

## Bis(2,3-diaminopyridinium) phthalate dihydrate

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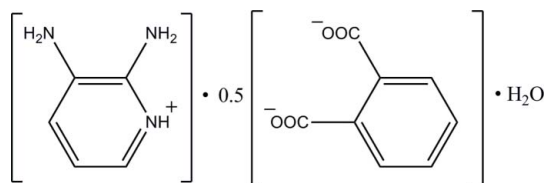
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.043;  $wR$  factor = 0.125; data-to-parameter ratio = 16.1.

The complete anion of the title hydrated molecular salt,  $2\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_8\text{H}_4\text{O}_4^-\cdot 2\text{H}_2\text{O}$ , is generated by a crystallographic twofold axis. In the crystal, the cations, anions and water molecules are connected by  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a three-dimensional network. The crystal structure also features  $\text{C}-\text{H}\cdots\pi$  interactions.

### Related literature

For background to hydrogen-bonding patterns of 2-amino-pyridine derivatives, see: Gellert & Hsu (1988); Banerjee & Murugavel (2004). For related structures, see: Hemamalini & Fun (2010*a,b,c*). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



### Experimental

#### Crystal data

$2\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_8\text{H}_4\text{O}_4^-\cdot 2\text{H}_2\text{O}$

$M_r = 420.43$

Monoclinic,  $C2/c$

$a = 15.795$  (5) Å

$b = 13.083$  (4) Å

$c = 11.012$  (4) Å

$\beta = 115.194$  (5)°

$V = 2059.2$  (11) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\mu = 0.10$  mm<sup>-1</sup>

$T = 100$  K

$0.42 \times 0.36 \times 0.03$  mm

#### Data collection

Bruker APEXII DUO CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.958$ ,  $T_{\max} = 0.997$

10343 measured reflections

2955 independent reflections

2148 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.125$

$S = 1.04$

2955 reflections

184 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.26$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$Cg1$  and  $Cg2$  are the centroids of the  $C6-C8/C6A-C8A$  and  $N1/C1-C5$  rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H5\cdots O2^i$	0.90 (2)	2.03 (2)	2.9155 (19)	169.0 (18)
$N1-H6\cdots O2^{ii}$	0.98 (2)	1.790 (19)	2.7565 (18)	170.3 (19)
$N2-H7\cdots O1^{ii}$	0.92 (2)	1.99 (2)	2.8976 (19)	168.1 (19)
$N3-H9\cdots O1W^{iii}$	0.89 (2)	2.09 (2)	2.978 (2)	179 (3)
$N3-H10\cdots O2^i$	0.89 (2)	2.23 (2)	3.078 (2)	158.8 (17)
$O1W-H11\cdots O1^{iv}$	0.95 (3)	1.86 (3)	2.7878 (18)	165 (3)
$O1W-H12\cdots O1^v$	0.92 (2)	1.99 (2)	2.8641 (18)	158.2 (19)
$C3-H2\cdots O1W^{vi}$	0.984 (17)	2.516 (18)	3.369 (2)	145.0 (14)
$C4-H8\cdots Cg1^{iii}$	1.01 (2)	2.76 (2)	3.629 (2)	144.3 (15)
$C6-H3\cdots Cg2^{vii}$	0.959 (18)	2.568 (18)	3.497 (2)	163.4 (14)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6574).

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**supplementary materials**

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## Bis(2,3-diaminopyridinium) phthalate dihydrate

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### Comment

2-Aminopyridine and its derivatives are among the most frequently used synthons in supramolecular chemistry based on hydrogen bonds (Gellert & Hsu, 1988; Banerjee & Murugavel, 2004). A series of similar complexes formed from 2-aminopyridine and carboxylates has been reported previously (Hemamalini & Fun, 2010*a,b,c*). The present work, 2,3-diaminopyridinium phthalate dihydrate, (2/1/1) (I), is a continuation of our structural study of complexes of the 2,3-diaminopyridinium system.

