

## Benzene-1,2-diaminium bis(hydrogen phosphonate)

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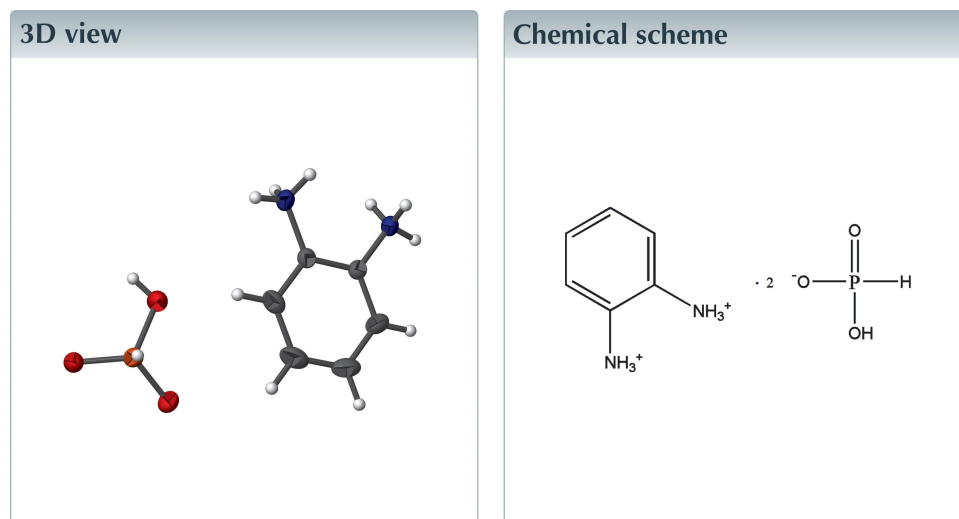
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Structural data: full structural data are available from iucrdata.iucr.org

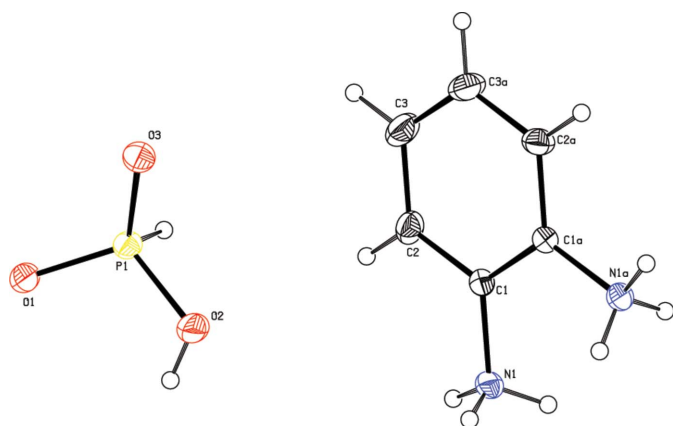
The asymmetric unit of the title molecular salt,  $C_6H_{10}N_2^{2+} \cdot 2H_2PO_3^-$ , contains half of a benzene-1,2-diaminium cation and a phosphite anion, the complete cation being generated by a crystallographic mirror plane. In the crystal,  $N-H \cdots O$  hydrogen bonds generate  $R_2^2(9)$  and  $R_2^2(8)$  ring motifs and  $O-H \cdots O$  hydrogen bonds generate an  $R_2^2(8)$  ring motif. Overall, these generate a three-dimensional framework. The crystal structure also features  $\pi-\pi$  interactions [centroid-to-centroid distance = 3.8642 (7) Å].



