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Bis(2-amino-5-bromopyridinium) fumarate dihydrate

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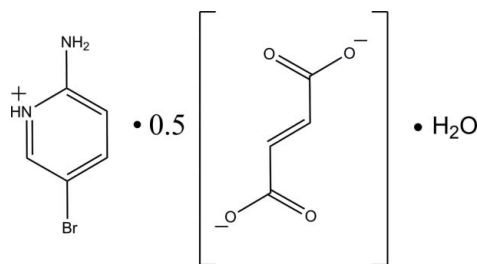
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.059; data-to-parameter ratio = 28.6.

In the title compound, $2\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-} \cdot 2\text{H}_2\text{O}$, the complete fumarate dianion is generated by crystallographic inversion symmetry. The cation is approximately planar, with a maximum deviation of 0.036 (1) Å. In the anion, the carboxylate group is twisted slightly away from the attached plane; the dihedral angle between carboxylate and (*E*)-but-2-ene planes is 6.11 (14)°. In the crystal, the carboxylate O atoms form bifurcated (N—H···O and C—H···O) and N—H···O hydrogen bonds with the cations. The crystal packing is stabilized by $R_2^2(8)$ ring motifs which are generated by pairs of N—H···O hydrogen bonds. The crystal structure is further consolidated by water molecules *via* O(water)—H···O and N—H···O(water) hydrogen bonds. The components are linked by these interactions into three-dimensional network.

Related literature

For details of hydrogen bonding, see: Goswami & Ghosh (1997); Goswami *et al.* (1998). For applications of fumaric acid, see: Batchelor *et al.* (2000). For related structures, see: Büyükgüngör *et al.* (2004); Büyükgüngör & Odabaşoğlu (20065); Hemamalini & Fun, (2010*a,b*); Quah *et al.* (2008; 2010*a,b*). 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). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$2\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-} \cdot \text{H}_2\text{O}$

$M_r = 498.14$

Monoclinic, $P2_1/c$

$a = 8.3717$ (1) Å

$b = 16.5354$ (2) Å

$c = 6.7846$ (1) Å

$\beta = 108.336$ (1)°

$V = 891.50$ (2) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 4.59$ mm⁻¹

$T = 100$ K

$0.39 \times 0.15 \times 0.12$ mm

Data collection

Bruker SMART APEXII CCD

area-detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.271$, $T_{\max} = 0.618$

15040 measured reflections

3942 independent reflections

3252 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.059$

$S = 1.03$

3942 reflections

138 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.54$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1N1···O1	0.902 (18)	1.815 (18)	2.7136 (14)	174.1 (19)
N2—H2N2···O1W ⁱ	0.82 (2)	2.11 (2)	2.9143 (16)	169.7 (19)
N2—H1N2···O2	0.893 (19)	1.946 (19)	2.8348 (15)	173.2 (19)
O1W—H2W1···O1 ⁱⁱⁱ	0.77 (2)	2.07 (2)	2.8213 (15)	169 (2)
O1W—H1W1···O1 ⁱⁱⁱ	0.82 (3)	1.99 (3)	2.7865 (14)	167 (3)
C3—H3A···O2 ^{iv}	0.93	2.41	3.3089 (17)	162

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

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: BT5312).

[‡] Thomson Reuters ResearcherID: A-5525-2009.

[§] Thomson Reuters ResearcherID: A-3561-2009.

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supporting information

Acta Cryst. (2010). E66, o2252–o2253 [https://doi.org/10.1107/S1600536810030989]

Bis(2-amino-5-bromopyridinium) fumarate dihydrate**Ching Kheng Quah, Madhukar Hemamalini and Hoong-Kun Fun****S1. Comment**

