Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 2-Aminopyridinium 4-methylbenzoate dihydrate

**Yun Liu and Jie Li***

Basic Experiment Teaching Center, Henan University, Kaifeng 475004, People's Republic of China
Correspondence e-mail: lijie_78@126.com

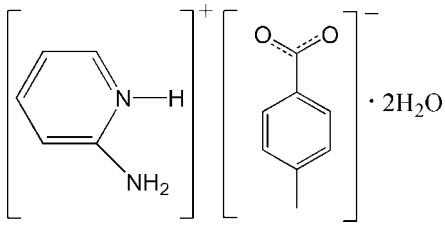
Received 28 September 2008; accepted 30 September 2008

Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.032; $wR$ factor = 0.089; data-to-parameter ratio = 9.0.

The crystal structure of the title salt, $C_5H_7N_2^+\cdot C_8H_7O_2^-\cdot 2H_2O$, contains a three-dimensional supramolecular framework constructed through N—H···O and O—H···O hydrogen bonds.

## Related literature

For a related structure, see: Wang & Wei (2005).



## Experimental

### Crystal data

$C_5H_7N_2^+\cdot C_8H_7O_2^-\cdot 2H_2O$
$M_r$ = 266.29
Monoclinic, $Cc$
$a$ = 12.2059 (14) Å
$b$ = 13.1531 (16) Å
$c$ = 8.9937 (11) Å
$\beta$ = 96.617 (2)°
$V$ = 1434.3 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 296 (2) K
0.23 × 0.18 × 0.16 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min}$ = 0.979, $T_{max}$ = 0.985
4203 measured reflections
1567 independent reflections
1406 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
$S$ = 1.04
1567 reflections
175 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.12 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.12 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$C$···O1$W^{i}$ | 0.86 | 2.06 | 2.906 (2) | 169 |
| N1—H1$A$···O1 | 0.86 | 1.82 | 2.676 (2) | 173 |
| N2—H2$B$···O2 | 0.86 | 1.98 | 2.826 (3) | 168 |
| O1$W$—H1$AW$···O2$W$ | 0.84 | 1.88 | 2.705 (2) | 168 |
| O1$W$—H1$BW$···O2 | 0.83 | 1.92 | 2.739 (2) | 169 |
| O2$W$—H2$AW$···O1$W^{ii}$ | 0.83 | 1.93 | 2.758 (2) | 172 |
| O2$W$—H2$BW$···O1$^{iii}$ | 0.83 | 1.93 | 2.732 (2) | 160 |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

This work was supported by the Basic Research Foundation for Natural Science of Henan University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2811).

## References

Bruker (2001). *SAINT-Plus* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wang, Z.-L. & Wei, L.-H. (2005). *Acta Cryst.* E**61**, o3129–o3130.

# supplementary materials

*Acta Cryst.* (2008). E**64**, o2057 [ **doi:10.1107/S160053680803153X** ]

# 2-Aminopyridinium 4-methylbenzoate dihydrate

**Y. Liu and J. Li**

## Comment

Currently, many groups are investigating supramolecular structures of cocrystals containing organic acids and organic bases resulting from hydrogen bonding (Wang & Wei, 2005). The asymmetric unit of the title compound, (I), is composed of 4-methylbenzoate anion, one 2-amino pyridinium cation and two water molecules in general positions (Fig. 1). The carboxyl group of 4-methylbenzoic acid is deprotonated. In the crystal, 2-amino pyridinium and 4-methylbenzoic acid anion together with water molecules are linked into a three-dimensional supramolecular framework by multiple N—H···O and O—H···O hydrogen bonds (Fig. 2 and Table 1).

## Experimental

4-Methylbenzoic acid (1 mmol, 0.135 g) and 2-aminopyridine (1 mmol, 0.094 g) were dissolved in 20 ml of distilled water. The solution was stirred for about 20 min at 353 K, avoiding evaporation of 2-aminopyridine. Colourless blocks of (I) were obtained from the filtrate after seven days.

## Refinement

Anomalous dispersion was negligible and Friedel pairs were merged before refinement.

The H atoms were geometrically placed with C—H = 0.93–0.96 Å, N—H = 0.86 Å and O—H = 0.83 Å, and were refined as riding with $U_{iso}(H)=1.2U_{eq}$(N and $C_{methylidyne}$) and $U_{iso}(H)=1.5U_{eq}$(O or $C_{methyl}$).