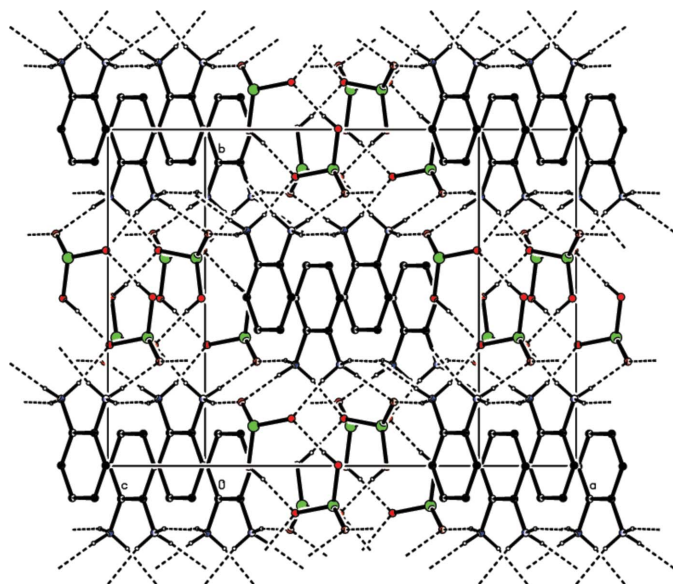
## Structure description

Inorganic-organic hybrid compounds provide a class of materials with interesting potential technological applications (Dai *et al.*, 2002). We report herein the synthesis and the crystal structure of the title molecular salt (Fig. 1). The salt contains half of a benzene-1,2-diaminium cation and a phosphite anion in the asymmetric unit, the complete cation being generated by a crystallographic mirror plane. The cation is protonated at the amine N atoms and the anion is deprotonated at a hydroxyl O atom. Bond lengths are comparable with those found in related structures (Idrissi *et al.*, 2002; Soudani *et al.*, 2013).

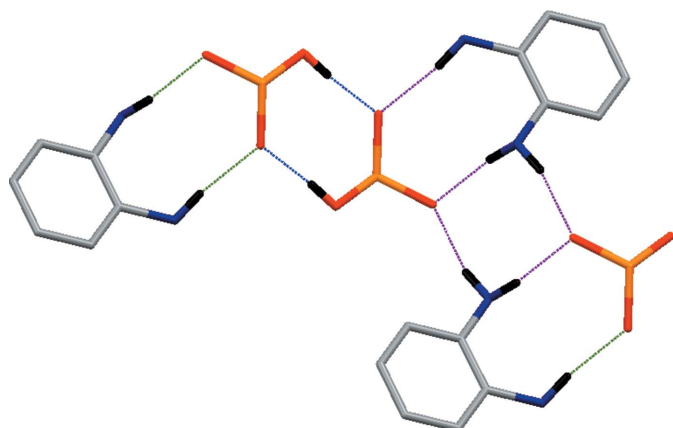
In the crystal, classical  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen bonds (Table 1, Fig. 2) which link the adjacent ions into an infinite three dimensional framework. The  $N1-H1A \cdots O1$  and  $N1-H1C \cdots O3$  hydrogen bonds generate an  $R_2^2(9)$  ring motif while an  $R_2^2(8)$  ring motif is generated by  $N1-H1C \cdots O3$  and  $N1-H1B \cdots O3$  hydrogen bonds and the  $O2-H2A \cdots O1$  hydrogen bonds generate an  $R_2^2(8)$  ring motif (Table 1, Fig. 3). The crystal structure also features  $\pi-\pi$  interactions [ $Cg1 \cdots Cg1^i$ ,  $Cg1 \cdots Cg1^{ii}$ ,  $Cg1 \cdots Cg1^{iii}$  and  $Cg1 \cdots Cg1^{iv}$  with equal distances of 3.8642 (7) Å;  $Cg1$  is the centroid of the  $C1/C2/C3/C1a/C2a/C3a$  ring; symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, 1-y, 2-z$ ; (iii)  $x, 1-y, -\frac{1}{2}+z$ ; (iv)  $x, 1-y, \frac{1}{2}+z$ ].



**Figure 1**  
The molecular structure of the title molecular salt, with atom labelling and 30% probability displacement ellipsoids. [Symmetry code: (a)  $1 - x, y, \frac{3}{2} - z$ .]



**Figure 2**  
The crystal packing of the title molecular salt viewed along the *c* axis. The hydrogen bonds are shown as dashed lines. H atoms not involving in hydrogen bonding have been omitted for clarity.



