relative to the other two P—O bonds.

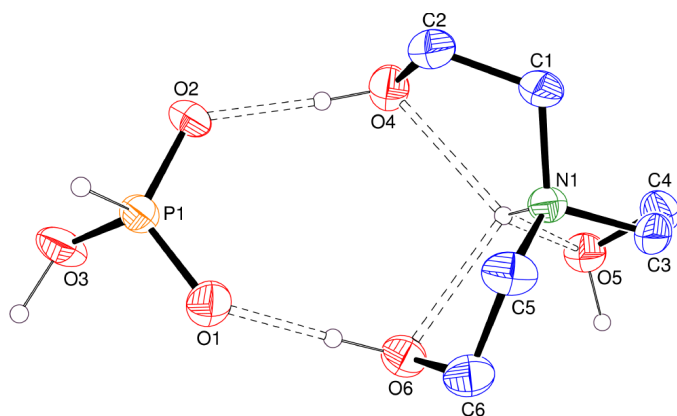


Figure 1

View of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and H bonds are indicated by dashed lines. Only the major orientation of the organic molecule is shown; all C–H hydrogen atoms have been omitted for clarity.

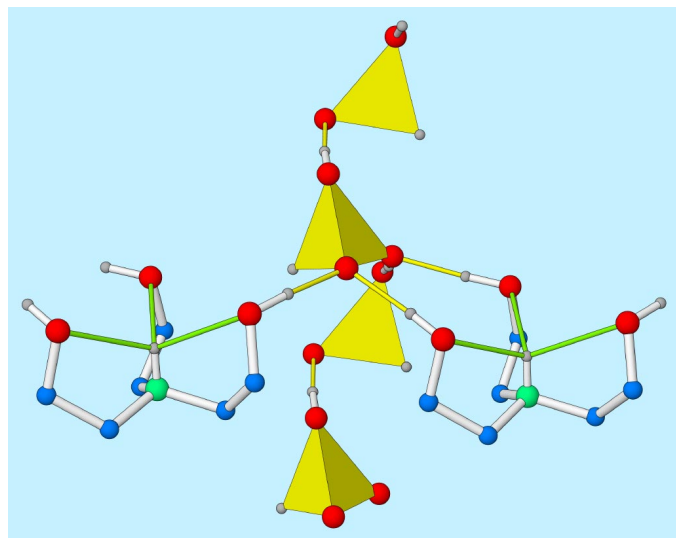


Figure 2

Detail of a dihydrogenphosphite chain and the pendant organic species (major orientation only) in (I). Colour key: $[\text{H}_2\text{PO}_3]^-$ pseudo-tetrahedra yellow, O atoms red, C atoms blue, N atoms purple, H atoms grey. The $\text{H}\cdots\text{O}$ portions of the $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds are highlighted in green and yellow, respectively. All C–H H atoms omitted for clarity.

The component species in (I) interact by means of an extensive network of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{H}\cdots\text{O}$ intermolecular contacts (Table 2). The H_2PO_3^- units are linked into a polymeric chain by $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonds in the polar [010] direction (Fig. 2). A similar dihydrogenphosphite chain was seen in $(\text{CN}_3\text{H}_6)(\text{H}_2\text{PO}_3)$ (Harrison, 2003). The organic species crosslink the chains in the **a** direction by way of $\text{O}_E-\text{H}\cdots\text{O}_P$ ($E = \text{ethanol}$ and $P = \text{phosphite}$) hydrogen bonds, such that each cation makes two hydrogen bonds to one adjacent phosphite moiety (Fig. 1). This results in (001) slabs (Fig. 3). The possible $\text{C}-\text{H}\cdots\text{O}$ interactions [$d_{\text{av}}(\text{H}\cdots\text{O}) = 2.45 \text{ \AA}$, $\theta_{\text{av}}(\text{C}-\text{H}\cdots\text{O}) = 158^\circ$ and $d_{\text{av}}(\text{C}\cdots\text{O}) = 3.364(4) \text{ \AA}$] were identified in a *PLATON*

(Spek, 2003) analysis of the structure. Those involving H5, H9 and H14 provide additional coherence between adjacent organic molecules, in the **c** direction for H5 and in the **b** direction for H9 and H14. The bond involving H10 links an $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ grouping with an $(\text{H}_2\text{PO}_3)^-$ anion in the **a** direction.

Triethanolammonium dihydrogenphosphate, $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3](\text{H}_2\text{PO}_4)$ (Demir *et al.*, 2003) crystallizes in the same space group and has a rather similar structure to (I), in which chains of $[\text{H}_2\text{PO}_4]^-$ anions are crosslinked into sheets by the triethanolammonium cations. However, the $(\text{H}_2\text{PO}_4)^-$ moieties in $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3](\text{H}_2\text{PO}_4)$ are linked together by a distinctly different hydrogen-bonding motif involving alternating single and double $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ links.

Experimental

H_3PO_3 (0.81 g, 1 mmol) and triethanolamine (1.49 g, 1 mmol) were dissolved in 20 ml deionized water in a Petri dish, resulting in a clear solution. Rod-shaped crystals of (I) grew as the water evaporated over the course of a few days. These colourless transparent crystals were rinsed with acetone and dried in air.

