

4,15-Dimethyl-7,12-diazoniatricyclo[10.4.0.0^{2,7}]-hexadeca-1(12),2,4,6,13,15-hexaene dibromide monohydrate

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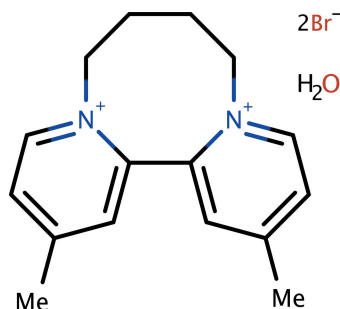
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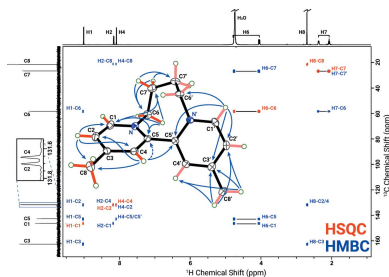
The title compound, C₁₆H₂₀N₂²⁺·2Br⁻·H₂O (**1**) is a member of the class of compounds called viologens. Viologens are quaternary salts of dipyrindyls and are especially useful as redox indicators as a result of their large negative one-electron reduction potentials. Compound **1** consists of a dication composed of a pair of 4-methylpyridine rings mutually joined at the 2-position, with a dihedral angle between the pyridine rings of 62.35 (4)°. In addition, the rings are tethered *via* the pyridine nitrogen atoms by a tetramethylene bridge. Charge balance is provided by a pair of bromide anions, which are hydrogen bonded to a single water molecule [*D*_{O...Br} = 3.3670 (15) and 3.3856 (15) Å]. The crystal structure of **1**, details of an improved synthesis, and a full analysis of its NMR spectra are presented.

1. Chemical context

The title compound (**1**) is a member of the class of compounds called viologens. Viologens are quaternary salts of dipyrindyls, which have proven useful as redox indicators as a result of their large negative one-electron reduction potentials (Anderson & Patel, 1984). The herbicides, paraquat, and diquat are viologens. We found that the literature synthesis of 4,4'-dimethyl-2,2'-dipyridyl-*N,N'*-tetramethylene dibromide, *i.e.*, **1** (Spotswood & Tanzer, 1967) could be improved by a change in the solvent. We report details of our improved synthesis of **1** along with the crystal structure and a full analysis of its NMR spectra.



Spotswood & Tanzer (1967) give general directions for the syntheses of a series of bridged dimethyl 2,2'-dipyridyl salts. Our attempts to make the title compound by their directions failed; only a salt of the starting dipyrindyl was recovered. Homer & Tomlinson (1960) noted that HBr is formed by dehydrohalogenation of the dibromide. We think that the conditions used by Anderson & Patel (1984), *i.e.*, refluxing



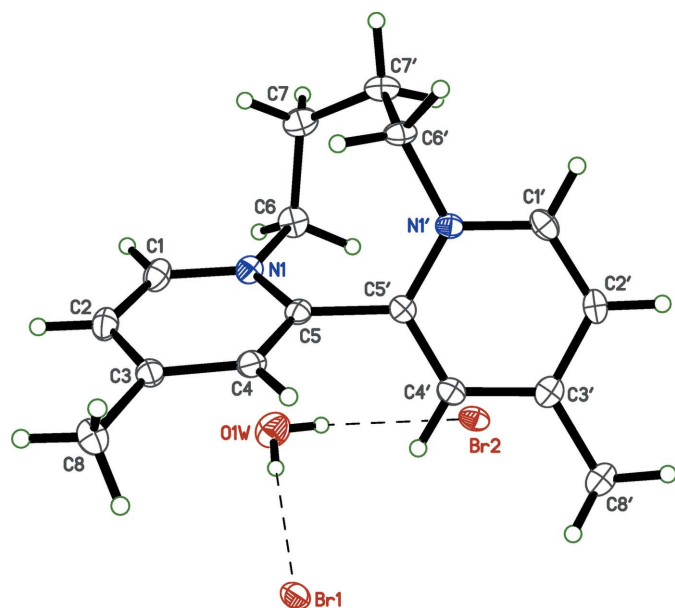


Figure 1
A view of **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds between water and Br^- are shown as dashed lines.

o-dichlorobenzene, b.p. 453 K, produced a good deal of HBr, which protonated the dipyrindyl, rendering it unreactive. Carrying out the reaction in refluxing xylene (mixed isomers, b.p. *ca* 413 K) does not produce HBr, but the reaction is slow; after five h, about 50% of the starting dipyrindyl was recovered. The quaternization of tertiary amines is known as the Menshutkin reaction (Menschutkin, 1890). The velocity of this reaction shows a strong dependence on solvent (Abraham

& Grellier, 1976), with about a 65,000-fold increase from hexane to DMSO. The addition of nitrobenzene to the solvent gave satisfactory yields of the product in a reasonable time (see *Synthesis and crystallization* section).