## Figures

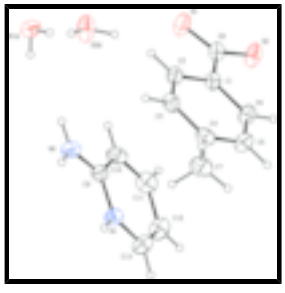


Fig. 1. The molecular structure of (I), with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

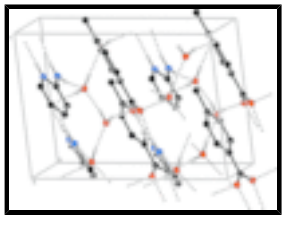


Fig. 2. Three-dimensional structure of (I), with H bonds indicated by dashed lines. For clarity, H atoms not involved in hydrogen bonds are omitted.

### 2-Aminopyridinium 4-methylbenzoate dihydrate

*Crystal data*

| | |
|---|---|
| $C_5H_7N_2^+·C_8H_7O_2^-·2H_2O$ | $F_{000}$ = 568 |
| $M_r$ = 266.29 | $D_x$ = 1.233 Mg m$^{-3}$ |
| Monoclinic, *Cc* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: C -2yc | Cell parameters from 1977 reflections |
| *a* = 12.2059 (14) Å | θ = 2.3–26.6º |
| *b* = 13.1531 (16) Å | μ = 0.09 mm$^{-1}$ |
| *c* = 8.9937 (11) Å | *T* = 296 (2) K |
| β = 96.617 (2)º | Block, colorless |
| *V* = 1434.3 (3) Å$^3$ | 0.23 × 0.18 × 0.16 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 1567 independent reflections |
| Radiation source: fine-focus sealed tube | 1406 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.019 |
| *T* = 296(2) K | $\theta_{max}$ = 27.0º |
| ω scans | $\theta_{min}$ = 2.3º |
| Absorption correction: Multi-scan (SADABS; Sheldrick, 2001) | *h* = −6→15 |
| $T_{min}$ = 0.979, $T_{max}$ = 0.985 | *k* = −16→16 |
| 4203 measured reflections | *l* = −11→11 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.032 | H-atom parameters constrained |
| $wR(F^2)$ = 0.089 | $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1161P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.04 | $(\Delta/\sigma)_{max} < 0.001$ |
| 1567 reflections | $\Delta\rho_{max}$ = 0.12 e Å$^{-3}$ |
| 175 parameters | $\Delta\rho_{min}$ = −0.11 e Å$^{-3}$ |
| 8 restraints | Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.019 (2) |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.48260 (16) | 0.20609 (14) | 0.6527 (2) | 0.0505 (4) |
| C2 | 0.43746 (18) | 0.28865 (16) | 0.7214 (2) | 0.0563 (5) |
| H2A | 0.4359 | 0.3522 | 0.6758 | 0.068* |
| C3 | 0.39515 (17) | 0.27745 (17) | 0.8558 (2) | 0.0606 (5) |
| H3A | 0.3662 | 0.3338 | 0.9000 | 0.073* |
| C4 | 0.39467 (17) | 0.18356 (19) | 0.9270 (2) | 0.0607 (5) |
| C5 | 0.4400 (2) | 0.10125 (18) | 0.8588 (3) | 0.0682 (6) |
| H5A | 0.4413 | 0.0377 | 0.9044 | 0.082* |
| C6 | 0.4834 (2) | 0.11256 (16) | 0.7238 (2) | 0.0625 (6) |
| H6A | 0.5135 | 0.0565 | 0.6803 | 0.075* |
| C7 | 0.3478 (3) | 0.1719 (2) | 1.0746 (4) | 0.0832 (7) |
| H7A | 0.3541 | 0.1023 | 1.1065 | 0.125* |
| H7B | 0.2715 | 0.1916 | 1.0626 | 0.125* |
| H7C | 0.3881 | 0.2145 | 1.1485 | 0.125* |
| C8 | 0.52854 (18) | 0.21761 (16) | 0.5061 (2) | 0.0559 (5) |
| C9 | 0.64742 (16) | 0.25294 (16) | 0.1096 (2) | 0.0540 (5) |
| C10 | 0.6947 (2) | 0.2780 (2) | −0.0219 (3) | 0.0662 (6) |
| H10A | 0.7279 | 0.2279 | −0.0741 | 0.079* |
| C11 | 0.6915 (2) | 0.3748 (2) | −0.0715 (3) | 0.0766 (7) |
| H11A | 0.7248 | 0.3912 | −0.1563 | 0.092* |

