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# Bis(2-amino-4-methylpyridinium) terephthalate tetrahydrate

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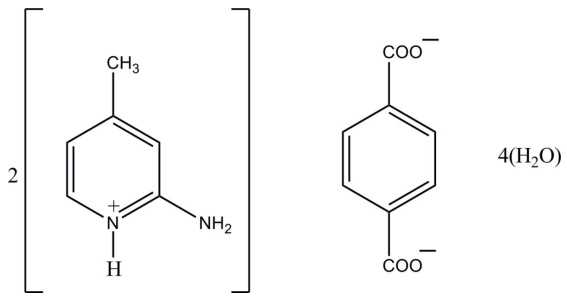
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.036; $wR$ factor = 0.101; data-to-parameter ratio = 9.4.

In the crystal structure of the title salt, $2C_6H_9N_2^+\cdot C_8H_4O_4^{2-}\cdot 4H_2O$, the terephthalate carboxylate groups interacts with the 2-amino-4-methylpyridinium cations *via* a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. The water molecules form an $R_6^6(12)$ ring motif through O—H···O hydrogen bonds and these motifs are fused, forming a supramolecular chain along the $c$ axis. The $R_2^2(8)$ and $R_6^6(12)$ ring motifs are connected *via* O—H···O hydrogen bonds. In addition, $\pi$–$\pi$ stacking interactions are observed between the pyridinium rings [centroid–centroid distance = 3.522 (12) Å].

## Related literature

For details of non-covalent interactions, see: Desiraju (2007); Corna *et al.* (2004); Aakeröy & Seddon (1993). For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For the applications of terephthalic acid, see: Serre *et al.* (2007); Mukherjee *et al.* (2004); Sun *et al.* (2000); Lynch & Jones (2004); Spencer *et al.* (2004); Devi & Muthiah (2007). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).




## Experimental

### Crystal data

$2C_6H_9N_2^+\cdot C_8H_4O_4^{2-}\cdot 4H_2O$
$M_r$ = 454.48
Monoclinic, *Cc*
$a$ = 17.6290 (16) Å
$b$ = 13.8091 (13) Å
$c$ = 9.2518 (9) Å
$\beta$ = 93.940 (2)°
$V$ = 2246.9 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.11 mm$^{-1}$
$T$ = 100 K
0.45 × 0.27 × 0.07 mm

### Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.955, $T_{max}$ = 0.992
12651 measured reflections
3275 independent reflections
3004 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
$S$ = 1.06
3275 reflections
347 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1$A$—H1$NA$···O2 | 0.95 (3) | 1.75 (3) | 2.698 (2) | 172 (3) |
| N2$A$—H2$NA$···O1 | 0.83 (3) | 2.10 (3) | 2.906 (2) | 165 (3) |
| N2$A$—H3$NA$···O1$^{i}$ | 0.91 (3) | 1.97 (3) | 2.866 (2) | 171 (2) |
| N1$B$—H1$NB$···O4$^{ii}$ | 1.02 (5) | 1.72 (5) | 2.723 (2) | 169 (3) |
| N2$B$—H2$NB$···O3$^{ii}$ | 0.90 (4) | 1.88 (4) | 2.765 (2) | 170 (3) |
| N2$B$—H3$NB$···O3$W^{iii}$ | 0.93 (3) | 1.97 (3) | 2.894 (2) | 174 (3) |
| O1$W$—H1$W1$···O3$W$ | 0.76 (4) | 2.03 (3) | 2.781 (2) | 174 (4) |
| O1$W$—H2$W1$···O4$W$ | 0.89 (4) | 1.91 (4) | 2.779 (2) | 167 (3) |
| O2$W$—H1$W2$···O4$^{iv}$ | 0.88 (3) | 1.86 (3) | 2.741 (2) | 175 (3) |
| O2$W$—H2$W2$···O4$W$ | 0.88 (3) | 1.90 (3) | 2.772 (2) | 176 (3) |
| O3$W$—H1$W3$···O3$^{v}$ | 0.77 (4) | 1.95 (4) | 2.721 (2) | 178 (5) |
| O3$W$—H2$W3$···O1$W^{vi}$ | 0.86 (4) | 1.89 (3) | 2.742 (2) | 168 (3) |
| O4$W$—H1$W4$···O2 | 0.92 (4) | 1.81 (4) | 2.689 (2) | 161 (3) |
| O4$W$—H2$W4$···O2$W^{vi}$ | 0.80 (3) | 1.93 (3) | 2.716 (2) | 171 (3) |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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: CI5123).

‡ Thomson Reuters ResearcherID: A-3561-2009.

