

4-Aza-1-azoniabicyclo[2.2.2]octane dihydrogenphosphite

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.037

wR factor = 0.098

Data-to-parameter ratio = 19.4

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

The title compound, $\text{C}_6\text{H}_{13}\text{N}^+\cdot\text{H}_2\text{PO}_3^-$, contains monoprotonated 4-aza-1-azoniabicyclo[2.2.2]octane (dabconium, $\text{C}_6\text{H}_{13}\text{N}^+$) cations and dihydrogenphosphite (H_2PO_3^-) anions. 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 $[100]$ direction. The dabconium cations are pendant to the dihydrogenphosphite chains by way of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and possible $\text{C}-\text{H}\cdots\text{O}$ interactions. The chains are crosslinked by means of van der Waals forces.

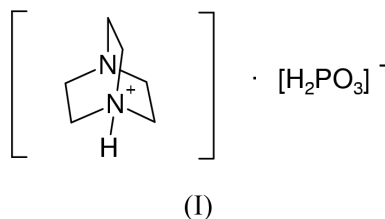
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Comment

The crystal structures of amine (hydrogen) phosphites containing HPO_3^{2-} or H_2PO_3^- ions are of interest in terms of the interplay between cation–anion and anion–anion hydrogen bonds and for comparison with their phosphate (HPO_4^{2-} or H_2PO_4^-) analogues (Averbuch-Pouchot, 1993*a,b*). Previous reports of phosphite-containing crystal structures have been recently surveyed by Idrissi *et al.* (2002).



The structure of (I) (Fig. 1) consists of monoprotonated 4-aza-1-azoniabicyclo[2.2.2]octane (dabconium, $\text{C}_6\text{H}_{13}\text{N}^+$) cations and dihydrogenphosphite (H_2PO_3^-) anions. The dabconium cation has typical (Bremner & Harrison, 2003) geometrical parameters [$d_{\text{av}}(\text{N}-\text{C}) = 1.470(3)\text{ \AA}$, $d_{\text{av}}(\text{C}-\text{C}) = 1.528(3)\text{ \AA}$ and $\theta_{\text{av}}(\text{C}-\text{N}-\text{C}) = 109.1(2)^\circ$]. The $(\text{HN}1)^+-\text{C}-\text{C}$ bond angles [$\theta_{\text{av}} = 108.2(2)^\circ$] are significantly smaller than the equivalent $\text{N}2-\text{C}-\text{C}$ values [$\theta_{\text{av}} = 111.1(2)^\circ$]. The

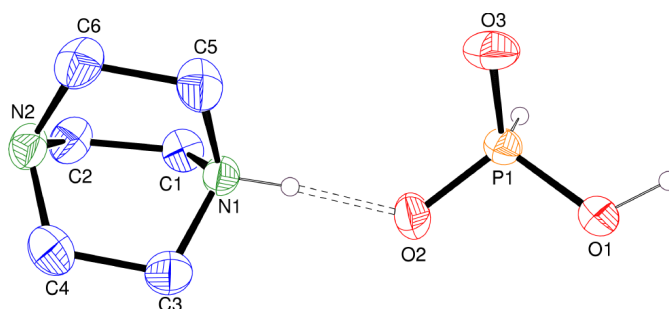
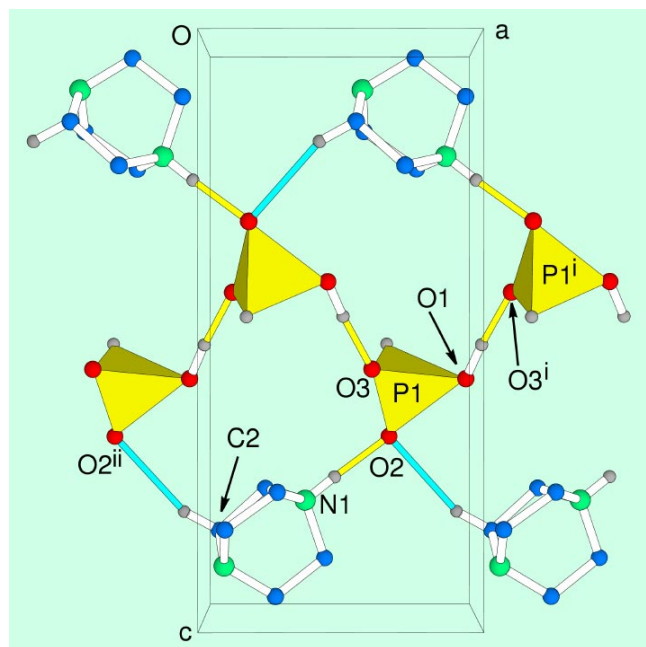