Crystal data

$\text{C}_6\text{H}_{16}\text{NO}_3^+\cdot\text{H}_2\text{PO}_3^-$
 $M_r = 231.18$
 Monoclinic, $P2_1$
 $a = 7.9280(7) \text{ \AA}$
 $b = 5.5192(5) \text{ \AA}$
 $c = 12.7940(11) \text{ \AA}$
 $\beta = 104.803(2)^\circ$
 $V = 541.24(8) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.419 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1408 reflections
 $\theta = 2.7\text{--}23.3^\circ$
 $\mu = 0.26 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Rod, colourless
 $0.52 \times 0.08 \times 0.07 \text{ mm}$

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.876$, $T_{\text{max}} = 0.977$
 3955 measured reflections

2362 independent reflections
 1743 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -10 \rightarrow 10$
 $k = -7 \rightarrow 7$
 $l = -11 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.087$
 $S = 0.94$
 2362 reflections
 140 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1128 Friedel pairs
 Flack parameter = 0.11 (12)

Table 1

Selected geometric parameters (\AA , $^\circ$).

P1–O1	1.4883 (19)	N1–C5	1.497 (4)
P1–O2	1.4901 (16)	N1–C1	1.503 (3)
P1–O3	1.563 (2)	N1–C3	1.509 (4)
O1–P1–O2	117.83 (11)	O2–P1–O3	107.14 (11)
O1–P1–O3	110.75 (12)		

Table 2

Hydrogen-bonding geometry and intermolecular C—H...O contacts (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—H2...O1 ⁱ	1.04	1.56	2.597 (3)	175
N1—H3...O6	0.91	2.27	2.760 (3)	114
N1—H3...O4	0.91	2.29	2.765 (3)	112
N1—H3...O5	0.91	2.37	2.850 (3)	113
O4—H8...O2	0.92	1.76	2.672 (2)	176
O6—H18...O1	1.01	1.69	2.702 (3)	176
O5—H13...O2 ⁱⁱ	1.06	1.68	2.731 (2)	175
C1—H5...O4 ⁱⁱⁱ	0.97	2.45	3.382 (4)	161
C3—H9...O5 ^{iv}	0.97	2.41	3.370 (4)	170
C3—H10...O3 ^v	0.97	2.58	3.478 (4)	154
C5—H14...O6 ^{iv}	0.97	2.36	3.227 (4)	148

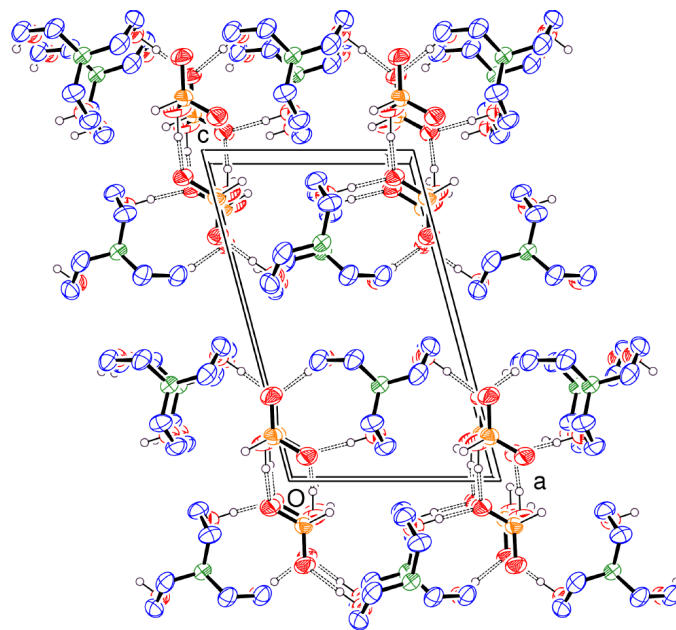
Symmetry codes: (i) $-x, \frac{1}{2} + y, -z$; (ii) $1 + x, y, z$; (iii) $1 - x, y - \frac{1}{2}, 1 - z$; (iv) $x, y - 1, z$; (v) $1 + x, y - 1, z$.

The site occupancies of the two conformations (C1, C3, C5 and their attached H atoms/C11, C13, C15 and their attached H atoms) of the partially disordered organic species were constrained to sum to unity. The O—H and N—H H atoms were found in difference maps and were refined as riding atoms. The H atoms bonded to carbon and phosphorus were placed in calculated positions [$d(\text{C—H}) = 0.97 \text{ \AA}$ and $d(\text{P—H}) = 1.32 \text{ \AA}$] and refined as riding. For all H atoms, the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ was applied.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE-Plus* (Bruker, 1999); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEP3* (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

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**Figure 3**

[010] projection of (I), showing the (001) sheet-like arrangement of $[\text{HN}(\text{C}_2\text{H}_4\text{OH})_3]^+$ (major orientation only) and $(\text{H}_2\text{PO}_3)^-$ moieties. Colour key as in Fig. 2. H3 and all C—H H atoms have been omitted for clarity.

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