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# supplementary materials

*Acta Cryst.* (2010). E**66**, o1925-o1926 [ **doi:10.1107/S1600536810025651** ]

# Bis(2-amino-4-methylpyridinium) terephthalate tetrahydrate

**M. Hemamalini and H.-K. Fun**

## Comment

Supramolecular architectures assembled *via* various delicate noncovalent interactions such as hydrogen bonds, π–π stacking and electrostatic interactions, etc., have attracted intense interest in recent years because of their fascinating structural diversity and potential applications for functional materials (Desiraju, 2007; Corna *et al.*, 2004). Especially, the application of intermolecular hydrogen bonds is a well known and efficient tool in the field of organic crystal design owing to its strength and directional properties (Aakeröy & Seddon, 1993). Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). They are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). Terephthalic acid ($H_2$TPA), a rod-like aromatic diacid, has often been used in the synthesis of metal-organic frameworks as a linker molecule (Serre *et al.*, 2007; Mukherjee *et al.*, 2004; Sun *et al.*, 2000). Recently, with the increase in interest in controlling the crystalline structures of organic-based solid-state materials, $H_2$TPA is being increasingly employed in constructing supramolecular structures (Lynch & Jones, 2004; Spencer *et al.*, 2004; Devi & Muthiah, 2007). Since our aim is to study some interesting hydrogen-bonding interactions, the crystal structure of the title compound is presented here.

The asymmetric unit of the title salt contains two 2-amino-4-methylpyridinium cations (A and B), one terephthalate anion and four water molecules (Fig. 1). Each 2-amino-4-methylpyridinium cation is planar, with a maximum deviation of 0.008 (2) Å for atom C2A (molecule A) and 0.005 (2) Å for atom C3B (molecule B). The protonation of atoms N1A and N1B lead to a slight increase in C1A—N1A—C5A [122.10 (16)°] and C1B—N1B—C5B [122.09 (16)°] angles. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal structure, the terephthalate carboxylate groups interacts with 2-amino-4-methylpyridinium cations *via* a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). An $R_6^6(12)$ ring motif is formed by water molecules through O—H···O (Table 1) hydrogen bonds and these motifs fuse to form a one-dimensional supramolecular chain along the *c*-axis (Fig. 2). Further, the $R_2^2(8)$ and $R_6^6(12)$ motifs are connected *via* O—H···O hydrogen bonds (Fig. 3). The crystal structure is further stabilized by π–π interactions between N1A/C1A–C5A and N1B/C1B–C5B pyridinium rings at (x, y, z) [centroid-to-centroid distance = 3.522 (1) Å].

## Experimental

A hot methanol solution (20 ml) of 2-amino-4-methylpyridine (54 mg, Aldrich) and terephthalic acid (83 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound appeared after a few days.

### Refinement

O- and N-bound H atoms were located from a difference Fourier map and were refined freely [N–H= 0.83 (3)–1.01 (5) Å and O–H = 0.75 (3)–0.92 (3) Å]. The remaining hydrogen atoms were positioned geometrically [C–H = 0.93 or 0.96 Å] and were refined using a riding model, with $U_{iso}$(H) = 1.2 or 1.5 $U_{eq}$(C). A rotating group model was used for the methyl groups. In the absence of significant anomalous dispersion, 2680 Friedel pairs were merged before the final refinement.

### Figures

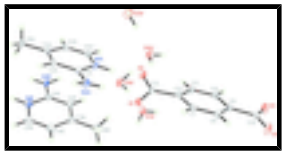

Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

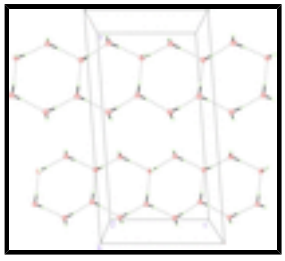

Fig. 2. View of the supramolecular chain made up of water molecules along the *c*-axis.

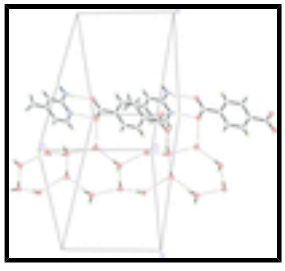

Fig. 3. Hydrogen bonding pattern in the title compound.

### Bis(2-amino-4-methylpyridinium) terephthalate tetrahydrate

*Crystal data*

| | |
|---|---|
| $2C_6H_9N_2^+·C_8H_4O_4^{2-}·4H_2O$ | $F(000) = 968$ |
| $M_r = 454.48$ | $D_x = 1.343$ Mg m$^{-3}$ |
| Monoclinic, *Cc* | Mo *K*α radiation, λ = 0.71073 Å |
| Hall symbol: C -2yc | Cell parameters from 4430 reflections |
| *a* = 17.6290 (16) Å | θ = 2.3–30.0° |
| *b* = 13.8091 (13) Å | μ = 0.11 mm$^{-1}$ |
| *c* = 9.2518 (9) Å | *T* = 100 K |
| β = 93.940 (2)° | Plate, colourless |
| *V* = 2246.9 (4) Å$^3$ | 0.45 × 0.27 × 0.07 mm |
| *Z* = 4 | |