2. Structural commentary

The molecular structure of **1** is shown in Fig. 1. It consists of a dication composed of a pair of 4-methylpyridine rings mutually joined at their 2-positions, with a dihedral angle between the pyridine rings of $62.35(4)^\circ$. In addition, the rings are tethered *via* the pyridine nitrogen atoms by a tetramethylene bridge. There are no unusual bond lengths or angles. As a result of the two bridges between the pyridine rings, **1** occurs as two optical isomers, and therefore provides an example of atropisomerism (Eliel *et al.*, 1994; Alkorta *et al.*, 2012; Mancinelli *et al.*, 2020). Crystals of **1**, however, were centrosymmetric, with space group $P2_1/n$, and are thus strictly racemic. Charge balance is provided by a pair of bromide anions, which are hydrogen bonded to a single water molecule of crystallization [$D_{\text{O}\cdots\text{Br}} = 3.3670(15)$ and $3.3856(15)$ Å] (Table 1).

3. Supramolecular features

Aside from the hydrogen bonds between the water molecule and bromide anions, the only other notable intermolecular contacts are interactions of type $\text{C}-\text{H}\cdots\text{Br}$ (Fig. 2, Table 1), with distances that range between $3.5765(17)$ and $3.7762(18)$ Å for type $\text{C}_{\text{pyridinyl}}\cdots\text{Br}$ and $3.6581(18)$ to $3.7700(19)$ Å for type $\text{C}_{\text{methylene}}\cdots\text{Br}$. For comparison, the

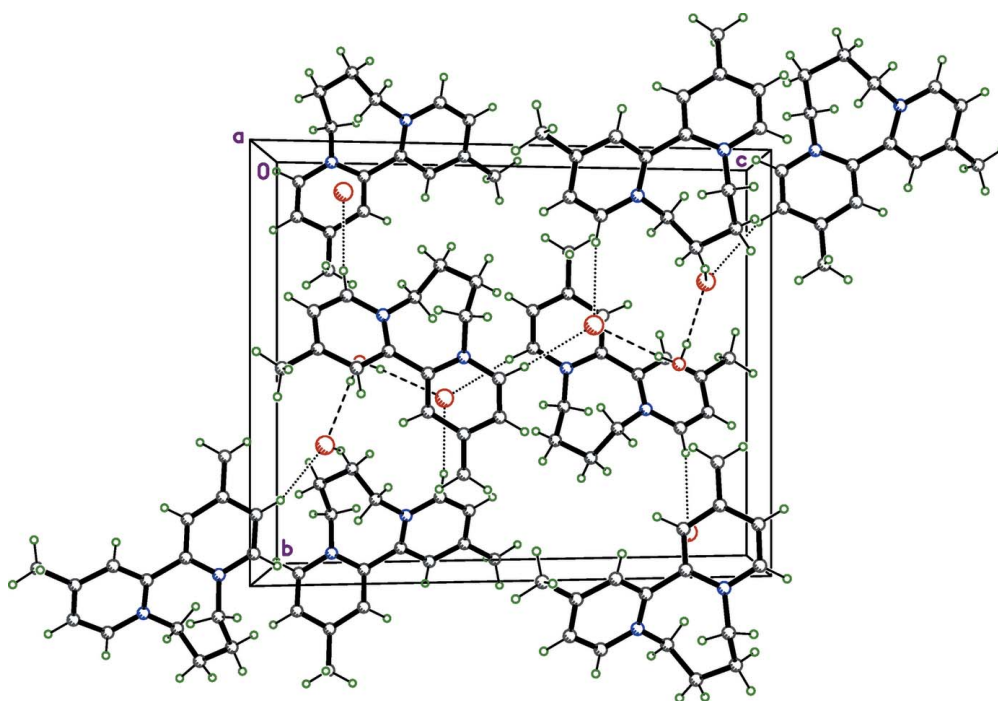


Figure 2
A packing plot of **1** viewed down the crystallographic *a* axis. Hydrogen bonds between water and Br^- are shown as dashed lines, while weaker $\text{C}-\text{H}\cdots\text{Br}$ interactions are shown as dotted lines.

