

# 2,2'-Bipyridin-1'-ium 1-oxide bromide monohydrate

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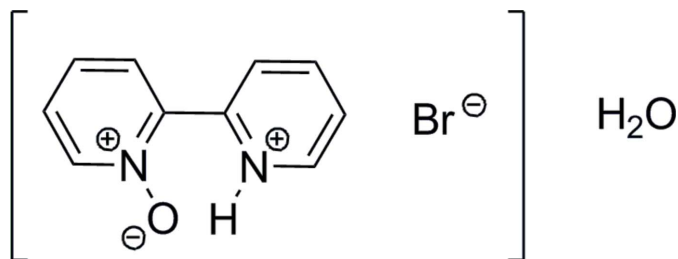
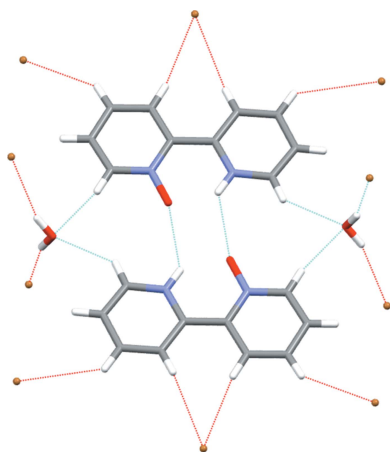
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The title compound 2,2'-bipyridin-1'-ium 1-oxide bromide crystallizes as a monohydrate,  $C_{10}H_9N_2^+ \cdot Br^- \cdot H_2O$ . Structural disorder is observed due to the fact that protonation, as well as oxidation, of the N atoms of 2,2'-bipyridine occurs at either of the N atoms. The disorder extends to the remainder of the cation, with a refined occupancy rate of 0.717 (4) for the major moiety. An intramolecular N—H...O hydrogen bond forces the bipyridine unit into an *s-cis* conformation. Each pair of neighbouring 2,2'-bipyridin-1'-ium ions forms a dimeric aggregate by hydrogen bonds between their respective N—O and the N—H functions. These dimers and hydrogen-bonding interactions with bromide ions and the water molecule give rise to a complex supramolecular arrangement.

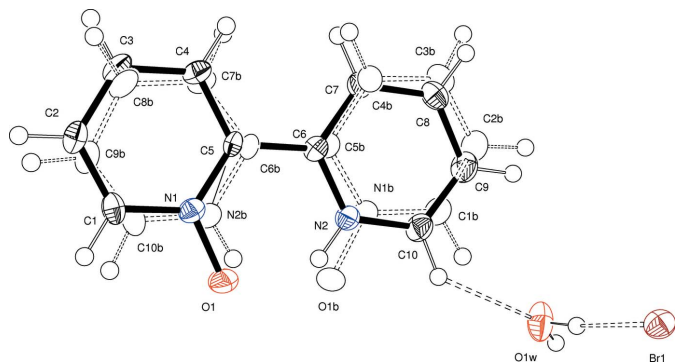
## 1. Chemical context

Bipyridine ligands are an important class of ligands with respect to the synthesis of transition metal complexes. They are especially well-known for their use in the development of complexes with specific photophysical (Thompson *et al.*, 2013; Sun *et al.*, 2015; Dongare *et al.*, 2017) and/or photocatalytic (Wenger, 2013; Fukuzumi *et al.*, 2016; Knoll *et al.*, 2015; Duan *et al.*, 2015; Pal & Hanan, 2014) properties or for the construction of dye-sensitized solar cells (Happ *et al.*, 2012; Bomben *et al.*, 2012; Robson *et al.*, 2012; Adeloye & Ajibade, 2014; Lu *et al.*, 2016; Omae, 2016). During our attempts to introduce substituents to 2,2'-bipyridines that would allow us to use them as monomers in copolymerization reactions (Heintz *et al.*, 2017), we treated 2,2'-bipyridine with a mixture of hydrobromic acid and hydrogen peroxide with the aim of getting direct access to 4-bromo-2,2'-bipyridine-1-oxide. After recrystallization, the title compound turned out to be the only isolable product.