*Data collection*

| | |
|---|---|
| Bruker APEXII DUO CCD area-detector diffractometer | 3275 independent reflections |
| Radiation source: fine-focus sealed tube | 3004 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.031$ |
| φ and ω scans | $\theta_{max} = 30.1°$, $\theta_{min} = 1.9°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | $h = -21 \rightarrow 24$ |
| $T_{min} = 0.955$, $T_{max} = 0.992$ | $k = -19 \rightarrow 13$ |
| 12651 measured reflections | $l = -13 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.101$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.06$ | $w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.2622P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3275 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 347 parameters | $\Delta\rho_{max} = 0.46$ e Å$^{-3}$ |
| 2 restraints | $\Delta\rho_{min} = -0.20$ e Å$^{-3}$ |

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1A | 0.73749 (9) | 0.27051 (12) | 0.16796 (17) | 0.0163 (3) |
| N2A | 0.75478 (10) | 0.43694 (12) | 0.17137 (18) | 0.0204 (3) |
| C1A | 0.73275 (10) | 0.35697 (14) | 0.09938 (19) | 0.0163 (4) |

| | | | | |
|---|---|---|---|---|
| C2A | 0.70424 (11) | 0.35868 (15) | −0.0481 (2) | 0.0187 (4) |
| H2AA | 0.7016 | 0.4170 | −0.0983 | 0.022* |
| C3A | 0.68056 (10) | 0.27471 (14) | −0.11685 (19) | 0.0173 (4) |
| C4A | 0.68604 (11) | 0.18620 (14) | −0.0396 (2) | 0.0188 (4) |
| H4AA | 0.6702 | 0.1286 | −0.0841 | 0.023* |
| C5A | 0.71489 (11) | 0.18657 (15) | 0.1009 (2) | 0.0202 (4) |
| H5AA | 0.7192 | 0.1285 | 0.1518 | 0.024* |
| C6A | 0.64919 (12) | 0.27652 (16) | −0.2720 (2) | 0.0230 (4) |
| H6AA | 0.6584 | 0.3389 | −0.3133 | 0.034* |
| H6AB | 0.5954 | 0.2645 | −0.2762 | 0.034* |
| H6AC | 0.6736 | 0.2274 | −0.3257 | 0.034* |
| N1B | 0.48583 (10) | 0.31843 (13) | −0.04463 (18) | 0.0195 (3) |
| N2B | 0.49724 (10) | 0.15247 (12) | −0.02353 (17) | 0.0184 (3) |
| C1B | 0.50869 (11) | 0.23962 (14) | 0.03428 (19) | 0.0169 (4) |
| C2B | 0.54266 (11) | 0.25447 (16) | 0.1759 (2) | 0.0183 (4) |
| H2BA | 0.5582 | 0.2015 | 0.2326 | 0.022* |
| C3B | 0.55264 (11) | 0.34599 (15) | 0.2296 (2) | 0.0200 (4) |
| C4B | 0.52752 (12) | 0.42658 (16) | 0.1435 (2) | 0.0230 (4) |
| H4BA | 0.5336 | 0.4894 | 0.1788 | 0.028* |
| C5B | 0.49433 (12) | 0.41005 (15) | 0.0082 (2) | 0.0220 (4) |
| H5BA | 0.4773 | 0.4622 | −0.0487 | 0.026* |
| C6B | 0.58818 (13) | 0.36063 (18) | 0.3806 (2) | 0.0271 (5) |
| H6BA | 0.6173 | 0.3043 | 0.4099 | 0.041* |
| H6BB | 0.5490 | 0.3707 | 0.4461 | 0.041* |
| H6BC | 0.6210 | 0.4162 | 0.3822 | 0.041* |
| O1 | 0.79418 (8) | 0.41120 (10) | 0.47912 (14) | 0.0196 (3) |
| O2 | 0.80222 (9) | 0.25260 (10) | 0.43950 (15) | 0.0196 (3) |
| O3 | 0.95157 (10) | 0.35431 (12) | 1.18466 (16) | 0.0258 (3) |
| O4 | 0.93553 (9) | 0.19471 (11) | 1.17111 (15) | 0.0227 (3) |
| C7 | 0.87740 (10) | 0.39144 (13) | 0.75006 (19) | 0.0156 (3) |
| H7A | 0.8791 | 0.4520 | 0.7063 | 0.019* |
| C8 | 0.90527 (10) | 0.37998 (14) | 0.89289 (19) | 0.0158 (3) |
| H8A | 0.9248 | 0.4331 | 0.9447 | 0.019* |
| C9 | 0.90425 (10) | 0.28948 (14) | 0.95947 (18) | 0.0148 (3) |
| C10 | 0.87640 (10) | 0.20985 (14) | 0.87956 (19) | 0.0153 (3) |
| H10A | 0.8771 | 0.1488 | 0.9219 | 0.018* |
| C11 | 0.84752 (11) | 0.22144 (13) | 0.73637 (19) | 0.0156 (3) |
| H11A | 0.8286 | 0.1681 | 0.6840 | 0.019* |
| C12 | 0.84683 (10) | 0.31250 (13) | 0.67150 (18) | 0.0138 (3) |
| C13 | 0.81214 (10) | 0.32704 (14) | 0.51865 (18) | 0.0147 (3) |
| C14 | 0.93282 (10) | 0.27846 (14) | 1.11620 (19) | 0.0165 (4) |
| O1W | 0.63068 (10) | 0.06139 (12) | 0.38459 (17) | 0.0271 (3) |
| O2W | 0.85423 (10) | 0.02585 (12) | 0.18024 (18) | 0.0268 (3) |
| O3W | 0.56061 (10) | 0.01269 (12) | 0.63491 (16) | 0.0242 (3) |
| O4W | 0.78771 (9) | 0.05874 (11) | 0.43863 (16) | 0.0224 (3) |
| H1NA | 0.7560 (17) | 0.265 (2) | 0.267 (3) | 0.024 (7)* |
| H2NA | 0.7743 (15) | 0.432 (2) | 0.255 (3) | 0.022 (6)* |
| H3NA | 0.7636 (14) | 0.489 (2) | 0.115 (3) | 0.019 (6)* |
| H1NB | 0.463 (3) | 0.307 (3) | −0.147 (5) | 0.077 (14)* |