Figure 1

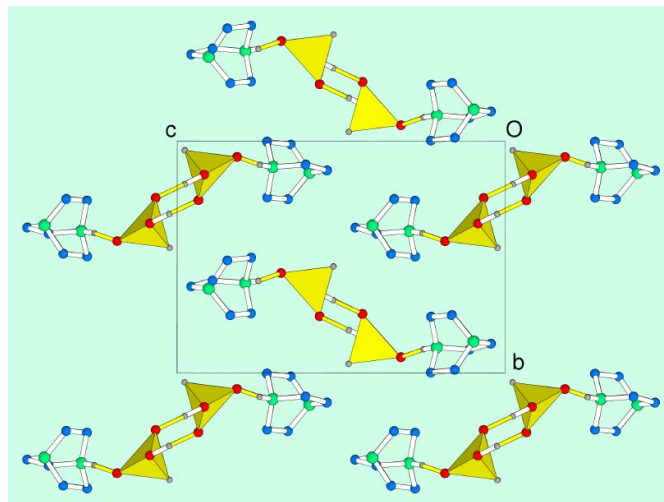
View of (I) (30% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and hydrogen bonds are indicated by dashed lines. All C–H H atoms have been omitted for clarity.

**Figure 2**

Detail of a [100] dihydrogen phosphite chain and pendant dabconium cations in (I). Colour key: $[\text{H}_2\text{PO}_3]^-$ tetrahedra yellow, O atoms red, C atoms blue, N atoms green, H atoms grey (all radii arbitrary). The $\text{H}\cdots\text{O}$ portions of the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{H}\cdots\text{O}$ interactions are highlighted in yellow and light blue, respectively. All $\text{C}-\text{H}$ H atoms except H5 have been omitted for clarity.

dihydrogenphosphite group shows its usual (Idrissi *et al.*, 2002) pseudo-pyramidal geometry [$d_{\text{av}}(\text{P}-\text{O}) = 1.508(2) \text{ \AA}$ and $\theta_{\text{av}}(\text{O}-\text{P}-\text{O}) = 111.9(2)^\circ$]. The protonated $\text{P}-\text{O}1$ vertex shows its expected lengthening relative to the other $\text{P}-\text{O}$ bonds, and the unprotonated $\text{O}2-\text{P}1-\text{O}3$ bond angle (Table 1) is notably larger than the corresponding $\text{O}-\text{P}-\text{OH}$ angles, as seen previously for the same anion in related compounds (Averbuch-Pouchot, 1993*a,b*; Harrison, 2003*b*).