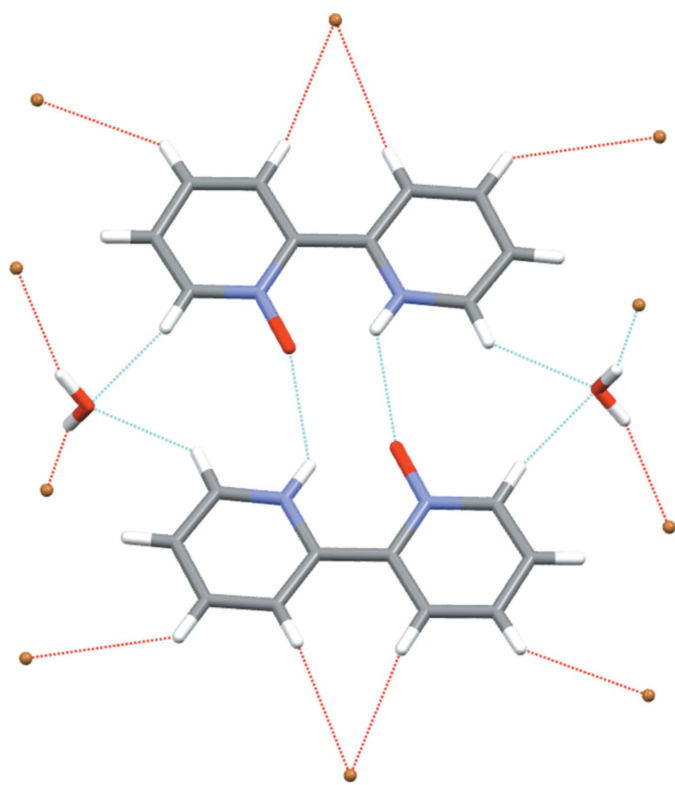
## 2. Structural commentary

The molecular structure of the cation of the title compound is depicted in Fig. 1, showing the disorder of the cations in which the oxygen atom and the proton are bonded to either N1 or N2. The two cation moieties are disordered over the same



**Figure 1**  
Molecular structure of the cation of the title compound. Non-hydrogen atoms showing displacement ellipsoids with octand shading represent the major component of the two disordered cations.

position in an approximate 3:1 ratio, with a refined occupancy for the major moiety of 0.717 (4). The disorder has been refined in terms of a whole molecule disorder, thus leading virtually identical bond lengths which, in addition, are of expected values. See the *Refinement* section for details of the refinement of the disorder. The two pyridine subunits of the 2,2'-bipyridine exhibit an *s-cis* conformation, which is stabilized by an intramolecular N—H···O hydrogen bond (Table 1). The *s-cis* conformation also allows the cations to arrange themselves into dimeric aggregates *via* additional N—H···O hydrogen bonds (*cf.* *Supramolecular features*).



**Figure 2**  
Dimer of cations formed by N—H···O hydrogen bonds (Table 1). Hydrogen-bonded bromide anions and water molecules are also shown. Disorder of the cation is omitted for clarity.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H1N2···O1	0.88	1.76	2.485 (4)	138
N2—H1N2···O1 <sup>i</sup>	0.88	2.41	3.089 (5)	134
C1—H1···O1W <sup>i</sup>	0.95	2.22	3.138 (6)	163
C4—H4···Br1 <sup>ii</sup>	0.95	2.75	3.687 (10)	167
C7—H7···Br1 <sup>ii</sup>	0.95	2.86	3.769 (10)	160
C10—H10···O1W	0.95	2.34	3.074 (5)	134
N2B—H2N2···O1B	0.88	1.81	2.500 (15)	134
N2B—H2N2···O1B <sup>i</sup>	0.88	2.35	3.117 (18)	146
C1B—H1B···O1W	0.95	2.09	2.979 (14)	156
C2B—H2B···Br1 <sup>iii</sup>	0.95	2.80	3.497 (15)	131
C4B—H4B···Br1 <sup>ii</sup>	0.95	2.77	3.70 (3)	168
C7B—H7B···Br1 <sup>ii</sup>	0.95	2.92	3.80 (3)	155
C10B—H10B···O1W <sup>i</sup>	0.95	2.40	3.246 (17)	147
O1W—H1W1···Br1	0.90 (3)	2.47 (3)	3.3475 (18)	165 (3)
O1W—H2W1···Br1 <sup>iv</sup>	0.84 (3)	2.57 (3)	3.3754 (17)	160 (3)