| | | | | |
|---|---|---|---|---|
| H2NB | 0.4765 (19) | 0.150 (2) | −0.115 (4) | 0.038 (8)* |
| H3NB | 0.5148 (17) | 0.100 (2) | 0.032 (3) | 0.033 (8)* |
| H1W1 | 0.6143 (17) | 0.050 (2) | 0.456 (4) | 0.025 (7)* |
| H2W1 | 0.680 (2) | 0.051 (2) | 0.404 (4) | 0.040 (9)* |
| H1W2 | 0.8800 (16) | 0.080 (2) | 0.172 (3) | 0.025 (7)* |
| H2W2 | 0.8348 (16) | 0.035 (2) | 0.264 (3) | 0.025 (7)* |
| H1W3 | 0.529 (2) | 0.049 (3) | 0.649 (4) | 0.059 (12)* |
| H2W3 | 0.5807 (17) | −0.003 (2) | 0.719 (4) | 0.034 (8)* |
| H1W4 | 0.7949 (18) | 0.123 (3) | 0.461 (3) | 0.035 (8)* |
| H2W4 | 0.8036 (18) | 0.029 (2) | 0.508 (4) | 0.031 (7)* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1A | 0.0186 (7) | 0.0172 (7) | 0.0128 (7) | −0.0016 (6) | −0.0011 (6) | 0.0010 (5) |
| N2A | 0.0271 (8) | 0.0185 (7) | 0.0147 (7) | −0.0044 (6) | −0.0042 (6) | 0.0014 (6) |
| C1A | 0.0166 (8) | 0.0170 (8) | 0.0151 (8) | −0.0016 (7) | −0.0005 (6) | 0.0016 (6) |
| C2A | 0.0203 (9) | 0.0220 (9) | 0.0136 (7) | −0.0013 (7) | −0.0008 (6) | 0.0026 (6) |
| C3A | 0.0146 (8) | 0.0234 (9) | 0.0140 (8) | 0.0014 (7) | 0.0007 (6) | 0.0006 (7) |
| C4A | 0.0200 (9) | 0.0182 (8) | 0.0182 (8) | −0.0020 (7) | 0.0015 (7) | −0.0031 (7) |
| C5A | 0.0209 (9) | 0.0184 (9) | 0.0215 (9) | 0.0021 (7) | 0.0024 (7) | 0.0027 (7) |
| C6A | 0.0234 (10) | 0.0321 (11) | 0.0125 (8) | −0.0007 (8) | −0.0051 (7) | −0.0014 (7) |
| N1B | 0.0219 (8) | 0.0207 (8) | 0.0153 (7) | −0.0009 (6) | −0.0021 (6) | 0.0001 (6) |
| N2B | 0.0225 (8) | 0.0195 (8) | 0.0127 (7) | −0.0017 (6) | −0.0024 (6) | −0.0006 (6) |
| C1B | 0.0162 (8) | 0.0211 (9) | 0.0135 (8) | −0.0020 (6) | 0.0013 (6) | 0.0009 (6) |
| C2B | 0.0172 (8) | 0.0240 (9) | 0.0137 (8) | −0.0006 (7) | 0.0002 (6) | 0.0005 (6) |
| C3B | 0.0174 (9) | 0.0295 (10) | 0.0133 (8) | −0.0029 (7) | 0.0020 (6) | −0.0019 (7) |
| C4B | 0.0250 (10) | 0.0221 (9) | 0.0217 (9) | −0.0004 (8) | −0.0004 (7) | −0.0039 (7) |
| C5B | 0.0232 (9) | 0.0227 (9) | 0.0198 (9) | 0.0027 (7) | −0.0003 (7) | −0.0001 (7) |
| C6B | 0.0282 (11) | 0.0370 (12) | 0.0151 (9) | 0.0003 (9) | −0.0048 (8) | −0.0064 (8) |
| O1 | 0.0276 (7) | 0.0164 (6) | 0.0140 (6) | 0.0043 (5) | −0.0034 (5) | 0.0006 (5) |
| O2 | 0.0293 (7) | 0.0149 (6) | 0.0138 (6) | 0.0008 (5) | −0.0032 (5) | −0.0006 (5) |
| O3 | 0.0373 (8) | 0.0238 (7) | 0.0151 (6) | −0.0085 (6) | −0.0064 (6) | 0.0005 (5) |
| O4 | 0.0309 (8) | 0.0196 (7) | 0.0165 (6) | −0.0048 (6) | −0.0053 (5) | 0.0033 (5) |
| C7 | 0.0165 (8) | 0.0154 (8) | 0.0146 (8) | 0.0003 (6) | −0.0007 (6) | 0.0007 (6) |
| C8 | 0.0160 (8) | 0.0173 (8) | 0.0138 (7) | −0.0027 (6) | −0.0014 (6) | −0.0012 (6) |
| C9 | 0.0143 (8) | 0.0198 (8) | 0.0103 (7) | 0.0005 (6) | −0.0001 (6) | 0.0015 (6) |
| C10 | 0.0183 (8) | 0.0152 (8) | 0.0124 (8) | 0.0010 (7) | 0.0002 (6) | 0.0017 (6) |
| C11 | 0.0180 (8) | 0.0161 (8) | 0.0126 (8) | 0.0004 (7) | −0.0006 (6) | −0.0006 (6) |