The asymmetric unit of the title compound, (I), contains one 2,3-diamino-pyridinium cation, a half of phthalate anion (which lies on a twofold axis;  $-x+1, y, -z+1/2$ ) and a water molecule as shown in Fig. 1. The dihedral angle between the pyridine (N1/C1–C5) and benzene (C6–C8/ C6A–C8A) ring is  $80.61(7)^\circ$ .

In the crystal structure (Fig. 2), the ion pairs and water molecules are connected *via* N—H $\cdots$ O, O—H $\cdots$ O and C—H $\cdots$ O (Table 1) hydrogen bonds forming a three-dimensional network. The crystal structure is further stabilized by C—H $\cdots$  $\pi$  interactions involving the centroids of the C6–C8/C6A–C8A (Cg1) and N1/C1–C5 (Cg2) rings.

### Experimental

A hot methanol solution (20 ml) of 2,3-diaminopyridine (27 mg, Aldrich) and phthalic acid (42 mg, Merck) were mixed and warmed over a magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and brown plates of the title compound appeared after a few days.

### Refinement

All hydrogen atoms were located from a difference Fourier maps and refined freely [N—H =  $0.89(2)$ – $0.98(2)$  Å; O—H =  $0.91(2)$ – $0.95(3)$  Å and C—H =  $0.959(18)$ – $1.01(2)$  Å]. The highest residual electron density peak is located at  $0.73$  Å from C9 and the deepest hole is located at  $0.78$  Å from C9.

### Figures

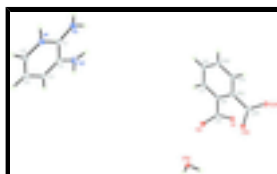


Fig. 1. The molecule of (I) with 30% probability displacement ellipsoids. Atoms labelled A are generated by  $-x+1, y, -z+1/2$ .

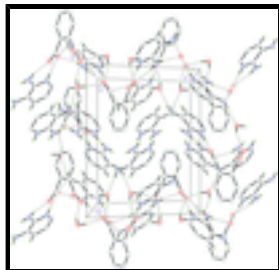
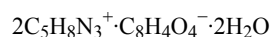


Fig. 2. The crystal packing of the title compound showing hydrogen-bonded (dashed lines) networks. H atoms not involved in hydrogen bond interactions are omitted for clarity.

## Bis(2,3-diaminopyridinium) benzene-1,2-dicarboxylate dihydrate

### Crystal data



$$M_r = 420.43$$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$$a = 15.795\ (5)\ \text{\AA}$$

$$b = 13.083\ (4)\ \text{\AA}$$

$$c = 11.012\ (4)\ \text{\AA}$$

$$\beta = 115.194\ (5)^\circ$$

$$V = 2059.2\ (11)\ \text{\AA}^3$$

$$Z = 4$$

$$F(000) = 888$$

$$D_x = 1.356\ \text{Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3390 reflections

$$\theta = 2.8\text{--}29.8^\circ$$

$$\mu = 0.10\ \text{mm}^{-1}$$

$$T = 100\ \text{K}$$

Plate, brown

$$0.42 \times 0.36 \times 0.03\ \text{mm}$$

### Data collection

Bruker APEXII DUO CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2009)

$$T_{\min} = 0.958, T_{\max} = 0.997$$

10343 measured reflections

2955 independent reflections

2148 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.042$$

$$\theta_{\max} = 29.9^\circ, \theta_{\min} = 2.1^\circ$$

$$h = -22 \rightarrow 22$$

$$k = -18 \rightarrow 18$$

$$l = -14 \rightarrow 14$$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.043$$

$$wR(F^2) = 0.125$$

$$S = 1.04$$

2955 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.7423P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