Table 3
 ^1H and ^{13}C NMR spectroscopic data for **1** recorded in D_2O at 298K.

Assignments	^{13}C (ppm)	^1H (ppm)	Couplings (Hz)
C^1/H^1	146.25	8.99	$^3J(\text{H}^1\text{H}^2)$ 6.4
C^2/H^2	131.70	8.14	$^4J(\text{H}^2\text{H}^4)$ 1.4
C^3	162.63		
C^4/H^4	131.66	8.07	
C^5	142.78		
$\text{C}^6/\text{H}^{6A}, \text{H}^{6B}$	58.26	$\text{H}^{6A,6B}$ 4.73, 4.03	$^2J(\text{H}^{6A}\text{H}^{6B})$ 14.5, $^3J(\text{H}^{6A}\text{H}^{7A})$ 6.1, $^3J(\text{H}^{6B}\text{H}^{7B})$ 11.3
$\text{C}^7/\text{H}^{7A}, \text{H}^{7B}$	26.72	$\text{H}^{7A,7B}$ 2.35, 2.05	$^2J(\text{H}^{7A}\text{H}^{7B})$ 11.1
C^8/H^8	21.62	2.68	
N^9	208.5		

The errors were estimated to be $\pm 0.02\text{ppm}$, $\pm 0.002\text{ppm}$, and $\pm 0.3\text{Hz}$, respectively, for the ^{13}C chemical shifts, ^1H chemical shifts, and J coupling constants.

methyl group exchange with deuterons in a base-catalyzed reaction (Zoltewicz & Jacobson, 1978). Our NMR sample, which also showed exchange, was neutral. Exchange was prevented by adjusting the 'pH' to ~ 1 with DCl. This exchange with solvent deuterium led to some deuterium couplings with both protons and carbon and hence multiplicities in the NMR spectra, which were initially puzzling. Calder *et al.* (1967) discuss the effect of the length of the bridging group on the NMR spectra and the mobility of the structures.

There are eight resonance signals in the ^1H NMR spectrum recorded in D_2O , including one on the downfield shoulder of the residual water resonance. All but one of the signals are of equal intensity and the one at 2.68 ppm is about three times larger. The ^{13}C NMR spectrum shows eight signals (C1–C8), two of which (C2 and C4) are barely separated. Quantitative measurement using inverse-gated decoupling with a long recycle delay (60 s) shows that the carbon signals are of equal intensity. The 1-D ^{13}C DEPT (Distortionless Enhancement by Polarization Transfer) and 2-D multiplicity-edited ^1H – ^{13}C HSQC (Heteronuclear Single Quantum Coherence) establish a ratio of 3:2:1 for CH, CH_2 , and CH_3 , respectively. Further analysis of 2-D ^1H COSY (Correlation Spectroscopy) and 2-D ^1H – ^{13}C HMBC (Heteronuclear Multiple-Bond Correlation spectroscopy) spectra led to the NMR assignments summarized in Table 3. A selective HMBC focusing on the C2/C4 region was recorded for unambiguous assignments of multiple-bond ^1H – ^{13}C correlations related to these two carbons. These details together with the 2-D ^1H – ^{15}N HMBC, which reveals stronger H2/N9 and H4/N9 cross-peaks than H1/N9, clearly establish a symmetric three-ring molecular structure, as shown in Fig. 3, in full agreement with the crystal structure (Fig. 1).

The stereospecific assignment of the methylene protons was achieved by a systematic recording of 1-D selective NOESY (Nuclear Overhauser Effect Spectroscopy) and COSY spectra. A stronger NOE was observed between the proton at 4.73 ppm and H1, and thus this resonance was assigned to H6A while the geminal one at 4.03 ppm to H6B. The 1-D selective homonuclear decoupling ^1H NMR spectra led to the extraction of J -coupling constants between these methylene protons (Table 3). A large 3J coupling exists between H6B and H7B (11.3 Hz), followed by a sizable 3J coupling between H6A

and H7A (6.1 Hz). As a result of the complexity of the spectra, the $^3J(\text{H}^{6A}\text{H}^{7B})$ and $^3J(\text{H}^{6B}\text{H}^{7A})$ could not be determined, but were estimated to be less than 2 Hz. Also, the 11.1 Hz coupling between H7A and H7B was tentatively assigned to the geminal coupling rather than the one across the C7–C7' bond.