| C12 | 0.0136 (8) | 0.0166 (8) | 0.0112 (7) | 0.0015 (6) | 0.0010 (6) | 0.0009 (6) |
| C13 | 0.0163 (8) | 0.0177 (8) | 0.0099 (7) | −0.0002 (6) | −0.0003 (6) | 0.0006 (6) |
| C14 | 0.0177 (8) | 0.0203 (9) | 0.0109 (7) | −0.0035 (7) | −0.0028 (6) | 0.0009 (6) |
| O1W | 0.0280 (8) | 0.0343 (9) | 0.0189 (7) | −0.0029 (7) | −0.0002 (6) | 0.0039 (6) |
| O2W | 0.0357 (9) | 0.0214 (7) | 0.0236 (7) | −0.0049 (6) | 0.0044 (6) | −0.0045 (6) |
| O3W | 0.0289 (8) | 0.0237 (7) | 0.0197 (7) | 0.0027 (6) | 0.0002 (6) | −0.0012 (5) |
| O4W | 0.0306 (8) | 0.0169 (7) | 0.0194 (7) | −0.0007 (6) | −0.0007 (6) | 0.0001 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1A—C1A | 1.352 (2) | C4B—H4BA | 0.93 |
| N1A—C5A | 1.361 (3) | C5B—H5BA | 0.93 |
| N1A—H1NA | 0.95 (3) | C6B—H6BA | 0.96 |
| N2A—C1A | 1.334 (2) | C6B—H6BB | 0.96 |
| N2A—H2NA | 0.83 (3) | C6B—H6BC | 0.96 |
| N2A—H3NA | 0.91 (3) | O1—C13 | 1.253 (2) |
| C1A—C2A | 1.421 (2) | O2—C13 | 1.267 (2) |
| C2A—C3A | 1.374 (3) | O3—C14 | 1.256 (2) |
| C2A—H2AA | 0.93 | O4—C14 | 1.263 (2) |
| C3A—C4A | 1.416 (3) | C7—C8 | 1.387 (2) |
| C3A—C6A | 1.503 (2) | C7—C12 | 1.398 (2) |
| C4A—C5A | 1.363 (3) | C7—H7A | 0.93 |
| C4A—H4AA | 0.93 | C8—C9 | 1.394 (3) |
| C5A—H5AA | 0.93 | C8—H8A | 0.93 |
| C6A—H6AA | 0.96 | C9—C10 | 1.395 (2) |
| C6A—H6AB | 0.96 | C9—C14 | 1.510 (2) |
| C6A—H6AC | 0.96 | C10—C11 | 1.395 (2) |
| N1B—C1B | 1.356 (2) | C10—H10A | 0.93 |
| N1B—C5B | 1.361 (3) | C11—C12 | 1.393 (2) |
| N1B—H1NB | 1.01 (5) | C11—H11A | 0.93 |
| N2B—C1B | 1.327 (3) | C12—C13 | 1.515 (2) |
| N2B—H2NB | 0.90 (3) | O1W—H1W1 | 0.75 (3) |
| N2B—H3NB | 0.93 (3) | O1W—H2W1 | 0.89 (3) |
| C1B—C2B | 1.418 (2) | O2W—H1W2 | 0.88 (3) |
| C2B—C3B | 1.365 (3) | O2W—H2W2 | 0.88 (3) |
| C2B—H2BA | 0.93 | O3W—H1W3 | 0.76 (5) |
| C3B—C4B | 1.421 (3) | O3W—H2W3 | 0.86 (3) |
| C3B—C6B | 1.505 (3) | O4W—H1W4 | 0.92 (3) |
| C4B—C5B | 1.364 (3) | O4W—H2W4 | 0.79 (3) |
| C1A—N1A—C5A | 122.10 (16) | C4B—C3B—C6B | 120.57 (19) |
| C1A—N1A—H1NA | 121.5 (17) | C5B—C4B—C3B | 118.71 (19) |
| C5A—N1A—H1NA | 116.4 (17) | C5B—C4B—H4BA | 120.6 |
| C1A—N2A—H2NA | 118.8 (19) | C3B—C4B—H4BA | 120.6 |
| C1A—N2A—H3NA | 115.1 (16) | N1B—C5B—C4B | 121.01 (18) |
| H2NA—N2A—H3NA | 122 (2) | N1B—C5B—H5BA | 119.5 |
| N2A—C1A—N1A | 119.37 (16) | C4B—C5B—H5BA | 119.5 |
| N2A—C1A—C2A | 122.50 (17) | C3B—C6B—H6BA | 109.5 |
| N1A—C1A—C2A | 118.13 (16) | C3B—C6B—H6BB | 109.5 |
| C3A—C2A—C1A | 120.45 (18) | H6BA—C6B—H6BB | 109.5 |
| C3A—C2A—H2AA | 119.8 | C3B—C6B—H6BC | 109.5 |
| C1A—C2A—H2AA | 119.8 | H6BA—C6B—H6BC | 109.5 |
| C2A—C3A—C4A | 119.13 (16) | H6BB—C6B—H6BC | 109.5 |
| C2A—C3A—C6A | 120.58 (18) | C8—C7—C12 | 120.35 (17) |
| C4A—C3A—C6A | 120.29 (18) | C8—C7—H7A | 119.8 |
| C5A—C4A—C3A | 119.09 (17) | C12—C7—H7A | 119.8 |
| C5A—C4A—H4AA | 120.5 | C7—C8—C9 | 120.59 (16) |