| | | | | |
|---|---|---|---|---|
| C12 | 0.6383 (3) | 0.4515 (2) | 0.0034 (3) | 0.0775 (7) |
| H12A | 0.6346 | 0.5180 | −0.0321 | 0.093* |
| C13 | 0.5934 (2) | 0.42557 (17) | 0.1272 (3) | 0.0679 (6) |
| H13A | 0.5575 | 0.4747 | 0.1780 | 0.082* |
| N1 | 0.59936 (16) | 0.32882 (13) | 0.17948 (19) | 0.0572 (4) |
| H1A | 0.5713 | 0.3152 | 0.2607 | 0.069* |
| N2 | 0.64687 (16) | 0.16065 (14) | 0.1677 (2) | 0.0616 (4) |
| H2B | 0.6164 | 0.1502 | 0.2479 | 0.074* |
| H2C | 0.6770 | 0.1110 | 0.1252 | 0.074* |
| O1 | 0.51630 (17) | 0.30246 (12) | 0.4395 (2) | 0.0748 (5) |
| O2 | 0.57598 (17) | 0.14398 (13) | 0.4549 (2) | 0.0774 (5) |
| O1W | 0.74860 (13) | 0.02177 (11) | 0.56348 (16) | 0.0631 (4) |
| H1AW | 0.7767 | 0.0431 | 0.6471 | 0.076* |
| H1BW | 0.7022 | 0.0649 | 0.5296 | 0.076* |
| O2W | 0.85359 (18) | 0.06355 (15) | 0.8382 (2) | 0.0886 (6) |
| H2AW | 0.8275 | 0.0340 | 0.9081 | 0.133* |
| H2BW | 0.8906 | 0.1114 | 0.8791 | 0.133* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0524 (10) | 0.0485 (10) | 0.0491 (10) | 0.0065 (8) | −0.0009 (8) | −0.0026 (8) |
| C2 | 0.0571 (11) | 0.0491 (10) | 0.0612 (12) | 0.0059 (8) | 0.0005 (9) | −0.0031 (9) |
| C3 | 0.0565 (11) | 0.0624 (12) | 0.0624 (13) | 0.0081 (9) | 0.0050 (10) | −0.0100 (10) |
| C4 | 0.0511 (11) | 0.0738 (14) | 0.0569 (13) | −0.0057 (10) | 0.0045 (9) | −0.0047 (10) |
| C5 | 0.0847 (16) | 0.0545 (11) | 0.0661 (13) | −0.0024 (11) | 0.0115 (11) | 0.0063 (10) |
| C6 | 0.0797 (15) | 0.0484 (10) | 0.0595 (12) | 0.0090 (10) | 0.0086 (11) | −0.0039 (9) |
| C7 | 0.0784 (16) | 0.104 (2) | 0.0709 (15) | −0.0051 (15) | 0.0234 (13) | 0.0001 (14) |
| C8 | 0.0607 (11) | 0.0550 (11) | 0.0516 (10) | 0.0136 (9) | 0.0042 (9) | 0.0013 (8) |
| C9 | 0.0496 (10) | 0.0573 (11) | 0.0529 (11) | 0.0052 (9) | −0.0032 (9) | −0.0067 (9) |
| C10 | 0.0607 (13) | 0.0826 (16) | 0.0561 (12) | 0.0112 (11) | 0.0105 (10) | −0.0046 (11) |
| C11 | 0.0808 (17) | 0.0914 (18) | 0.0589 (13) | −0.0001 (13) | 0.0133 (12) | 0.0119 (13) |
| C12 | 0.101 (2) | 0.0654 (14) | 0.0632 (14) | −0.0019 (13) | −0.0014 (12) | 0.0081 (11) |
| C13 | 0.0905 (16) | 0.0550 (12) | 0.0565 (12) | 0.0086 (11) | 0.0007 (11) | −0.0039 (10) |
| N1 | 0.0655 (10) | 0.0568 (9) | 0.0492 (9) | 0.0060 (8) | 0.0060 (7) | −0.0021 (7) |
| N2 | 0.0652 (10) | 0.0570 (10) | 0.0627 (10) | 0.0110 (8) | 0.0080 (8) | −0.0044 (8) |
| O1 | 0.0988 (12) | 0.0615 (9) | 0.0686 (10) | 0.0280 (9) | 0.0295 (9) | 0.0155 (8) |
| O2 | 0.1095 (13) | 0.0620 (9) | 0.0638 (9) | 0.0332 (9) | 0.0228 (8) | 0.0046 (7) |
| O1W | 0.0750 (9) | 0.0564 (8) | 0.0593 (8) | 0.0100 (7) | 0.0137 (7) | −0.0006 (7) |
| O2W | 0.1081 (15) | 0.0954 (13) | 0.0626 (9) | −0.0426 (12) | 0.0114 (10) | −0.0026 (9) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C6 | 1.386 (3) | C9—N1 | 1.349 (3) |
| C1—C2 | 1.394 (3) | C9—C10 | 1.414 (3) |
| C1—C8 | 1.499 (3) | C10—C11 | 1.347 (4) |
| C2—C3 | 1.375 (3) | C10—H10A | 0.9300 |
| C2—H2A | 0.9300 | C11—C12 | 1.412 (4) |
| C3—C4 | 1.391 (3) | C11—H11A | 0.9300 |