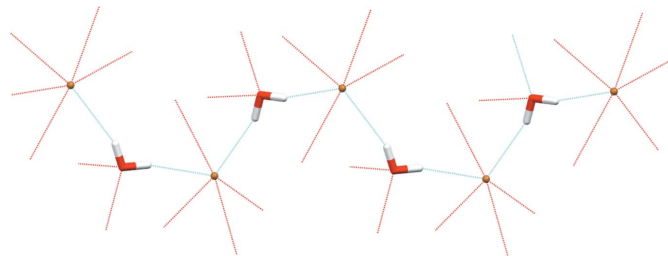
Symmetry codes: (i)  $-x, -y, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x + 1, y, z$ ; (iv)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ .

### 3. Supramolecular features

Fig. 2 shows a dimeric aggregate built up by two cations of the title compound *via* N—H···O hydrogen bonds (Table 1). In addition, the figure shows that hydrogen atoms in the 3, 3', 4 and 4' positions of each bipyridine unit are engaged in C—H···Br hydrogen bonds (Desiraju & Steiner, 2001) with the interactions of the 3 and 3' hydrogen atoms being part of a bifurcated hydrogen bond towards the bromide anion. Hydrogen atoms in the 6 and 6' positions are part of bifurcated hydrogen bonds towards the water molecule. Moreover, the hydrogen atoms of the water molecules are involved in hydrogen bonds of the O—H···Br type. Bromide anions and water molecules form zigzag chains along the *b*-axis direction (Fig. 3). In summary, a complex network structure is realized by hydrogen bonds linking the constituents of this zigzag chain into dimers of cations.

### 4. Database survey

According to a CSD survey (Version 5.38; Groom *et al.*, 2016) and in contrast to 2,2'-bipyridine or 2,2'-bipyridine-1-oxide, there are no metal complexes reported in which a protonated 2,2'-bipyridine-1-oxide acts as a ligand. Nevertheless, there are several closely related compounds that show different counter-ions. There are entries involving the hydrogensulfate (ESUMEL; Najafpour *et al.*, 2010), the perrhenate (PEPDAP;



**Figure 3**  
Zigzag chain of water molecules and bromide anions parallel to the *b* axis.

Englert *et al.*, 1993) and the triiodide (SINBIB; Lin *et al.*, 2007). All of these compounds, as well as the title compound itself, show an *s-cis* conformation of the bipyridine. Moreover, in all compounds, both rings of the bipyridine show an almost perfect coplanar arrangement with dihedral angles well below 10° [title compound: molecule 1: 1.2 (6)°, molecule 2: 2(2)°; ESUMEL 5.9°; PEPDAP 3.9°; SINBIB 2.7°]. This arrangement is most probably caused by the short intramolecular N—H...O hydrogen bond between the protonated nitrogen atom and the oxygen atom (title compound: molecule 1 1.76, molecule 2; 1.81 Å; ESUMEL 1.73 Å; PEPDAP 1.71 Å; SINBIB 1.73 Å). The supramolecular arrangement in ESUMEL and PEPDAP is identical, with the cations also forming hydrogen-bonded dimers. Nevertheless, in contrast to the title compound, these dimers are formed by weak C—H...O hydrogen bonds of aromatic C—H functions towards the oxygen atom. All other hydrogen bonds are realized by oxygen atoms of the counter-ions acting as the hydrogen-bond acceptor sites. In SINBIB, the cations form an infinite plane realized by bifurcated hydrogen bonds of the oxygen atoms with aromatic C—H functions. In addition, each cation shows a weak C—H...I interaction. In ESUMEL and SINBIB, the protonated N—H groups are not involved in the hydrogen-bond network, whereas in PEPDAP there is an N—H...O hydrogen bond to one of the perchlorate counter-ions. In summary, the hydrogen-bond network observed for the title compound is unique compared to the situation for other closely related crystal structures.