| | | | |
|---|---|---|---|
| C3A—C4A—H4AA | 120.5 | C7—C8—H8A | 119.7 |
| N1A—C5A—C4A | 121.08 (18) | C9—C8—H8A | 119.7 |
| N1A—C5A—H5AA | 119.5 | C8—C9—C10 | 119.16 (15) |
| C4A—C5A—H5AA | 119.5 | C8—C9—C14 | 120.08 (15) |
| C3A—C6A—H6AA | 109.5 | C10—C9—C14 | 120.77 (16) |
| C3A—C6A—H6AB | 109.5 | C11—C10—C9 | 120.31 (16) |
| H6AA—C6A—H6AB | 109.5 | C11—C10—H10A | 119.8 |
| C3A—C6A—H6AC | 109.5 | C9—C10—H10A | 119.8 |
| H6AA—C6A—H6AC | 109.5 | C12—C11—C10 | 120.29 (16) |
| H6AB—C6A—H6AC | 109.5 | C12—C11—H11A | 119.9 |
| C1B—N1B—C5B | 122.09 (16) | C10—C11—H11A | 119.9 |
| C1B—N1B—H1NB | 118 (3) | C11—C12—C7 | 119.24 (15) |
| C5B—N1B—H1NB | 120 (3) | C11—C12—C13 | 120.85 (15) |
| C1B—N2B—H2NB | 117 (2) | C7—C12—C13 | 119.90 (16) |
| C1B—N2B—H3NB | 116.5 (19) | O1—C13—O2 | 124.18 (16) |
| H2NB—N2B—H3NB | 126 (3) | O1—C13—C12 | 118.25 (16) |
| N2B—C1B—N1B | 118.66 (16) | O2—C13—C12 | 117.57 (16) |
| N2B—C1B—C2B | 123.14 (18) | O3—C14—O4 | 124.01 (16) |
| N1B—C1B—C2B | 118.19 (18) | O3—C14—C9 | 117.32 (16) |
| C3B—C2B—C1B | 120.39 (19) | O4—C14—C9 | 118.66 (16) |
| C3B—C2B—H2BA | 119.8 | H1W1—O1W—H2W1 | 103 (3) |
| C1B—C2B—H2BA | 119.8 | H1W2—O2W—H2W2 | 101 (3) |
| C2B—C3B—C4B | 119.60 (17) | H1W3—O3W—H2W3 | 106 (4) |
| C2B—C3B—C6B | 119.81 (19) | H1W4—O4W—H2W4 | 106 (3) |
| C5A—N1A—C1A—N2A | 179.05 (18) | C3B—C4B—C5B—N1B | −0.6 (3) |
| C5A—N1A—C1A—C2A | −1.0 (3) | C12—C7—C8—C9 | 0.9 (3) |
| N2A—C1A—C2A—C3A | −178.48 (19) | C7—C8—C9—C10 | 1.5 (3) |
| N1A—C1A—C2A—C3A | 1.6 (3) | C7—C8—C9—C14 | −178.37 (18) |
| C1A—C2A—C3A—C4A | −1.0 (3) | C8—C9—C10—C11 | −2.2 (3) |
| C1A—C2A—C3A—C6A | 178.99 (18) | C14—C9—C10—C11 | 177.62 (17) |
| C2A—C3A—C4A—C5A | −0.2 (3) | C9—C10—C11—C12 | 0.5 (3) |
| C6A—C3A—C4A—C5A | 179.84 (18) | C10—C11—C12—C7 | 1.9 (3) |
| C1A—N1A—C5A—C4A | −0.2 (3) | C10—C11—C12—C13 | −176.98 (17) |
| C3A—C4A—C5A—N1A | 0.8 (3) | C8—C7—C12—C11 | −2.6 (3) |
| C5B—N1B—C1B—N2B | 178.77 (19) | C8—C7—C12—C13 | 176.24 (17) |
| C5B—N1B—C1B—C2B | −0.2 (3) | C11—C12—C13—O1 | 161.04 (18) |
| N2B—C1B—C2B—C3B | −179.74 (19) | C7—C12—C13—O1 | −17.8 (3) |
| N1B—C1B—C2B—C3B | −0.8 (3) | C11—C12—C13—O2 | −18.0 (3) |
| C1B—C2B—C3B—C4B | 1.1 (3) | C7—C12—C13—O2 | 163.16 (17) |
| C1B—C2B—C3B—C6B | 179.48 (19) | C8—C9—C14—O3 | 5.2 (3) |
| C2B—C3B—C4B—C5B | −0.4 (3) | C10—C9—C14—O3 | −174.63 (18) |
| C6B—C3B—C4B—C5B | −178.8 (2) | C8—C9—C14—O4 | −175.75 (19) |
| C1B—N1B—C5B—C4B | 0.9 (3) | C10—C9—C14—O4 | 4.4 (3) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1A—H1NA···O2 | 0.95 (3) | 1.75 (3) | 2.698 (2) | 172 (3) |
| N2A—H2NA···O1 | 0.83 (3) | 2.10 (3) | 2.906 (2) | 165 (3) |