184 parameters

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

### Special details

**Experimental.** The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.23077 (8)	0.94380 (9)	1.03746 (11)	0.0227 (3)
N2	0.30262 (8)	0.94315 (10)	0.89459 (13)	0.0256 (3)
N3	0.17815 (10)	0.78666 (11)	0.74285 (14)	0.0330 (3)
C1	0.23819 (9)	0.90400 (10)	0.93023 (13)	0.0192 (3)
C2	0.17516 (9)	0.82430 (9)	0.85688 (13)	0.0210 (3)
C3	0.11106 (9)	0.79131 (11)	0.90331 (14)	0.0249 (3)
C4	0.10585 (11)	0.83570 (13)	1.01540 (15)	0.0313 (3)
C5	0.16621 (11)	0.91224 (13)	1.08149 (15)	0.0310 (3)
O1	0.43751 (6)	0.07071 (7)	0.10193 (9)	0.0225 (2)
O2	0.32273 (6)	0.12167 (7)	0.15491 (9)	0.0225 (2)
C6	0.45346 (10)	0.41720 (10)	0.20469 (14)	0.0242 (3)
C7	0.40590 (9)	0.32537 (10)	0.16012 (13)	0.0201 (3)
C8	0.45249 (8)	0.23274 (9)	0.20552 (12)	0.0160 (2)
C9	0.40094 (8)	0.13405 (9)	0.15149 (12)	0.0168 (2)
O1W	0.45043 (8)	0.10881 (8)	0.86130 (12)	0.0315 (3)
H1	0.3388 (12)	0.3242 (12)	0.0959 (17)	0.028 (4)*
H2	0.0692 (11)	0.7346 (13)	0.8557 (17)	0.026 (4)*
H3	0.4209 (12)	0.4807 (14)	0.1749 (17)	0.032 (4)*
H4	0.1689 (13)	0.9496 (15)	1.160 (2)	0.043 (5)*
H5	0.3138 (13)	0.9165 (14)	0.8275 (19)	0.033 (5)*
H6	0.2697 (12)	1.0029 (15)	1.0806 (18)	0.036 (5)*
H7	0.3468 (13)	0.9879 (15)	0.9506 (19)	0.039 (5)*
H8	0.0557 (13)	0.8149 (14)	1.044 (2)	0.042 (5)*
H9	0.1404 (14)	0.7328 (17)	0.712 (2)	0.046 (5)*
H10	0.2265 (14)	0.7967 (14)	0.723 (2)	0.040 (5)*
H11	0.4555 (16)	0.1035 (17)	0.950 (3)	0.064 (7)*
H12	0.4828 (16)	0.0542 (18)	0.850 (2)	0.062 (7)*

## supplementary materials

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0235 (6)	0.0244 (6)	0.0181 (5)	-0.0068 (5)	0.0070 (4)	-0.0020 (4)
N2	0.0237 (6)	0.0281 (6)	0.0260 (6)	-0.0104 (5)	0.0116 (5)	-0.0096 (5)
N3	0.0323 (7)	0.0332 (7)	0.0364 (7)	-0.0153 (6)	0.0174 (6)	-0.0188 (6)
C1	0.0186 (6)	0.0182 (6)	0.0175 (6)	-0.0001 (4)	0.0043 (5)	0.0016 (4)
C2	0.0195 (6)	0.0181 (6)	0.0197 (6)	-0.0001 (5)	0.0028 (5)	0.0004 (5)
C3	0.0232 (6)	0.0223 (6)	0.0224 (6)	-0.0060 (5)	0.0033 (5)	0.0024 (5)
C4	0.0312 (7)	0.0392 (8)	0.0237 (7)	-0.0138 (6)	0.0119 (6)	0.0001 (6)
C5	0.0348 (8)	0.0393 (8)	0.0223 (7)	-0.0128 (6)	0.0153 (6)	-0.0043 (6)
O1	0.0229 (5)	0.0220 (5)	0.0222 (5)	-0.0006 (4)	0.0093 (4)	-0.0059 (4)
O2	0.0205 (4)	0.0227 (5)	0.0253 (5)	-0.0041 (4)	0.0106 (4)	-0.0029 (4)
C6	0.0252 (7)	0.0173 (6)	0.0297 (7)	0.0038 (5)	0.0113 (6)	0.0033 (5)
C7	0.0191 (6)	0.0200 (6)	0.0196 (6)	0.0017 (5)	0.0068 (5)	0.0022 (4)
C8	0.0180 (6)	0.0171 (6)	0.0140 (5)	-0.0005 (4)	0.0078 (4)	-0.0002 (4)
C9	0.0178 (5)	0.0173 (6)	0.0124 (5)	0.0007 (4)	0.0036 (4)	0.0006 (4)
O1W	0.0361 (6)	0.0276 (6)	0.0363 (6)	0.0102 (4)	0.0208 (5)	0.0120 (4)

