

## 2-Aminoanilinium phosphite

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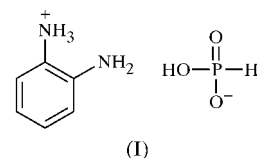
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The solid-state structure of the title compound, alternatively called 2-aminoanilinium hydrogen phosphonate,  $C_6H_9N_2^+ \cdot H_2PO_3^-$ , shows the monoprotonated diamine molecule to be multiply hydrogen bonded to  $HPO_3H^-$  anions. There is no inter-phosphite hydrogen bonding, contrary to previous solid-state observations of the species.

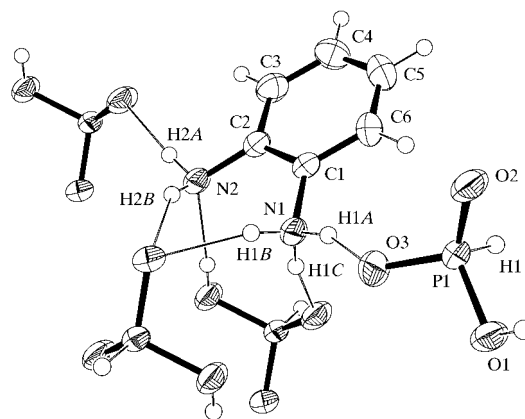
### Comment

Dihydrogen phosphite ( $HPO_3H_2$ ) has been observed in the solid state both in its monoanionic and dianionic forms. There have been observations of the doubly deprotonated form ( $HPO_3^{2-}$ ) with metallic cations in  $Mg(HPO_3) \cdot 6H_2O$  (Corbridge, 1956),  $Na_2(HPO_3) \cdot 5H_2O$  (Colton & Henn, 1971),  $Cu(HPO_3) \cdot 2H_2O$  (Handlovič, 1969),  $Al_2(HPO_3)_3 \cdot Ga_2(HPO_3)_3$  (Morris *et al.*, 1994) and  $Ga_2(HPO_3)_3 \cdot 4H_2O$  (Morris *et al.*, 1992). The single known structure of an organic cation and  $HPO_3^{2-}$  is  $(NH_4)_2(HPO_3) \cdot 5H_2O$  (Rafiq *et al.*, 1982). The monoanionic form has been observed in the solid state with metallic cations in  $Ca(HPO_3H) \cdot 2H_2O$  (Larbot *et al.*, 1984),  $Cd(HPO_3H) \cdot 2H_2O$  (Loub *et al.*, 1978),  $Nd(HPO_3H) \cdot 2H_2O$  (Loukili *et al.*, 1988),  $Fe(HPO_3H)_3$  (Sghyar *et al.*, 1991) and  $Zn(HPO_3H) \cdot 0.333H_2O$  (Durand *et al.*, 1992), and with organic cations in isopropyl ammonium  $HPO_3H^-$  (Averbuch-Pouchot, 1993a), anilinium  $HPO_3H^-$  (Adrissi *et al.*, 2000), and glycinium  $HPO_3H^-$  and glycyglycinium  $HPO_3H^-$  (Averbuch-Pouchot, 1993b). The organic examples show the two different types of hydrogen bonding possible in the solid state. In isopropyl ammonium  $HPO_3H^-$  (Averbuch-Pouchot, 1993a), glycinium  $HPO_3H^-$  and glycyglycinium  $HPO_3H^-$  (Averbuch-Pouchot, 1993b), the monoanions are linked in a polymeric chain by hydrogen bonding. In anilinium  $HPO_3H^-$  (Adrissi *et al.*, 2000), the phosphite groups are hydrogen bonded in pairs which resemble the doubly hydrogen-bonded pairs normally observed in carboxylic acid species. In both arrangements, ammonium groups serve as hydrogen-bond donors in additional hydrogen bonding. We have examined the solid-state structure of the salt of the monoanionic form of  $HPO_3H_2$  with