Hydrogen bonding plays a key role in molecular recognition (Goswami & Ghosh, 1997) and crystal engineering research (Goswami *et al.*, 1998). Fumaric acid, the *E* isomer of butenedioic acid, is of interest since it is known to form supramolecular assemblies with *N*-aromatic compounds (Batchelor *et al.*, 2000). It tends to form infinite chains arranged in a nearly coplanar manner *via* pairs of strong O—H \cdots O hydrogen bonds. The crystal structures of 2-aminopyridinium-fumarate-fumaric acid (2/1/1) (Büyükgüngör *et al.*, 2004) and 2,6-diamino pyridinium hydrogen fumarate (Büyükgüngör & Odabaşoğlu, 2006) have been reported in the literature. We have recently reported the crystal structures of 2-amino-5-chloropyridine-fumaric acid (1/2) (Hemamalini & Fun, 2010*a*) and 2-amino-4-methylpyridinium (*E*)-3-carboxyprop-2-enoate (Hemamalini & Fun, 2010*b*) from our laboratory. In order to study some interesting hydrogen bonding interactions, the synthesis and structure of the title compound, (I), is presented here.

The asymmetric unit of title compound (Fig. 1), consist of a protonated 2-amino-5-bromopyridinium cation, a half molecule of fumarate anion and a water molecule. The fumarate anion is lying about an inversion center (symmetry code: $-x + 1, -y + 1, -z$). In the 2-amino-5-bromopyridinium cation, protonation of N1 atom has lead to a slight increase in the C1–N1–C5 angle to 122.64 (11)°. The 2-amino-5-bromopyridinium cation is approximately planar, with a maximum deviation of 0.036 (1) Å for atom N2. In fumarate anion, C6/C7/C6A/C7A plane is planar with an r.m.s deviation of <0.001 (1) Å. This plane makes a dihedral angle of 6.90 (6)° with 2-amino-5-bromopyridinium cation. In the anion, the carboxylate group is twisted slightly away from the attached plane; the dihedral angle between C6/C7/C6A/C7A and O1/O2/C6/C7 planes is 6.11 (14)°.

In the crystal packing (Fig. 2), the carboxylate oxygen atoms, O2 and O3 form bifurcated (N2–H1N2 \cdots O2 and C3–H3A \cdots O2) and N1–H1N1 \cdots O1 hydrogen bonds, respectively, with cations. The crystal packing is stabilized by $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995) which are generated by pairs of N–H \cdots O hydrogen bonds (Table 1). The crystal structure is further consolidated by water molecules *via* O1W–H1W1 \cdots O1, O1W–H2W1 \cdots O1 and N2–H2N2 \cdots O1W hydrogen bonds. The anions, cations and water molecules are linked by these interactions into three-dimensional network.

S2. Experimental

A hot methanol solution (20 ml) of 2-amino-5-bromopyridine (86 mg, Aldrich) and fumaric acid (58 mg, Merck) was mixed and warmed over a 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.

S3. Refinement

O– and N– bound H atoms were located in a difference Fourier map and allowed to refined freely. The rest of the hydrogen atoms were positioned geometrically and refined using a riding model with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The highest residual electron density peak is located at 0.66 Å from C6 and the deepest hole is located at 1.19 Å

from Br1.

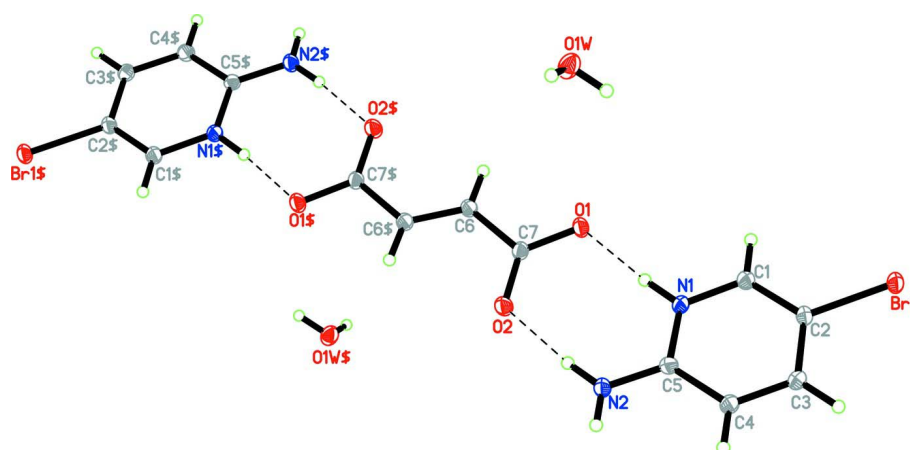


Figure 1

The molecular structure of the title compound showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Symmetry code: (\$) $-x + 1, -y + 1, -z$. Intramolecular interactions are shown as dashed lines.