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

N1—C1	1.3404 (17)	C4—H8	1.01 (2)
N1—C5	1.3663 (18)	C5—H4	0.98 (2)
N1—H6	0.98 (2)	O1—C9	1.2596 (15)
N2—C1	1.3388 (17)	O2—C9	1.2623 (15)
N2—H5	0.899 (19)	C6—C6 <sup>i</sup>	1.382 (3)
N2—H7	0.92 (2)	C6—C7	1.3910 (19)
N3—C2	1.3683 (19)	C6—H3	0.959 (18)
N3—H9	0.89 (2)	C7—C8	1.3954 (17)
N3—H10	0.89 (2)	C7—H1	0.993 (17)
C1—C2	1.4304 (18)	C8—C8 <sup>i</sup>	1.400 (2)
C2—C3	1.383 (2)	C8—C9	1.5072 (17)
C3—C4	1.398 (2)	O1W—H11	0.95 (3)
C3—H2	0.983 (17)	O1W—H12	0.91 (2)
C4—C5	1.360 (2)		
C1—N1—C5	123.61 (12)	C5—C4—H8	119.7 (11)
C1—N1—H6	117.6 (11)	C3—C4—H8	121.0 (11)
C5—N1—H6	118.5 (10)	C4—C5—N1	119.44 (14)
C1—N2—H5	122.2 (12)	C4—C5—H4	126.7 (11)
C1—N2—H7	120.2 (11)	N1—C5—H4	113.8 (11)
H5—N2—H7	116.0 (16)	C6 <sup>i</sup> —C6—C7	120.25 (8)
C2—N3—H9	111.0 (13)	C6 <sup>i</sup> —C6—H3	119.9 (10)
C2—N3—H10	122.9 (13)	C7—C6—H3	119.8 (10)
H9—N3—H10	121.6 (18)	C6—C7—C8	120.03 (12)
N2—C1—N1	118.16 (12)	C6—C7—H1	121.1 (10)
N2—C1—C2	123.13 (12)	C8—C7—H1	118.9 (10)
N1—C1—C2	118.67 (12)	C7—C8—C8 <sup>i</sup>	119.70 (7)

N3—C2—C3	122.93 (12)	C7—C8—C9	119.26 (11)
N3—C2—C1	119.54 (12)	C8 <sup>i</sup> —C8—C9	120.95 (6)
C3—C2—C1	117.49 (12)	O1—C9—O2	124.30 (11)
C2—C3—C4	121.61 (13)	O1—C9—C8	117.67 (11)
C2—C3—H2	118.0 (10)	O2—C9—C8	117.99 (11)
C4—C3—H2	120.4 (10)	H11—O1W—H12	105.6 (19)
C5—C4—C3	119.14 (13)		
C5—N1—C1—N2	178.22 (13)	C3—C4—C5—N1	-0.3 (2)
C5—N1—C1—C2	0.2 (2)	C1—N1—C5—C4	0.6 (2)
N2—C1—C2—N3	-1.5 (2)	C6 <sup>i</sup> —C6—C7—C8	-0.9 (2)
N1—C1—C2—N3	176.36 (12)	C6—C7—C8—C8 <sup>i</sup>	-0.9 (2)
N2—C1—C2—C3	-179.27 (13)	C6—C7—C8—C9	-177.35 (12)
N1—C1—C2—C3	-1.39 (18)	C7—C8—C9—O1	126.40 (13)
N3—C2—C3—C4	-175.91 (14)	C8 <sup>i</sup> —C8—C9—O1	-50.01 (19)
C1—C2—C3—C4	1.8 (2)	C7—C8—C9—O2	-51.38 (16)
C2—C3—C4—C5	-0.9 (2)	C8 <sup>i</sup> —C8—C9—O2	132.22 (15)

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

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

Cg1 and Cg2 are the centroids of the C6—C8/C6A—C8A and N1/C1—C5 rings, respectively.