| | | | | |
|---|---|---|---|---|
| N2A—H3NA···O1$^{i}$ | 0.91 (3) | 1.97 (3) | 2.866 (2) | 171 (2) |
| N1B—H1NB···O4$^{ii}$ | 1.02 (5) | 1.72 (5) | 2.723 (2) | 169 (3) |
| N2B—H2NB···O3$^{ii}$ | 0.90 (4) | 1.88 (4) | 2.765 (2) | 170 (3) |
| N2B—H3NB···O3W$^{iii}$ | 0.93 (3) | 1.97 (3) | 2.894 (2) | 174 (3) |
| O1W—H1W1···O3W | 0.76 (4) | 2.03 (3) | 2.781 (2) | 174 (4) |
| O1W—H2W1···O4W | 0.89 (4) | 1.91 (4) | 2.779 (2) | 167 (3) |
| O2W—H1W2···O4$^{iv}$ | 0.88 (3) | 1.86 (3) | 2.741 (2) | 175 (3) |
| O2W—H2W2···O4W | 0.88 (3) | 1.90 (3) | 2.772 (2) | 176 (3) |
| O3W—H1W3···O3$^{v}$ | 0.77 (4) | 1.95 (4) | 2.721 (2) | 178 (5) |
| O3W—H2W3···O1W$^{vi}$ | 0.86 (4) | 1.89 (3) | 2.742 (2) | 168 (3) |
| O4W—H1W4···O2 | 0.92 (4) | 1.81 (4) | 2.689 (2) | 161 (3) |
| O4W—H2W4···O2W$^{vi}$ | 0.80 (3) | 1.93 (3) | 2.716 (2) | 171 (3) |