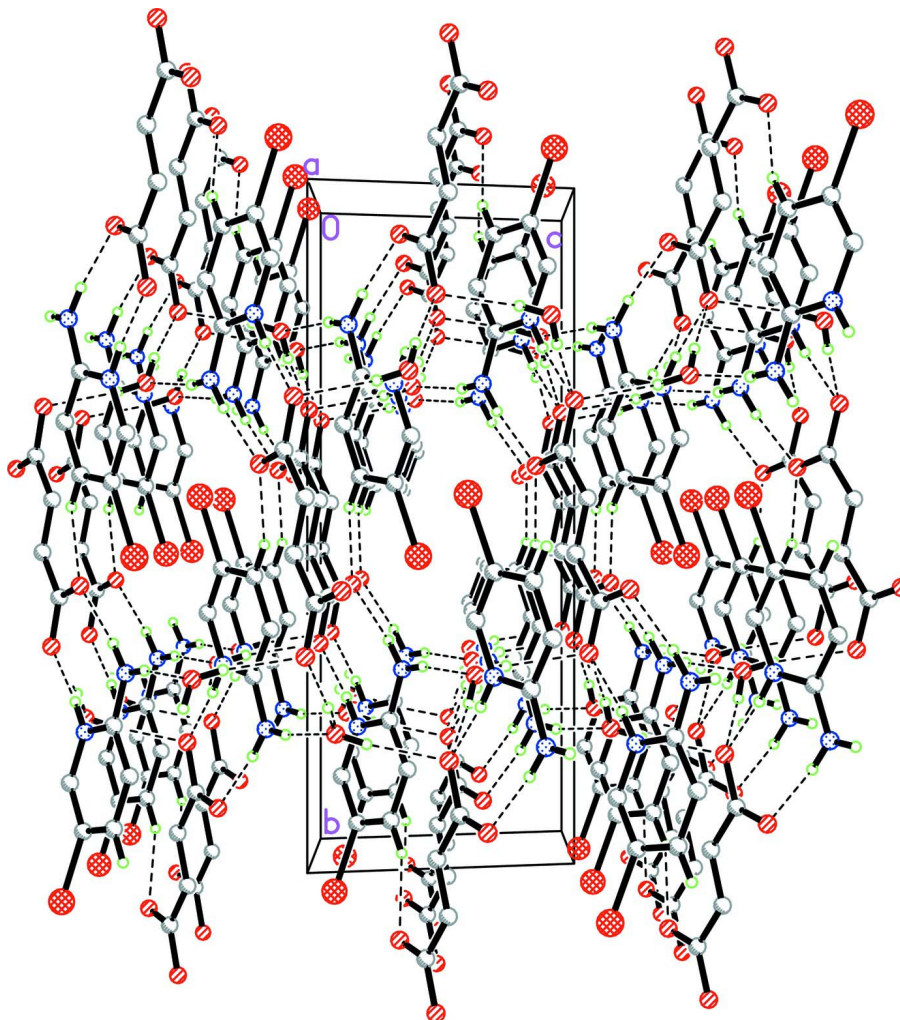


Figure 2

The crystal structure of the title compound viewed along the *a* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

Bis(2-amino-5-bromopyridinium) fumarate dihydrate

Crystal data

$2\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-} \cdot 2\text{H}_2\text{O}$

$M_r = 498.14$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 8.3717\ (1)\ \text{\AA}$