## 5. Synthesis and crystallization

2,2'-Bipyridine (1 g, 6.5 mmol) was dissolved in 15 mL methanol. Then hydrobromic acid (0.58 g, 7.2 mmol) and a 30% solution of hydrogen peroxide (0.74 mL, 6.5 mmol) were added at 283 K. The solution was stirred at room temperature for 20 h. The clear solution turned yellow and a fine precipitate was formed, which dissolved again during the reaction time. After the solvent had evaporated, the colourless residue was dissolved in ethanol. Then water was added until a fine precipitate was formed. Storing the solution in the refrigerator (277 K) overnight led to the formation of crystals suitable for x-ray diffraction (yield: 126 mg, 0.3 mmol, 46%).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Data were corrected for Lorentz and polarization effects. Water H atoms were freely refined. All other hydrogen atoms were placed in idealized positions (N—H = 0.88, C—H = 0.95 Å) and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$ . The disorder was refined in terms of a whole molecule disorder. The geometry of major and minor moieties were restrained to be similar (SAME restraint in *SHELXL*) and anisotropic displacement parameters of equivalent atoms in the two moieties were constrained to be identical. Site-occupation factors of the

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{10}\text{H}_9\text{N}_2\text{O}^+\cdot\text{Br}^-\cdot\text{H}_2\text{O}$
$M_r$	271.12
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	133
$a, b, c$ (Å)	5.7882 (1), 9.2095 (2), 20.2485 (4)
$\beta$ (°)	91.701 (1)
$V$ (Å <sup>3</sup> )	1078.90 (4)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	3.79
Crystal size (mm)	0.05 × 0.04 × 0.03
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2002)
$T_{\text{min}}, T_{\text{max}}$	0.557, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12419, 2465, 2226
$R_{\text{int}}$	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.052, 1.07
No. of reflections	2465
No. of parameters	190
No. of restraints	32
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.46, -0.51

Computer programs: *COLLECT* (Nonius, 1998), *DENZO* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006).

atoms of the two disordered cations were refined using the FVAR instruction and were calculated to be 0.717 (4) (O1 to H10) and 0.283 (4) (O1B to H10B).

## Funding information

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## supporting information

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## 2,2'-Bipyridin-1'-ium 1-oxide bromide monohydrate

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## Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2006).

## 2,2'-Bipyridin-1'-ium 1-oxide bromide monohydrate

## Crystal data

$C_{10}H_9N_2O^+ \cdot Br^- \cdot H_2O$

$M_r = 271.12$

Monoclinic,  $P2_1/c$

$a = 5.7882$  (1) Å

$b = 9.2095$  (2) Å

$c = 20.2485$  (4) Å

$\beta = 91.701$  (1)°

$V = 1078.90$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 544$

$D_x = 1.669$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 12419 reflections

$\theta = 2.0$ – $27.5$ °

$\mu = 3.79$  mm<sup>-1</sup>

$T = 133$  K

Prism, colourless

$0.05 \times 0.04 \times 0.03$  mm

## Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\phi$ – $\omega$ –scan

Absorption correction: multi-scan

(SADABS; Sheldrick, 2002)