Symmetry codes: (i) *x*, −*y*+1, *z*−1/2; (ii) *x*−1/2, −*y*+1/2, *z*−3/2; (iii) *x*, −*y*, *z*−1/2; (iv) *x*, *y*, *z*−1; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) *x*, −*y*, *z*+1/2.

**Fig. 1**

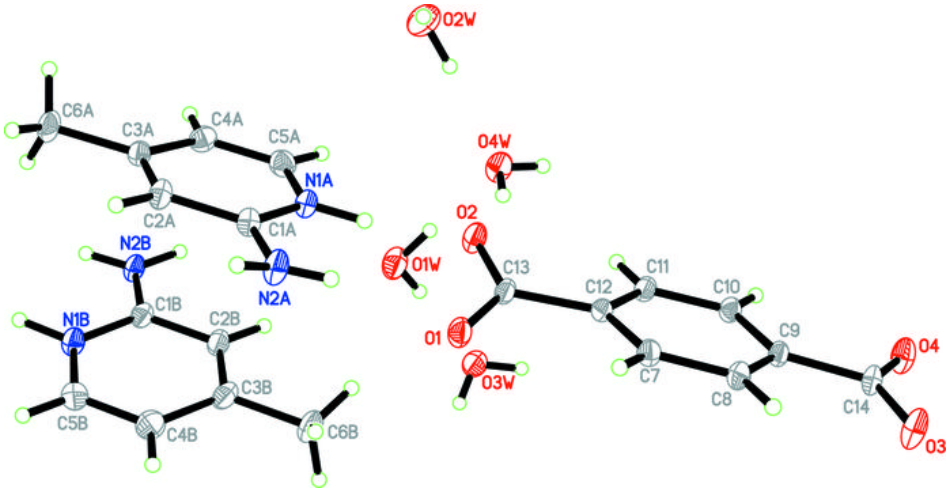
O2W
C6A
C3A
C4A
C5A
N1A
C2A
C1A
N2B
N2A
C1B
N1B
C2B
C3B
C5B
C4B
C6B
O4W
O2
O1W
C13
C12
C11
C10
C9
O1
O3W
C7
C8
C14
O4
O3

**Fig. 2**

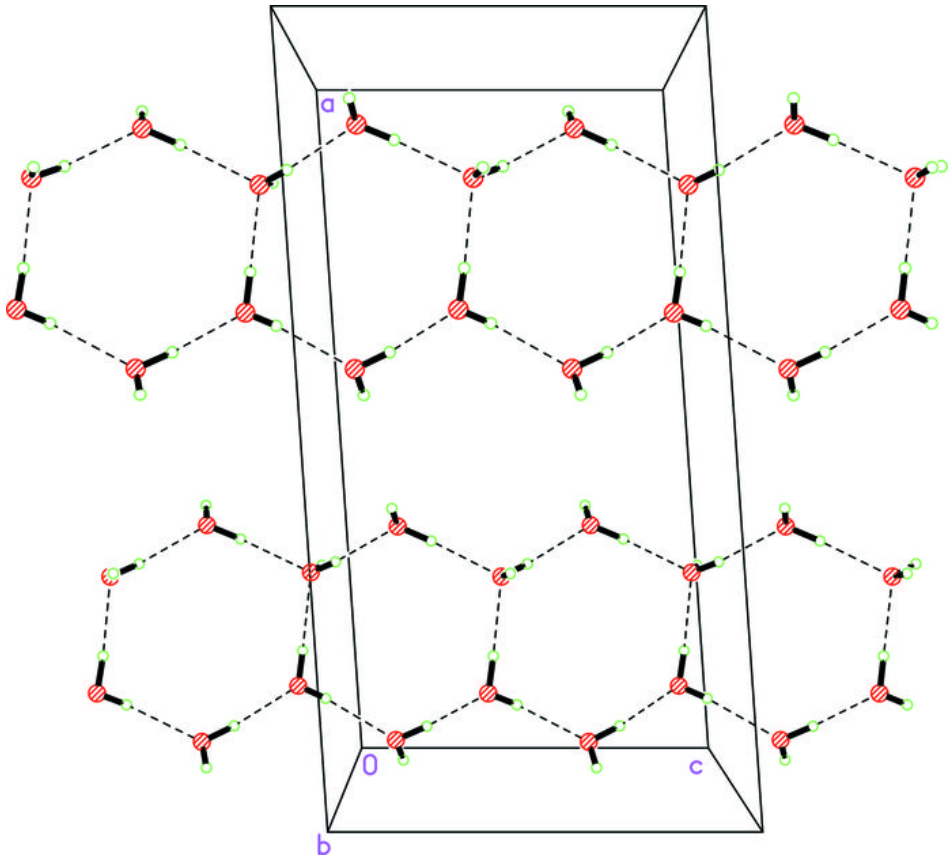

**Fig. 3**