| | | | |
|---|---|---|---|
| C3—H3A | 0.9300 | C12—C13 | 1.341 (4) |
| C4—C5 | 1.390 (4) | C12—H12A | 0.9300 |
| C4—C7 | 1.513 (4) | C13—N1 | 1.356 (3) |
| C5—C6 | 1.388 (4) | C13—H13A | 0.9300 |
| C5—H5A | 0.9300 | N1—H1A | 0.8600 |
| C6—H6A | 0.9300 | N2—H2B | 0.8600 |
| C7—H7A | 0.9600 | N2—H2C | 0.8600 |
| C7—H7B | 0.9600 | O1W—H1AW | 0.8386 |
| C7—H7C | 0.9600 | O1W—H1BW | 0.8339 |
| C8—O2 | 1.244 (3) | O2W—H2AW | 0.8328 |
| C8—O1 | 1.267 (3) | O2W—H2BW | 0.8345 |
| C9—N2 | 1.322 (3) | | |
| C6—C1—C2 | 118.00 (19) | O2—C8—C1 | 118.96 (18) |
| C6—C1—C8 | 120.78 (17) | O1—C8—C1 | 117.98 (18) |
| C2—C1—C8 | 121.22 (17) | N2—C9—N1 | 118.26 (19) |
| C3—C2—C1 | 120.9 (2) | N2—C9—C10 | 124.5 (2) |
| C3—C2—H2A | 119.5 | N1—C9—C10 | 117.3 (2) |
| C1—C2—H2A | 119.5 | C11—C10—C9 | 119.9 (2) |
| C2—C3—C4 | 121.4 (2) | C11—C10—H10A | 120.0 |
| C2—C3—H3A | 119.3 | C9—C10—H10A | 120.0 |
| C4—C3—H3A | 119.3 | C10—C11—C12 | 121.0 (2) |
| C5—C4—C3 | 117.7 (2) | C10—C11—H11A | 119.5 |
| C5—C4—C7 | 121.2 (2) | C12—C11—H11A | 119.5 |
| C3—C4—C7 | 121.0 (2) | C13—C12—C11 | 117.9 (2) |
| C6—C5—C4 | 120.9 (2) | C13—C12—H12A | 121.0 |
| C6—C5—H5A | 119.5 | C11—C12—H12A | 121.0 |
| C4—C5—H5A | 119.5 | C12—C13—N1 | 121.1 (2) |
| C1—C6—C5 | 121.0 (2) | C12—C13—H13A | 119.4 |
| C1—C6—H6A | 119.5 | N1—C13—H13A | 119.4 |
| C5—C6—H6A | 119.5 | C9—N1—C13 | 122.8 (2) |
| C4—C7—H7A | 109.5 | C9—N1—H1A | 118.6 |
| C4—C7—H7B | 109.5 | C13—N1—H1A | 118.6 |
| H7A—C7—H7B | 109.5 | C9—N2—H2B | 120.0 |
| C4—C7—H7C | 109.5 | C9—N2—H2C | 120.0 |
| H7A—C7—H7C | 109.5 | H2B—N2—H2C | 120.0 |
| H7B—C7—H7C | 109.5 | H1AW—O1W—H1BW | 106.9 |
| O2—C8—O1 | 123.1 (2) | H2AW—O2W—H2BW | 104.7 |
| C6—C1—C2—C3 | 0.1 (3) | C2—C1—C8—O2 | 174.2 (2) |
| C8—C1—C2—C3 | 179.8 (2) | C6—C1—C8—O1 | 173.5 (2) |
| C1—C2—C3—C4 | −0.7 (3) | C2—C1—C8—O1 | −6.2 (3) |
| C2—C3—C4—C5 | 0.9 (3) | N2—C9—C10—C11 | −179.6 (2) |
| C2—C3—C4—C7 | −179.9 (2) | N1—C9—C10—C11 | 0.7 (3) |
| C3—C4—C5—C6 | −0.5 (3) | C9—C10—C11—C12 | −2.1 (4) |
| C7—C4—C5—C6 | −179.6 (2) | C10—C11—C12—C13 | 1.5 (4) |
| C2—C1—C6—C5 | 0.4 (3) | C11—C12—C13—N1 | 0.4 (4) |
| C8—C1—C6—C5 | −179.3 (2) | N2—C9—N1—C13 | −178.5 (2) |
| C4—C5—C6—C1 | −0.2 (4) | C10—C9—N1—C13 | 1.2 (3) |
| C6—C1—C8—O2 | −6.0 (3) | C12—C13—N1—C9 | −1.8 (4) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2C···O1W$^{i}$ | 0.86 | 2.06 | 2.906 (2) | 169 |
| N1—H1A···O1 | 0.86 | 1.82 | 2.676 (2) | 173 |
| N2—H2B···O2 | 0.86 | 1.98 | 2.826 (3) | 168 |
| O1W—H1AW···O2W | 0.84 | 1.88 | 2.705 (2) | 168 |
| O1W—H1BW···O2 | 0.83 | 1.92 | 2.739 (2) | 169 |
| O2W—H2AW···O1W$^{ii}$ | 0.83 | 1.93 | 2.758 (2) | 172 |
| O2W—H2BW···O1$^{iii}$ | 0.83 | 1.93 | 2.732 (2) | 160 |