$T_{\min} = 0.557$ ,  $T_{\max} = 0.746$

12419 measured reflections

2465 independent reflections

2226 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.0$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 11$

$l = -26 \rightarrow 26$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.052$

$S = 1.07$

2465 reflections

190 parameters

32 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0113P)^2 + 0.9881P]$

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

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

$\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.51$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	-0.09302 (3)	0.63110 (2)	0.65415 (2)	0.02577 (7)	
O1	0.0960 (3)	-0.0036 (2)	0.43461 (9)	0.0270 (5)	0.717 (4)
N1	0.2649 (12)	0.0073 (8)	0.3908 (2)	0.0199 (9)	0.717 (4)
N2	0.3050 (9)	0.1763 (6)	0.5057 (2)	0.0206 (7)	0.717 (4)
H1N2	0.188837	0.116543	0.497651	0.025*	0.717 (4)
C1	0.2378 (9)	-0.0729 (6)	0.33445 (16)	0.0236 (8)	0.717 (4)
H1	0.103588	-0.130999	0.327701	0.028*	0.717 (4)
C2	0.4039 (8)	-0.0697 (6)	0.2875 (2)	0.0252 (9)	0.717 (4)
H2	0.385065	-0.126508	0.248510	0.030*	0.717 (4)
C3	0.5987 (11)	0.0160 (10)	0.2967 (4)	0.0254 (8)	0.717 (4)
H3	0.716054	0.016114	0.264870	0.031*	0.717 (4)
C4	0.620 (2)	0.1013 (15)	0.3526 (4)	0.0211 (11)	0.717 (4)
H4	0.748457	0.165180	0.358187	0.025*	0.717 (4)
C5	0.4539 (15)	0.0933 (9)	0.4009 (4)	0.0162 (9)	0.717 (4)
C6	0.4718 (14)	0.1856 (12)	0.4606 (3)	0.0174 (9)	0.717 (4)
C7	0.6635 (19)	0.2733 (8)	0.4752 (5)	0.0217 (11)	0.717 (4)
H7	0.791700	0.274957	0.447024	0.026*	0.717 (4)
C8	0.6624 (8)	0.3582 (9)	0.5321 (3)	0.0254 (9)	0.717 (4)
H8	0.783428	0.426128	0.540232	0.031*	0.717 (4)
C9	0.4864 (8)	0.3452 (6)	0.5776 (3)	0.0276 (11)	0.717 (4)
H9	0.491253	0.398271	0.617799	0.033*	0.717 (4)
C10	0.3066 (7)	0.2532 (5)	0.5621 (2)	0.0254 (9)	0.717 (4)
H10	0.182364	0.243774	0.591417	0.030*	0.717 (4)
O1B	0.1468 (8)	0.1100 (5)	0.5162 (2)	0.0283 (14)	0.283 (4)
N1B	0.330 (3)	0.1968 (18)	0.5193 (7)	0.0206 (7)	0.283 (4)
N2B	0.263 (3)	0.018 (2)	0.4059 (7)	0.0199 (9)	0.283 (4)
H2N2	0.165293	0.014377	0.438408	0.024*	0.283 (4)
C1B	0.361 (2)	0.2832 (16)	0.5724 (6)	0.0254 (9)	0.283 (4)
H1B	0.251328	0.281476	0.606250	0.030*	0.283 (4)
C2B	0.546 (3)	0.3722 (19)	0.5783 (8)	0.0276 (11)	0.283 (4)
H2B	0.556963	0.436182	0.615077	0.033*	0.283 (4)
C3B	0.716 (3)	0.373 (3)	0.5334 (10)	0.0254 (9)	0.283 (4)
H3B	0.858710	0.421752	0.541526	0.031*	0.283 (4)
C4B	0.668 (5)	0.299 (3)	0.4753 (13)	0.0217 (11)	0.283 (4)
H4B	0.756541	0.319587	0.437556	0.026*	0.283 (4)