Apart from electrostatic forces, the component species in (I) interact by means of $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2), and possibly a $\text{C}-\text{H}\cdots\text{O}$ interaction (see below). 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 [100] direction (Fig. 2), resulting in a $\text{P}1\cdots\text{P}1^i$ [symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$] separation of $4.7846(8) \text{ \AA}$. Similar inter-anion linkages have been seen in a number of amine phosphites, for example, isopropylammonium dihydrogenphosphite, $(\text{C}_3\text{H}_{10}\text{N})(\text{H}_2\text{PO}_3)$ (Averbuch-Pouchot, 1993*a*), guanidinium dihydrogenphosphite, $(\text{CH}_6\text{N}_3)(\text{H}_2\text{PO}_3)$ (Harrison, 2003*a*), and triethanolammonium dihydrogenphosphite, $(\text{C}_6\text{H}_{16}\text{NO}_3)(\text{H}_2\text{PO}_3)$ (Harrison, 2003*b*). In all these cases, a 2_1 screw axis generates the dihydrogenphosphite chain from a single distinct H_2PO_3^- moiety. The organic species are pendant to the chains by way of the $\text{N}1-\text{H}3\cdots\text{O}2$ hydrogen bonds. A short $\text{C}2-\text{H}6\cdots\text{O}2^{\text{ii}}$ [symmetry code: (ii) $1 - x, y, z$] interaction was identified in a *PLATON* (Spek, 2003) analysis of the structure [$d(\text{C}-\text{H}) = 0.97 \text{ \AA}$, $d(\text{H}\cdots\text{O}) = 2.53 \text{ \AA}$, $d(\text{C}\cdots\text{O}) = 3.450(3) \text{ \AA}$ and $\theta(\text{C}-\text{H}\cdots\text{O}) = 158^\circ$]. If it is not merely a packing artefact, it may provide some additional coherence between the phosphite

**Figure 3**

[100] projection of (I). Colour key as in Fig. 2. All $\text{C}-\text{H}$ hydrogen atoms have been omitted for clarity.

backbone and the pendant dabconium cations (Fig. 2). Inter-chain connectivity normal to [100] (Fig. 3) is mediated by van der Waals forces.

Experimental

H_3PO_3 (0.82 g, 1 mmol) and dabco (1,4-diazoniabicyclo[2.2.2]octane, $\text{C}_6\text{H}_{12}\text{N}_2$; 1.12 g, 1 mmol) were dissolved in 20 ml deionized water, giving a clear solution. Slab- and block-shaped crystals of (I) grew as the water evaporated from the increasingly viscous liquors over the course of several weeks. These colourless transparent crystals were washed with acetone and dried in air. The same phase, adopting a more platy morphology, can also be crystallized from a 1:1 mixture of H_3PO_3 and dabco in methanol.

Crystal data

$\text{C}_6\text{H}_{13}\text{N}_2^+\cdot\text{H}_2\text{PO}_3^-$
 $M_r = 194.17$
 Orthorhombic, $P2_12_12_1$
 $a = 6.6418(4) \text{ \AA}$
 $b = 9.9428(6) \text{ \AA}$
 $c = 14.0575(8) \text{ \AA}$
 $V = 928.33(10) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.389 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 3200 reflections
 $\theta = 2.5-27.3^\circ$
 $\mu = 0.27 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Slab, colourless
 $0.45 \times 0.15 \times 0.07 \text{ mm}$

Data collection

Bruker SMART1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.886$, $T_{\text{max}} = 0.990$
 6962 measured reflections

2139 independent reflections
 1861 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -7 \rightarrow 8$
 $k = -10 \rightarrow 12$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.098$
 $S = 1.04$
 2139 reflections
 110 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.0257P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 881 Friedel pairs
 Flack parameter = 0.15 (12)

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.4774 (19)	P1—O1	1.5561 (18)
P1—O2	1.4910 (16)		
O3—P1—O2	116.25 (11)	O2—P1—O1	106.34 (10)
O3—P1—O1	112.98 (12)		

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>
O1—H2...O3 ⁱ	0.98	1.55	2.528 (2)	176
N1—H3...O2	0.91	1.67	2.580 (2)	174

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

The O—H H atom was found in a difference map and refined using the riding model in its as-found position. The N—H H atom was found in a difference map and refined by riding in an idealized position [$d(\text{N—H}) = 0.91 \text{ \AA}$]. H atoms bonded to C and P atoms were placed in calculated positions [$d(\text{C—H}) = 0.97 \text{ \AA}$ and $d(\text{P—H}) =$

1.32 \AA] and refined by the riding model. 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* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

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