All NMR spectra were recorded on a Bruker Ascend 700 MHz spectrometer equipped with a TXO cryoprobe at 298 K. Spectra were indirectly referenced to the deuterium lock frequency, set to 4.7 ppm.

6. Synthesis and crystallization

The starting materials were standard commercial samples of 95–98% purity. 4,4'-Dimethyl-2,2'-dipyridyl (0.92 g, 5 mmol) and 1,4-dibromobutane (0.6 mL, 1.08g, 5 mmol) were added to a mixture of 5 mL each of xylene (mixed isomers, b.p. *ca* 413 K) and nitrobenzene (b.p. 483 K). The mixture was refluxed for about 5 h, during which time a heavy precipitate formed. After cooling, the crude material was filtered and washed with acetone to yield 1.1 g of a tan-colored powder. Paper electrophoresis of this material at pH 7.5 showed (*via* UV) a small amount of starting material at R_f *ca* zero and product at R_f –2.2 (R_f is movement relative to picric acid). Crystallization from methanol–acetone gave 0.5–0.6 g (*ca* 50%) of reddish crystals, m.p. 528–530 K [lit. 528–533 K; Spotswood & Tanzer (1967)], $U_{\text{max}}(\text{water})$ 271 nm. IR(Nujol): 3456, 3414, 3372, 1632, 1582, 1566, 1514 1312, 1159, 1032, 853 cm^{-1} .

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All hydrogen atoms were found in difference-Fourier maps. Those attached to carbon were subsequently included in the refinement using riding models, with constrained distances set to 0.95 Å (Csp^2H), 0.98 Å (RCH_3), and 0.99 Å (R_2CH_2). Water hydrogen coordinates were refined, but subject to a restraint on the O–H distances (*SHELXL* command SADI). $U_{\text{iso}}(\text{H})$ parameters were set to values of either $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ (RCH_3 only) of the attached atom.

Table 4

Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₂₀ N ₂ ²⁺ ·2(Br ⁻)·H ₂ O
<i>M_r</i>	418.17
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	90
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6402 (2), 13.7578 (3), 16.7691 (3)
β (°)	101.162 (1)
<i>V</i> (Å ³)	1729.30 (7)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	4.69
Crystal size (mm)	0.16 × 0.12 × 0.07
Data collection	
Diffractometer	Bruker D8 Venture dual source
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.562, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	26025, 3959, 3527
<i>R_{int}</i>	0.029
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.020, 0.043, 1.06
No. of reflections	3959
No. of parameters	198
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.38, -0.38

Computer programs: *APEX3* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008), *SHELX* (Sheldrick, 2008), *CIFFIX* (Parkin, 2013), and *pubCIF* (Westrip, 2010).

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4,15-Dimethyl-7,12-diazoniatriacyclo[10.4.0.0^{2,7}]hexadeca-1(12),2,4,6,13,15-hexaene dibromide monohydrate

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *APEX3* (Bruker, 2016); data reduction: *APEX3* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELX* (Sheldrick, 2008), *CIFFIX* (Parkin, 2013), and *publCIF* (Westrip, 2010).

4,15-Dimethyl-7,12-diazoniatriacyclo[10.4.0.0^{2,7}]hexadeca-1(12),2,4,6,13,15-hexaene dibromide monohydrate

Crystal data

$C_{16}H_{20}N_2^{2+} \cdot 2(Br^-) \cdot H_2O$
 $M_r = 418.17$
 Monoclinic, $P2_1/n$
 $a = 7.6402$ (2) Å
 $b = 13.7578$ (3) Å
 $c = 16.7691$ (3) Å
 $\beta = 101.162$ (1)°
 $V = 1729.30$ (7) Å³
 $Z = 4$

$F(000) = 840$
 $D_x = 1.606$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9914 reflections
 $\theta = 2.8$ – 27.5 °
 $\mu = 4.69$ mm⁻¹
 $T = 90$ K
 Irregular shard, pink
 $0.16 \times 0.12 \times 0.07$ mm

Data collection

Bruker D8 Venture dual source
 diffractometer
 Radiation source: microsource
 Detector resolution: 7.41 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Krause *et al.*, 2015)
 $T_{\min} = 0.562$, $T_{\max} = 0.746$

26025 measured reflections
 3959 independent reflections
 3527 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 27.5$ °, $\theta_{\text{min}} = 2.5$ °
 $h = -9 \rightarrow 9$
 $k = -17 \rightarrow 17$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.043$
 $S = 1.06$
 3959 reflections
 198 parameters
 1 restraint
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0121P)^2 + 1.4994P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 progress was checked using *Platon* (Spek, 2009) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