C5B	0.493 (4)	0.196 (3)	0.4710 (10)	0.0174 (9)	0.283 (4)
C6B	0.450 (4)	0.112 (3)	0.4118 (11)	0.0162 (9)	0.283 (4)
C7B	0.607 (6)	0.094 (4)	0.3618 (13)	0.0211 (11)	0.283 (4)
H7B	0.754015	0.139492	0.366763	0.025*	0.283 (4)
C8B	0.558 (3)	0.015 (3)	0.3049 (11)	0.0254 (8)	0.283 (4)
H8B	0.657616	0.018628	0.268447	0.031*	0.283 (4)
C9B	0.361 (3)	-0.0716 (19)	0.3024 (7)	0.0252 (9)	0.283 (4)
H9B	0.324956	-0.132271	0.265541	0.030*	0.283 (4)
C10B	0.224 (3)	-0.0649 (19)	0.3544 (5)	0.0236 (8)	0.283 (4)
H10B	0.089399	-0.124292	0.353836	0.028*	0.283 (4)
O1W	0.1320 (3)	0.31147 (18)	0.70149 (8)	0.0383 (4)	
H1W1	0.067 (6)	0.400 (4)	0.6970 (16)	0.075 (10)*	
H2W1	0.117 (5)	0.288 (3)	0.7415 (16)	0.064 (9)*	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02760 (10)	0.02744 (12)	0.02241 (10)	0.00035 (7)	0.00334 (7)	0.00392 (7)
O1	0.0252 (10)	0.0336 (11)	0.0225 (10)	-0.0067 (8)	0.0068 (7)	-0.0001 (8)
N1	0.0208 (8)	0.0207 (15)	0.019 (3)	0.0010 (8)	0.0034 (18)	0.002 (2)
N2	0.0220 (15)	0.024 (2)	0.016 (2)	-0.0026 (11)	0.0018 (14)	-0.0009 (14)
C1	0.0280 (13)	0.0231 (12)	0.019 (2)	-0.0009 (10)	-0.006 (2)	-0.004 (2)
C2	0.030 (2)	0.0272 (11)	0.018 (2)	0.0045 (15)	0.0008 (13)	-0.0047 (17)
C3	0.022 (3)	0.0337 (11)	0.021 (2)	0.0066 (19)	0.0064 (15)	-0.0024 (15)
C4	0.0189 (17)	0.0273 (17)	0.017 (3)	0.0011 (11)	0.0040 (17)	0.003 (2)
C5	0.0186 (8)	0.015 (3)	0.015 (3)	0.0039 (14)	0.0018 (16)	-0.0031 (14)
C6	0.0199 (18)	0.0198 (19)	0.012 (3)	0.0021 (12)	-0.0014 (18)	0.0032 (18)
C7	0.0259 (10)	0.017 (3)	0.0225 (9)	0.000 (2)	0.0028 (7)	0.0005 (19)
C8	0.025 (3)	0.025 (2)	0.0259 (10)	-0.004 (2)	-0.005 (2)	-0.0014 (11)
C9	0.037 (3)	0.028 (3)	0.0183 (10)	0.000 (2)	0.0029 (19)	-0.0003 (15)
C10	0.030 (2)	0.029 (2)	0.0179 (18)	-0.0004 (15)	0.0043 (14)	-0.0005 (14)
O1B	0.025 (2)	0.034 (3)	0.026 (3)	-0.011 (2)	0.0061 (19)	-0.004 (2)
N1B	0.0220 (15)	0.024 (2)	0.016 (2)	-0.0026 (11)	0.0018 (14)	-0.0009 (14)
N2B	0.0208 (8)	0.0207 (15)	0.019 (3)	0.0010 (8)	0.0034 (18)	0.002 (2)
C1B	0.030 (2)	0.029 (2)	0.0179 (18)	-0.0004 (15)	0.0043 (14)	-0.0005 (14)
C2B	0.037 (3)	0.028 (3)	0.0183 (10)	0.000 (2)	0.0029 (19)	-0.0003 (15)
C3B	0.025 (3)	0.025 (2)	0.0259 (10)	-0.004 (2)	-0.005 (2)	-0.0014 (11)
C4B	0.0259 (10)	0.017 (3)	0.0225 (9)	0.000 (2)	0.0028 (7)	0.0005 (19)
C5B	0.0199 (18)	0.0198 (19)	0.012 (3)	0.0021 (12)	-0.0014 (18)	0.0032 (18)
C6B	0.0186 (8)	0.015 (3)	0.015 (3)	0.0039 (14)	0.0018 (16)	-0.0031 (14)
C7B	0.0189 (17)	0.0273 (17)	0.017 (3)	0.0011 (11)	0.0040 (17)	0.003 (2)
C8B	0.022 (3)	0.0337 (11)	0.021 (2)	0.0066 (19)	0.0064 (15)	-0.0024 (15)
C9B	0.030 (2)	0.0272 (11)	0.018 (2)	0.0045 (15)	0.0008 (13)	-0.0047 (17)
C10B	0.0280 (13)	0.0231 (12)	0.019 (2)	-0.0009 (10)	-0.006 (2)	-0.004 (2)
O1W	0.0614 (10)	0.0280 (8)	0.0259 (8)	0.0023 (8)	0.0041 (7)	-0.0044 (7)