**Figure 3**  
A partial view of the crystal packing showing different ring motifs.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

<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>
N1—H1A···O1 <sup>i</sup>	0.88 (2)	1.85 (2)	2.7217 (14)	171 (2)
N1—H1B···O3 <sup>ii</sup>	0.87 (1)	1.87 (1)	2.7220 (13)	165 (1)
N1—H1C···O3 <sup>iii</sup>	0.86 (2)	1.87 (2)	2.7193 (14)	169 (1)
O2—H2A···O1 <sup>iv</sup>	0.81 (2)	1.80 (2)	2.5959 (14)	166 (2)

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

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{H}_2\text{PO}_3^-$
<i>M<sub>r</sub></i>	272.13
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	295
<i>a, b, c</i> ( $\text{\AA}$ )	13.6564 (6), 12.3755 (4), 7.7281 (3)
$\beta$ ( $^\circ$ )	117.586 (1)
<i>V</i> ( $\text{\AA}^3$ )	1157.61 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	0.39
Crystal size (mm)	0.26 $\times$ 0.24 $\times$ 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)
<i>T<sub>min</sub>, T<sub>max</sub></i>	0.699, 0.747
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	8958, 2065, 1822
<i>R<sub>int</sub></i>	0.021
( $\sin \theta/\lambda$ ) <sub>max</sub> ( $\text{\AA}^{-1}$ )	0.766
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.092, 1.07
No. of reflections	2065
No. of parameters	93
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.35, $-0.28$

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

## Synthesis and crystallization

*o*-Phenylenediamine (0.5 g) and phosphorous acid (1.6 g) were dissolved in 10 ml of Millipore water and allowed to evaporate slowly at room temperature. Good quality crystals suitable for X-ray intensity data collection were collected after a period of one week.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

The authors acknowledge the SAIF, IIT, Madras, for the data collection.

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## full crystallographic data

*IUCrData* (2016). **1**, x161591 [https://doi.org/10.1107/S2414314616015911]

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*Crystal data*

$C_6H_{10}N_2^{2+} \cdot 2H_2PO_3^-$

$M_r = 272.13$

Monoclinic,  $C2/c$

$a = 13.6564$  (6) Å

$b = 12.3755$  (4) Å

$c = 7.7281$  (3) Å

$\beta = 117.586$  (1)°

$V = 1157.61$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 568$

$D_x = 1.561$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4562 reflections

$\theta = 2.9$ – $32.4$ °

$\mu = 0.39$  mm<sup>-1</sup>

$T = 295$  K

Block, colourless

$0.26 \times 0.24 \times 0.20$  mm

*Data collection*

Bruker Kappa APEXII CCD  
diffractometer

$\omega$  and  $\phi$  scan

Absorption correction: multi-scan  
(SADABS; Bruker, 2004)

$T_{\min} = 0.699$ ,  $T_{\max} = 0.747$

8958 measured reflections

2065 independent reflections

1822 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 33.0$ °,  $\theta_{\min} = 2.4$ °

$h = -18 \rightarrow 20$

$k = -18 \rightarrow 18$

$l = -11 \rightarrow 11$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.092$

$S = 1.07$

2065 reflections

93 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.3312P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>

