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2-Aminopyridinium 4-methylbenzoate dihydrate

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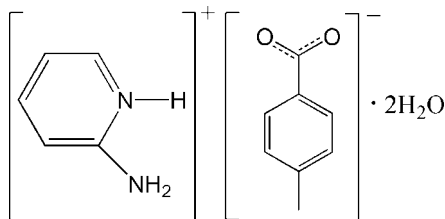
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.089; data-to-parameter ratio = 9.0.

The crystal structure of the title salt, $\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_8\text{H}_7\text{O}_2^- \cdot 2\text{H}_2\text{O}$, contains a three-dimensional supramolecular framework constructed through $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

Related literature

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



Experimental

Crystal data

 $\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_8\text{H}_7\text{O}_2^- \cdot 2\text{H}_2\text{O}$
 $M_r = 266.29$

 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) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.09$ mm⁻¹
 $T = 296$ (2) K

 $0.23 \times 0.18 \times 0.16$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

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

 $\Delta\rho_{\text{max}} = 0.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

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

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supporting information

Acta Cryst. (2008). E64, o2057 [doi:10.1107/S160053680803153X]

2-Aminopyridinium 4-methylbenzoate dihydrate

Yun Liu and Jie Li

S1. 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 \cdots O and O—H \cdots O hydrogen bonds (Fig. 2 and Table 1).

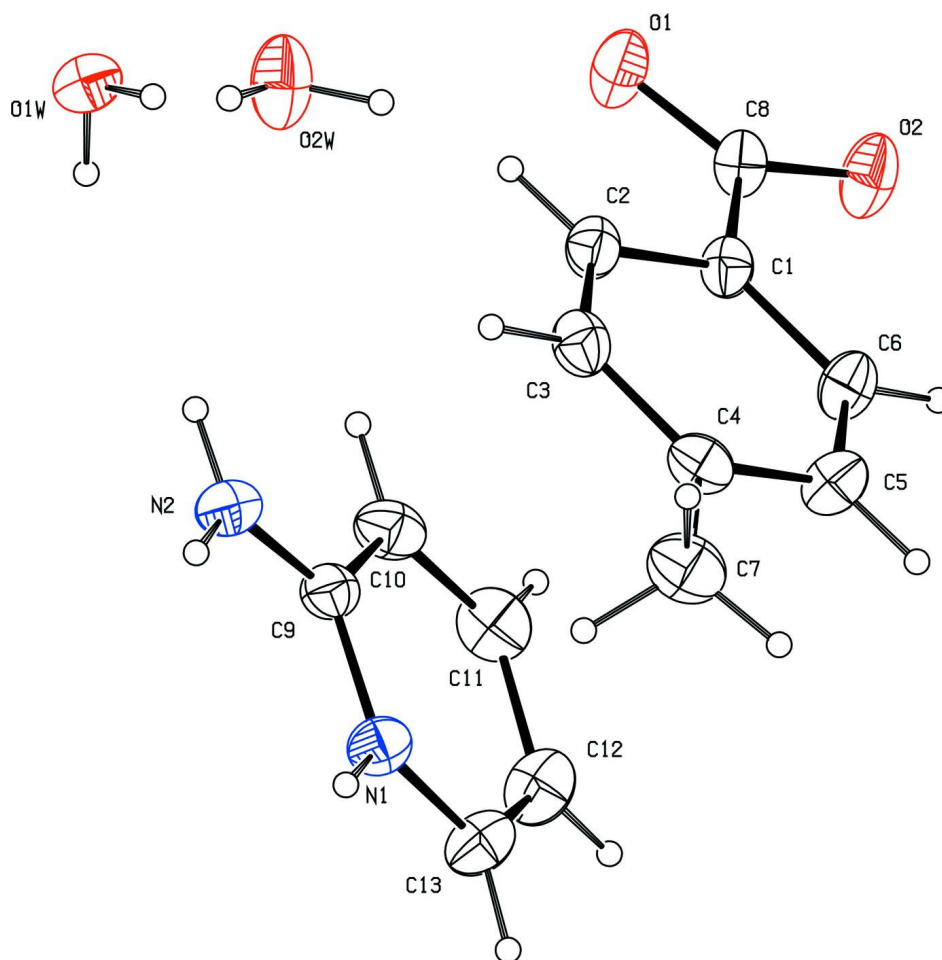
S2. Experimental

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.