*Geometric parameters (Å, °)*

O1—N1	1.343 (6)	N1B—C1B	1.345 (12)
N1—C5	1.361 (7)	N1B—C5B	1.378 (19)
N1—C1	1.364 (4)	N2B—C10B	1.307 (12)
N2—C10	1.344 (4)	N2B—C6B	1.386 (19)
N2—C6	1.351 (7)	N2B—H2N2	0.8800
N2—H1N2	0.8800	C1B—C2B	1.347 (11)
C1—C2	1.373 (4)	C1B—H1B	0.9500
C1—H1	0.9500	C2B—C3B	1.362 (17)
C2—C3	1.384 (7)	C2B—H2B	0.9500
C2—H2	0.9500	C3B—C4B	1.38 (2)
C3—C4	1.381 (8)	C3B—H3B	0.9500
C3—H3	0.9500	C4B—C5B	1.392 (19)
C4—C5	1.396 (7)	C4B—H4B	0.9500
C4—H4	0.9500	C5B—C6B	1.444 (12)
C5—C6	1.478 (4)	C6B—C7B	1.390 (19)
C6—C7	1.397 (8)	C7B—C8B	1.39 (2)
C7—C8	1.393 (8)	C7B—H7B	0.9500
C7—H7	0.9500	C8B—C9B	1.390 (17)
C8—C9	1.398 (6)	C8B—H8B	0.9500
C8—H8	0.9500	C9B—C10B	1.339 (11)
C9—C10	1.371 (4)	C9B—H9B	0.9500
C9—H9	0.9500	C10B—H10B	0.9500
C10—H10	0.9500	O1W—H1W1	0.90 (3)
O1B—N1B	1.330 (12)	O1W—H2W1	0.84 (3)
O1—N1—C5	122.8 (4)	O1B—N1B—C5B	121.8 (11)
O1—N1—C1	116.4 (5)	C1B—N1B—C5B	119.5 (12)
C5—N1—C1	120.8 (5)	C10B—N2B—C6B	123.3 (15)
C10—N2—C6	123.6 (4)	C10B—N2B—H2N2	118.4
C10—N2—H1N2	118.2	C6B—N2B—H2N2	118.4
C6—N2—H1N2	118.2	N1B—C1B—C2B	121.2 (14)
N1—C1—C2	120.2 (5)	N1B—C1B—H1B	119.4
N1—C1—H1	119.9	C2B—C1B—H1B	119.4
C2—C1—H1	119.9	C1B—C2B—C3B	122.1 (15)
C1—C2—C3	120.2 (4)	C1B—C2B—H2B	119.0
C1—C2—H2	119.9	C3B—C2B—H2B	119.0
C3—C2—H2	119.9	C2B—C3B—C4B	115.9 (15)
C4—C3—C2	119.3 (5)	C2B—C3B—H3B	122.1
C4—C3—H3	120.4	C4B—C3B—H3B	122.1
C2—C3—H3	120.4	C3B—C4B—C5B	121 (2)
C3—C4—C5	119.8 (7)	C3B—C4B—H4B	119.4
C3—C4—H4	120.1	C5B—C4B—H4B	119.4
C5—C4—H4	120.1	N1B—C5B—C4B	117.6 (17)
N1—C5—C4	119.6 (5)	N1B—C5B—C6B	119.0 (17)
N1—C5—C6	119.6 (6)	C4B—C5B—C6B	121.9 (19)
C4—C5—C6	120.6 (7)	N2B—C6B—C7B	113.1 (16)