$b = 16.5354\ (2)\ \text{\AA}$

$c = 6.7846\ (1)\ \text{\AA}$

$\beta = 108.336\ (1)^\circ$

$V = 891.50\ (2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 496$

$D_x = 1.856\ \text{Mg m}^{-3}$

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

Cell parameters from 5779 reflections

$\theta = 2.6\text{--}34.6^\circ$

$\mu = 4.59\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, colourless

$0.39 \times 0.15 \times 0.12\ \text{mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

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

$T_{\min} = 0.271$, $T_{\max} = 0.618$

15040 measured reflections

3942 independent reflections

3252 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 35.2^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -13 \rightarrow 12$

$k = -26 \rightarrow 23$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.059$

$S = 1.03$

3942 reflections

138 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 0.2048P]$

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

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

$\Delta\rho_{\max} = 0.54 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$

Special details

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

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.741696 (15)	1.042853 (7)	0.08809 (2)	0.01677 (4)
N1	0.78272 (13)	0.79718 (7)	0.17705 (16)	0.01325 (19)
H1N1	0.712 (2)	0.7551 (11)	0.133 (3)	0.022 (4)*
N2	0.99471 (14)	0.70859 (7)	0.34946 (18)	0.0152 (2)
H2N2	1.091 (3)	0.7028 (12)	0.426 (3)	0.031 (5)*
H1N2	0.926 (2)	0.6673 (12)	0.296 (3)	0.036 (5)*
C1	0.72188 (15)	0.87250 (8)	0.11482 (19)	0.0142 (2)
H1A	0.6112	0.8790	0.0301	0.017*
C2	0.82285 (16)	0.93842 (8)	0.1764 (2)	0.0139 (2)
C3	0.99045 (15)	0.92827 (8)	0.3065 (2)	0.0148 (2)
H3A	1.0606	0.9729	0.3486	0.018*
C4	1.04836 (15)	0.85246 (8)	0.36957 (19)	0.0144 (2)
H4A	1.1575	0.8455	0.4585	0.017*
C5	0.94285 (15)	0.78397 (8)	0.30010 (18)	0.0127 (2)

O1W	0.34331 (12)	0.71054 (7)	0.61811 (17)	0.0206 (2)
H2W1	0.392 (3)	0.6972 (13)	0.729 (3)	0.038 (6)*
H1W1	0.396 (3)	0.7487 (15)	0.594 (4)	0.043 (6)*
O1	0.55652 (11)	0.67725 (5)	0.02333 (15)	0.01630 (18)
O2	0.75988 (11)	0.58655 (6)	0.15601 (16)	0.01766 (18)
C6	0.48381 (16)	0.53893 (7)	-0.0202 (2)	0.0139 (2)
H6AA	0.3763	0.5537	-0.1026	0.017*
C7	0.61164 (15)	0.60438 (7)	0.06033 (19)	0.0127 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01516 (6)	0.01024 (6)	0.02259 (7)	0.00028 (4)	0.00262 (4)	0.00195 (5)
N1	0.0112 (4)	0.0107 (5)	0.0165 (5)	-0.0015 (4)	0.0023 (4)	-0.0004 (4)
N2	0.0124 (5)	0.0108 (5)	0.0201 (5)	-0.0002 (4)	0.0017 (4)	0.0006 (4)
C1	0.0128 (5)	0.0124 (5)	0.0161 (5)	0.0000 (4)	0.0027 (4)	0.0010 (4)
C2	0.0137 (5)	0.0103 (5)	0.0170 (5)	0.0005 (4)	0.0040 (4)	0.0008 (4)
C3	0.0129 (5)	0.0123 (5)	0.0182 (6)	-0.0025 (4)	0.0035 (4)	-0.0017 (4)
C4	0.0117 (5)	0.0129 (6)	0.0162 (5)	-0.0016 (4)	0.0011 (4)	-0.0019 (4)
C5	0.0111 (5)	0.0128 (5)	0.0139 (5)	-0.0003 (4)	0.0036 (4)	-0.0005 (4)
O1W	0.0163 (5)	0.0189 (5)	0.0221 (5)	-0.0039 (4)	-0.0003 (4)	0.0050 (4)
O1	0.0134 (4)	0.0097 (4)	0.0228 (5)	0.0004 (3)	0.0014 (3)	-0.0001 (3)
O2	0.0120 (4)	0.0126 (4)	0.0245 (5)	0.0001 (3)	0.0002 (3)	-0.0001 (4)
C6	0.0112 (5)	0.0111 (5)	0.0176 (5)	-0.0005 (4)	0.0016 (4)	-0.0011 (4)
C7	0.0130 (5)	0.0105 (5)	0.0138 (5)	-0.0010 (4)	0.0030 (4)	-0.0001 (4)