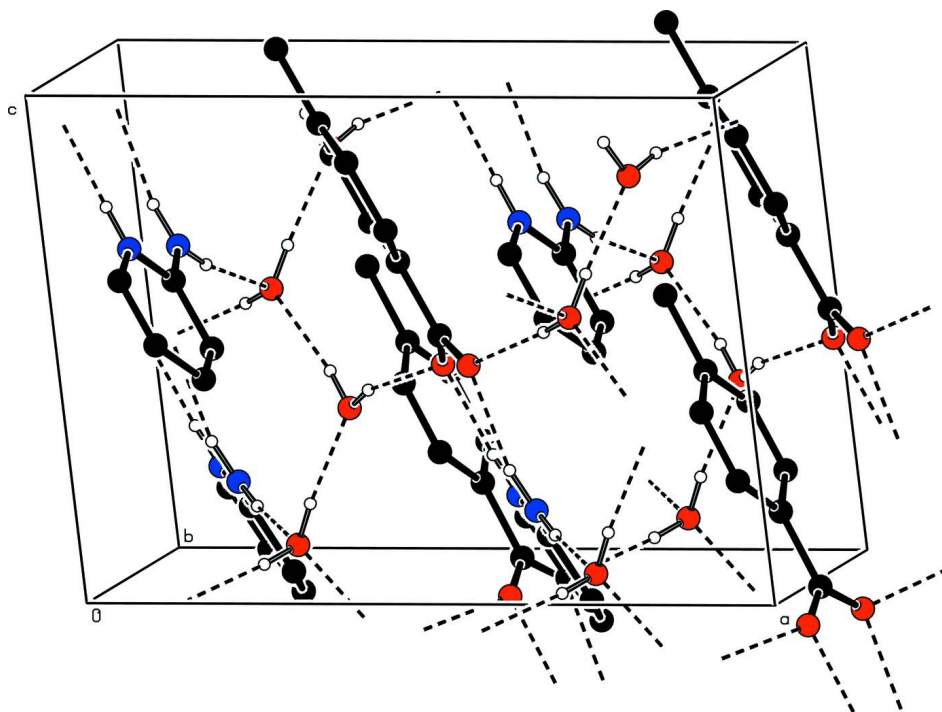
S3. Refinement

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 $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{N and C}_{\text{methylidyne}})$ and $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O or C}_{\text{methyl}})$.

**Figure 1**

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

**Figure 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

$C_5H_7N_2^+ \cdot C_8H_7O_2^- \cdot 2H_2O$

$M_r = 266.29$

Monoclinic, Cc

Hall symbol: $C -2yc$

$a = 12.2059 (14) \text{ \AA}$

$b = 13.1531 (16) \text{ \AA}$

$c = 8.9937 (11) \text{ \AA}$

$\beta = 96.617 (2)^\circ$

$V = 1434.3 (3) \text{ \AA}^3$

$Z = 4$

$F(000) = 568$

$D_x = 1.233 \text{ Mg m}^{-3}$

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

Cell parameters from 1977 reflections

$\theta = 2.3\text{--}26.6^\circ$

$\mu = 0.09 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colorless

$0.23 \times 0.18 \times 0.16 \text{ mm}$

Data collection

Bruker SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2001)

$T_{\min} = 0.979$, $T_{\max} = 0.985$

4203 measured reflections

1567 independent reflections

1406 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -6 \rightarrow 15$

$k = -16 \rightarrow 16$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.089$
 $S = 1.04$
 1567 reflections
 175 parameters
 8 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1161P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.12 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 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	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å²)

	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, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
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) $x+1/2, -y+1/2, z+1/2$.