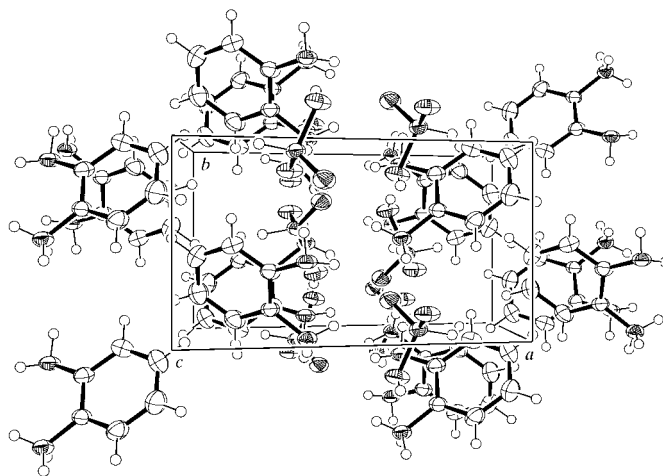
*o*-phenylenediamine, (I), and find that contrary to previous observations, there is no hydrogen bonding between the  $HPO_3H^-$  anions.



The H atom on the phosphite O1 atom is donated to the amino group,  $H11 \cdots N2$ . The ammonium group of the 2-aminoanilinium species serves as a donor to the remaining phosphite O atoms, *viz.*  $H1A \cdots O3$ ,  $H1B \cdots O3^i$  and  $H1C \cdots O2^{ii}$  (see Table 2 for details). The two H atoms of the amino group are similarly involved in hydrogen bonding to these O atoms;  $N2-H2A \cdots O2$  and  $N2-H2B \cdots O3$  (Fig. 1). The packing shows an alternation of the cationic and anionic species on planes perpendicular to the *c* direction. Other structural details are normal. However, the average C—C distance in the



**Figure 1**  
The hydrogen bonding in  $C_6H_9N_2^+ \cdot H_2PO_3^-$ . Displacement ellipsoids are shown at the 50% probability level.



**Figure 2**  
Projection on the (001) plane of the packing of  $C_6H_9N_2^+ \cdot H_2PO_3^-$  in the unit cell showing the alternation of  $C_6H_9N_2^+$  and  $H_2PO_3^-$  moieties.

phenyl ring is 1.36 Å and the C5—C6 distance is 1.346 (5) Å. The reason for these deviations from the expected values of 1.395 Å is unclear. Bond lengths (Table 1) reveal the protonated O1 atom to have a longer P—O bond [1.534 (2) Å] than both P1—O2 [1.461 (3) Å] and P1—O3 [1.471 (2) Å], which are of similar length as a result of delocalization of the negative charge between them. The C—NH<sub>3</sub><sup>+</sup> bond [1.422 (4) Å] is longer than the C—NH<sub>2</sub> bond [1.384 (4) Å], as predicted by charge considerations.

## Experimental

A single crystal of the title salt was prepared by slow evaporation of a 1:1 aqueous solution of phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) and 1,2-diaminobenzene.

### Crystal data

C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup> ·H <sub>2</sub> PO <sub>3</sub> <sup>-</sup>	$D_x = 1.517 \text{ Mg m}^{-3}$
$M_r = 190.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 11.212 (8) \text{ \AA}$	$\theta = 4.1\text{--}9.3^\circ$
$b = 5.992 (5) \text{ \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$c = 13.204 (14) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 110.16 (3)^\circ$	Block, colorless
$V = 832.7 (13) \text{ \AA}^3$	$0.1 \times 0.1 \times 0.1 \text{ mm}$
$Z = 4$	

### Data collection

Siemens P4 four-circle diffractometer	$\theta_{\text{max}} = 26.4^\circ$
$\theta$ – $2\theta$ scans	$h = -14 \rightarrow 1$
2306 measured reflections	$k = -7 \rightarrow 1$
1672 independent reflections	$l = -15 \rightarrow 16$
1359 reflections with $I > 2\sigma(I)$	3 standard reflections every 97 reflections
$R_{\text{int}} = 0.066$	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1328P)^2 + 0.2326P]$
$R(F) = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.167$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.91$	$\Delta\rho_{\text{max}} = 0.10 \text{ e \AA}^{-3}$
1672 reflections	$\Delta\rho_{\text{min}} = -0.09 \text{ e \AA}^{-3}$
111 parameters	
H-atom parameters constrained	

The H atoms on N, P and O atoms were located from a difference Fourier synthesis. The H atoms of the aromatic ring were given idealized geometry, with C—H distances of 0.93 Å. The  $U_{\text{iso}}$  values were fixed at  $0.05 \text{ \AA}^2$  for all H atoms.