<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>
N2—H5 $\cdots$ O2 <sup>ii</sup>	0.90 (2)	2.03 (2)	2.9155 (19)	169.0 (18)
N1—H6 $\cdots$ O2 <sup>iii</sup>	0.98 (2)	1.790 (19)	2.7565 (18)	170.3 (19)
N2—H7 $\cdots$ O1 <sup>iii</sup>	0.92 (2)	1.99 (2)	2.8976 (19)	168.1 (19)
N3—H9 $\cdots$ O1W <sup>iv</sup>	0.89 (2)	2.09 (2)	2.978 (2)	179 (3)
N3—H10 $\cdots$ O2 <sup>ii</sup>	0.89 (2)	2.23 (2)	3.078 (2)	158.8 (17)
O1W—H11 $\cdots$ O1 <sup>v</sup>	0.95 (3)	1.86 (3)	2.7878 (18)	165 (3)
O1W—H12 $\cdots$ O1 <sup>vi</sup>	0.92 (2)	1.99 (2)	2.8641 (18)	158.2 (19)
C3—H2 $\cdots$ O1W <sup>vii</sup>	0.984 (17)	2.516 (18)	3.369 (2)	145.0 (14)
C4—H8 $\cdots$ Cg1 <sup>iv</sup>	1.01 (2)	2.76 (2)	3.629 (2)	144.3 (15)
C6—H3 $\cdots$ Cg2 <sup>viii</sup>	0.959 (18)	2.568 (18)	3.497 (2)	163.4 (14)

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

Fig. 1

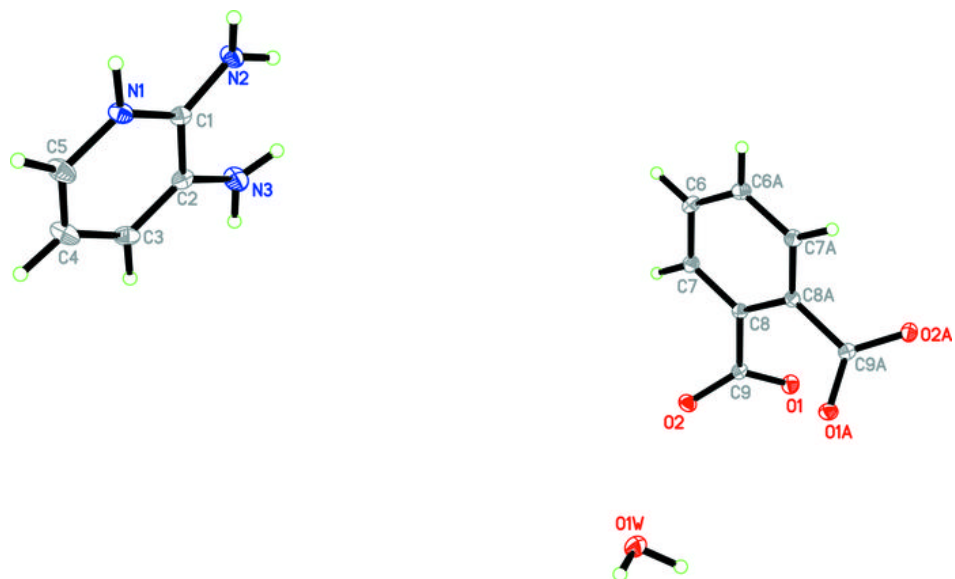




Fig. 2