Geometric parameters (Å, °)

Br1—C2	1.8832 (13)	C3—H3A	0.9300
N1—C5	1.3556 (15)	C4—C5	1.4223 (17)
N1—C1	1.3616 (16)	C4—H4A	0.9300
N1—H1N1	0.899 (18)	O1W—H2W1	0.77 (2)
N2—C5	1.3278 (16)	O1W—H1W1	0.81 (2)
N2—H2N2	0.81 (2)	O1—C7	1.2863 (15)
N2—H1N2	0.89 (2)	O2—C7	1.2416 (14)
C1—C2	1.3620 (17)	C6—C6 ⁱ	1.326 (2)
C1—H1A	0.9300	C6—C7	1.4990 (17)
C2—C3	1.4130 (17)	C6—H6AA	0.9300
C3—C4	1.3635 (18)		
C5—N1—C1	122.64 (11)	C2—C3—H3A	120.3
C5—N1—H1N1	119.8 (11)	C3—C4—C5	120.37 (11)
C1—N1—H1N1	117.5 (12)	C3—C4—H4A	119.8
C5—N2—H2N2	116.7 (14)	C5—C4—H4A	119.8
C5—N2—H1N2	119.8 (13)	N2—C5—N1	119.22 (11)
H2N2—N2—H1N2	123.4 (19)	N2—C5—C4	122.97 (11)
N1—C1—C2	120.10 (11)	N1—C5—C4	117.81 (11)
N1—C1—H1A	119.9	H2W1—O1W—H1W1	105 (2)

C2—C1—H1A	120.0	C6 ⁱ —C6—C7	123.34 (14)
C1—C2—C3	119.67 (12)	C6 ⁱ —C6—H6AA	118.3
C1—C2—Br1	120.62 (9)	C7—C6—H6AA	118.3
C3—C2—Br1	119.71 (9)	O2—C7—O1	124.24 (11)
C4—C3—C2	119.37 (11)	O2—C7—C6	120.03 (11)
C4—C3—H3A	120.3	O1—C7—C6	115.72 (11)
C5—N1—C1—C2	-0.12 (18)	C1—N1—C5—N2	-178.04 (12)
N1—C1—C2—C3	-0.51 (19)	C1—N1—C5—C4	1.59 (17)
N1—C1—C2—Br1	178.98 (9)	C3—C4—C5—N2	177.11 (13)
C1—C2—C3—C4	-0.42 (19)	C3—C4—C5—N1	-2.50 (18)
Br1—C2—C3—C4	-179.92 (10)	C6 ⁱ —C6—C7—O2	6.0 (2)
C2—C3—C4—C5	1.93 (19)	C6 ⁱ —C6—C7—O1	-173.89 (16)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N1 ⁱ ...O1	0.902 (18)	1.815 (18)	2.7136 (14)	174.1 (19)
N2—H2N2 ⁱ ...O1W ⁱⁱ	0.82 (2)	2.11 (2)	2.9143 (16)	169.7 (19)
N2—H1N2 ⁱ ...O2	0.893 (19)	1.946 (19)	2.8348 (15)	173.2 (19)
O1W—H2W1 ⁱ ...O1 ⁱⁱⁱ	0.77 (2)	2.07 (2)	2.8213 (15)	169 (2)
O1W—H1W1 ⁱ ...O1 ^{iv}	0.82 (3)	1.99 (3)	2.7865 (14)	167 (3)
C3—H3A ⁱ ...O2 ^v	0.93	2.41	3.3089 (17)	162

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