N2—C6—C7	118.2 (6)	N2B—C6B—C5B	121.5 (18)
N2—C6—C5	118.8 (6)	C7B—C6B—C5B	124 (2)
C7—C6—C5	122.8 (7)	C8B—C7B—C6B	123 (2)
C8—C7—C6	118.5 (8)	C8B—C7B—H7B	118.5
C8—C7—H7	120.7	C6B—C7B—H7B	118.5
C6—C7—H7	120.7	C7B—C8B—C9B	118.6 (16)
C7—C8—C9	121.2 (5)	C7B—C8B—H8B	120.7
C7—C8—H8	119.4	C9B—C8B—H8B	120.7
C9—C8—H8	119.4	C10B—C9B—C8B	116.8 (14)
C10—C9—C8	117.8 (5)	C10B—C9B—H9B	121.6
C10—C9—H9	121.1	C8B—C9B—H9B	121.6
C8—C9—H9	121.1	N2B—C10B—C9B	124.2 (16)
N2—C10—C9	120.4 (4)	N2B—C10B—H10B	117.9
N2—C10—H10	119.8	C9B—C10B—H10B	117.9
C9—C10—H10	119.8	H1W1—O1W—H2W1	106 (3)
O1B—N1B—C1B	118.7 (12)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N2 $\cdots$ O1	0.88	1.76	2.485 (4)	138
N2—H1N2 $\cdots$ O1 <sup>i</sup>	0.88	2.41	3.089 (5)	134
C1—H1 $\cdots$ O1W <sup>i</sup>	0.95	2.22	3.138 (6)	163
C4—H4 $\cdots$ Br1 <sup>ii</sup>	0.95	2.75	3.687 (10)	167
C7—H7 $\cdots$ Br1 <sup>ii</sup>	0.95	2.86	3.769 (10)	160
C10—H10 $\cdots$ O1W	0.95	2.34	3.074 (5)	134
N2B—H2N2 $\cdots$ O1B	0.88	1.81	2.500 (15)	134
N2B—H2N2 $\cdots$ O1B <sup>i</sup>	0.88	2.35	3.117 (18)	146
C1B—H1B $\cdots$ O1W	0.95	2.09	2.979 (14)	156
C2B—H2B $\cdots$ Br1 <sup>iii</sup>	0.95	2.80	3.497 (15)	131
C4B—H4B $\cdots$ Br1 <sup>ii</sup>	0.95	2.77	3.70 (3)	168
C7B—H7B $\cdots$ Br1 <sup>ii</sup>	0.95	2.92	3.80 (3)	155
C10B—H10B $\cdots$ O1W <sup>i</sup>	0.95	2.40	3.246 (17)	147
O1W—H1W1 $\cdots$ Br1	0.90 (3)	2.47 (3)	3.3475 (18)	165 (3)
O1W—H2W1 $\cdots$ Br1 <sup>iv</sup>	0.84 (3)	2.57 (3)	3.3754 (17)	160 (3)

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