Extinction correction: SHELXL2016 (Sheldrick  
2015),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0168 (18)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.44886 (8)	0.40189 (8)	0.66686 (14)	0.02418 (18)
C2	0.39713 (9)	0.49869 (9)	0.58591 (17)	0.0325 (2)
H2	0.328163	0.498858	0.476438	0.039*
C3	0.44871 (12)	0.59530 (9)	0.6689 (2)	0.0408 (3)
H3	0.414075	0.660483	0.615223	0.049*
N1	0.39441 (7)	0.30090 (7)	0.57724 (13)	0.02768 (18)
O1	0.00568 (7)	0.64051 (7)	0.50188 (13)	0.0394 (2)
O2	0.15544 (8)	0.49792 (7)	0.63278 (16)	0.0452 (2)
O3	0.20193 (7)	0.68978 (7)	0.73819 (12)	0.0366 (2)
P1	0.12641 (2)	0.61846 (2)	0.57358 (4)	0.02759 (10)
H1	0.1469 (14)	0.6272 (12)	0.429 (2)	0.040 (4)*
H1A	0.4365 (11)	0.2541 (11)	0.558 (2)	0.039 (4)*
H1B	0.3384 (9)	0.3133 (11)	0.4632 (14)	0.031 (3)*
H1C	0.3696 (12)	0.2700 (12)	0.649 (2)	0.040 (4)*
H2A	0.1013 (12)	0.4605 (15)	0.573 (3)	0.059*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0213 (4)	0.0239 (4)	0.0272 (4)	0.0007 (3)	0.0111 (3)	0.0009 (3)
C2	0.0324 (5)	0.0294 (5)	0.0371 (5)	0.0081 (4)	0.0172 (4)	0.0080 (4)
C3	0.0518 (7)	0.0244 (5)	0.0538 (7)	0.0067 (4)	0.0308 (6)	0.0068 (5)
N1	0.0201 (4)	0.0267 (4)	0.0277 (4)	-0.0007 (3)	0.0039 (3)	0.0014 (3)
O1	0.0259 (4)	0.0282 (4)	0.0485 (5)	0.0018 (3)	0.0041 (3)	-0.0065 (3)
O2	0.0287 (4)	0.0268 (4)	0.0617 (6)	0.0019 (3)	0.0053 (4)	0.0001 (4)
O3	0.0281 (4)	0.0352 (4)	0.0350 (4)	-0.0029 (3)	0.0048 (3)	-0.0104 (3)
P1	0.02555 (15)	0.02557 (15)	0.02480 (14)	-0.00026 (8)	0.00585 (10)	-0.00370 (8)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—C2	1.3843 (13)	N1—H1B	0.872 (9)
C1—C1 <sup>i</sup>	1.3928 (19)	N1—H1C	0.861 (9)
C1—N1	1.4552 (12)	O1—P1	1.5012 (9)
C2—C3	1.3852 (17)	O2—P1	1.5569 (9)
C2—H2	0.9300	O2—H2A	0.811 (9)
C3—C3 <sup>i</sup>	1.381 (3)	O3—P1	1.4987 (8)
C3—H3	0.9300	P1—H1	1.276 (16)
N1—H1A	0.876 (9)		
C2—C1—C1 <sup>i</sup>	120.05 (6)	H1A—N1—H1B	106.3 (14)
C2—C1—N1	119.13 (9)	C1—N1—H1C	110.0 (11)
C1 <sup>i</sup> —C1—N1	120.81 (5)	H1A—N1—H1C	107.5 (15)
C1—C2—C3	119.61 (11)	H1B—N1—H1C	107.8 (14)
C1—C2—H2	120.2	P1—O2—H2A	109.8 (15)
C3—C2—H2	120.2	O3—P1—O1	114.38 (5)

C3 <sup>i</sup> —C3—C2	120.32 (7)	O3—P1—O2	109.47 (5)
C3 <sup>i</sup> —C3—H3	119.8	O1—P1—O2	111.67 (5)
C2—C3—H3	119.8	O3—P1—H1	110.5 (7)
C1—N1—H1A	114.7 (10)	O1—P1—H1	108.1 (8)
C1—N1—H1B	110.2 (9)	O2—P1—H1	102.1 (7)
C1 <sup>i</sup> —C1—C2—C3	1.30 (18)	C1—C2—C3—C3 <sup>i</sup>	0.2 (2)
N1—C1—C2—C3	-179.38 (10)		

Symmetry code: (i)  $-x+1, y, -z+3/2$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1A $\cdots$ O1 <sup>ii</sup>	0.88 (2)	1.85 (2)	2.7217 (14)	171 (2)
N1—H1B $\cdots$ O3 <sup>iii</sup>	0.87 (1)	1.87 (1)	2.7220 (13)	165 (1)
N1—H1C $\cdots$ O3 <sup>iv</sup>	0.86 (2)	1.87 (2)	2.7193 (14)	169 (1)
O2—H2A $\cdots$ O1 <sup>v</sup>	0.81 (2)	1.80 (2)	2.5959 (14)	166 (2)

Symmetry codes: (ii)  $x+1/2, y-1/2, z$ ; (iii)  $x, -y+1, z-1/2$ ; (iv)  $-x+1/2, y-1/2, -z+3/2$ ; (v)  $-x, -y+1, -z+1$ .