Data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997).

**Table 1**

Selected geometric parameters (Å, °).

P1—O1	1.534 (2)	C1—C2	1.370 (4)
P1—O2	1.461 (3)	C2—C3	1.365 (4)
P1—O3	1.471 (2)	C3—C4	1.352 (5)
N1—C1	1.422 (4)	C4—C5	1.352 (5)
N2—C2	1.384 (4)	C5—C6	1.346 (5)
C1—C6	1.359 (4)		
O1—P1—O2	111.72 (12)	C3—C2—N2	121.3 (3)
O1—P1—O3	107.12 (13)	C1—C2—N2	121.0 (3)
O2—P1—O3	117.08 (14)	C4—C3—C2	121.0 (3)
C6—C1—C2	120.9 (3)	C3—C4—C5	120.6 (3)
C6—C1—N1	120.4 (3)	C4—C5—C6	119.4 (3)
C2—C1—N1	118.5 (3)	C1—C6—C5	120.4 (3)
C3—C2—C1	117.6 (3)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1A $\cdots$ O3	0.90	1.84	2.690 (3)	157
N1—H1B $\cdots$ O3 <sup>i</sup>	0.90	1.90	2.741 (4)	155
N1—H1C $\cdots$ O2 <sup>ii</sup>	0.90	1.79	2.669 (4)	164
N2—H2A $\cdots$ O2 <sup>iii</sup>	0.90	1.96	2.855 (4)	172
N2—H2B $\cdots$ O3 <sup>i</sup>	0.90	2.22	3.061 (4)	156
O1—H11 $\cdots$ N2 <sup>iv</sup>	0.85	1.88	2.719 (4)	168

Symmetry codes: (i)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $x, \frac{3}{2} - y, z - \frac{1}{2}$ ; (iv)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1382). Services for accessing these data are described at the back of the journal.

## References

- Adrissi, A. K., Saadi, M. & Rafiq, M. (2000). *Ann. Chim. Sci. Mater.* **25**, S121–S124.
- Averbuch-Pouchot, M.-T. (1993a). *Acta Cryst.* **C49**, 813–815.
- Averbuch-Pouchot, M.-T. (1993b). *Acta Cryst.* **C49**, 815–818.
- Colton, R. H. & Henn, D. E. (1971). *J. Chem. Soc. A*, pp. 1207–1209.
- Corbridge, D. E. C. (1956). *Acta Cryst.* **9**, 991–994.
- Durand, J., Cot, L., Sghyar, M. & Rafiq, R. (1992). *Acta Cryst.* **C48**, 1171–1173.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Handlovič, M. (1969). *Acta Cryst.* **B25**, 227–231.
- Larbot, A., Durand, J. & Cot, L. (1984). *Z. Anorg. Allg. Chem.* **508**, 154–158.
- Loub, J., Podlahova, J. & Jecny, J. (1978). *Acta Cryst.* **B34**, 32–34.
- Loukili, M., Durand, J., Cot, L. & Rafiq, M. (1988). *Acta Cryst.* **C44**, 6–8.
- Morris, R. E., Attfield, M. P. & Cheetham, A. K. (1994). *Acta Cryst.* **C50**, 473–476.
- Morris, R. E., Harrison, W. T. A., Wilkinson, A. P., Nicol, J. M. & Cheetham, A. K. (1992). *Nature (London)*, **359**, 519–522.
- Rafiq, M., Durand, J. & Cot, L. (1982). *Z. Anorg. Allg. Chem.* **484**, 187–194.
- Sghyar, M., Durand, J., Cot, L. & Rafiq, M. (1991). *Acta Cryst.* **C47**, 8–10.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.