Symmetry codes: (i) *x*, −*y*, *z*−1/2; (ii) *x*, −*y*, *z*+1/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2.

**Fig. 1**

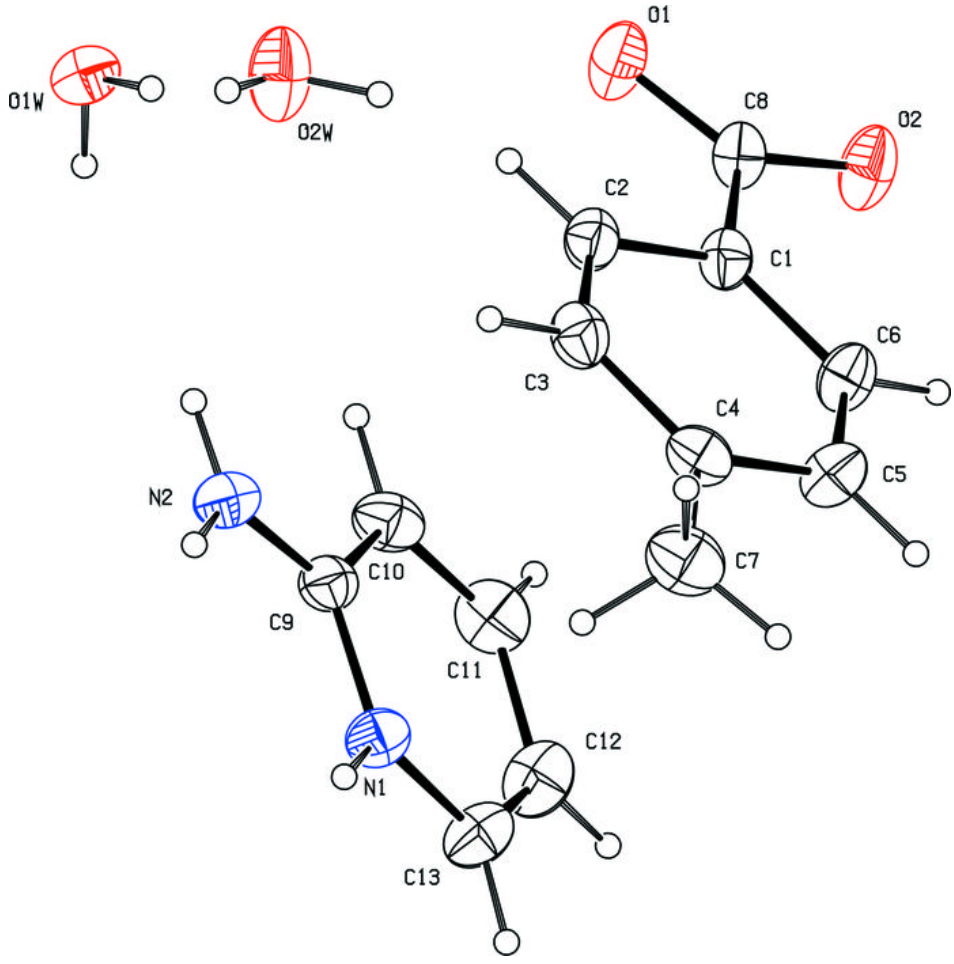


**Fig. 2**