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	0.38758 (2)	0.69802 (2)	0.11426 (2)	0.01809 (5)
Br2	0.09621 (2)	0.58825 (2)	0.34885 (2)	0.01872 (5)
N1	0.54040 (19)	0.38619 (10)	0.23392 (9)	0.0157 (3)
C1	0.5310 (2)	0.34004 (13)	0.16231 (11)	0.0193 (4)
H1	0.470042	0.279632	0.153665	0.023*
C2	0.6074 (2)	0.37819 (13)	0.10161 (11)	0.0190 (4)
H2	0.598713	0.344145	0.051717	0.023*
C3	0.6973 (2)	0.46646 (13)	0.1128 (1)	0.0164 (3)
C4	0.7082 (2)	0.51161 (13)	0.18795 (10)	0.0159 (3)
H4	0.771186	0.571265	0.198231	0.019*
C5	0.6300 (2)	0.47175 (12)	0.24753 (10)	0.0140 (3)
C6	0.4467 (2)	0.34092 (13)	0.29478 (11)	0.0188 (4)
H6A	0.337285	0.307919	0.266189	0.023*
H6B	0.410854	0.392247	0.329762	0.023*
C7	0.5666 (2)	0.26732 (13)	0.34768 (12)	0.0215 (4)
H7B	0.489315	0.219545	0.368381	0.026*
H7A	0.635324	0.231572	0.312750	0.026*
C8	0.7795 (3)	0.51217 (14)	0.04805 (11)	0.0232 (4)
H8A	0.750594	0.473388	-0.001783	0.035*
H8B	0.909326	0.514930	0.066178	0.035*
H8C	0.732611	0.578163	0.037298	0.035*
N1'	0.72247 (18)	0.4864 (1)	0.39609 (8)	0.0136 (3)
C1'	0.7337 (2)	0.53707 (13)	0.46545 (10)	0.0172 (4)
H1'	0.792782	0.508916	0.515149	0.021*
C2'	0.6619 (2)	0.62861 (13)	0.46625 (10)	0.0170 (3)
H2'	0.673762	0.663389	0.515955	0.020*
C3'	0.5719 (2)	0.67031 (13)	0.39448 (11)	0.0161 (3)
C4'	0.5608 (2)	0.61627 (12)	0.32318 (10)	0.0154 (3)
H4'	0.500590	0.642672	0.272967	0.018*
C5'	0.6360 (2)	0.52515 (12)	0.32479 (10)	0.0135 (3)
C6'	0.8162 (2)	0.39082 (12)	0.40077 (11)	0.0169 (4)
H6A'	0.925433	0.393784	0.443492	0.020*
H6B'	0.852567	0.377516	0.348290	0.020*

C7'	0.6976 (2)	0.30844 (13)	0.41992 (11)	0.0198 (4)
H7A'	0.629120	0.332138	0.460449	0.024*
H7B'	0.775237	0.254877	0.445511	0.024*
C8'	0.4859 (2)	0.76805 (13)	0.39343 (12)	0.0210 (4)
H8A'	0.500384	0.803271	0.344334	0.031*
H8B'	0.542276	0.804908	0.441597	0.031*
H8C'	0.358509	0.760037	0.393689	0.031*
O1W	0.1964 (2)	0.49717 (11)	0.17678 (9)	0.0297 (3)
H1W	0.240 (3)	0.5445 (16)	0.1598 (16)	0.044*
H2W	0.168 (3)	0.5155 (19)	0.2183 (13)	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01962 (9)	0.02036 (9)	0.01455 (8)	0.00295 (7)	0.00397 (6)	0.00357 (7)
Br2	0.01603 (9)	0.01993 (9)	0.01935 (9)	-0.00218 (7)	0.00129 (6)	0.00533 (7)
N1	0.0134 (7)	0.0157 (7)	0.0178 (7)	-0.0010 (6)	0.0022 (6)	-0.0013 (6)
C1	0.0155 (8)	0.0185 (9)	0.0229 (9)	-0.0014 (7)	0.0012 (7)	-0.0065 (7)
C2	0.0166 (8)	0.0215 (9)	0.0181 (8)	0.0020 (7)	0.0012 (7)	-0.0056 (7)
C3	0.0146 (8)	0.0189 (9)	0.0153 (8)	0.0046 (7)	0.0020 (6)	0.0001 (7)
C4	0.0158 (8)	0.0140 (8)	0.0173 (8)	0.0006 (6)	0.0017 (6)	0.0005 (7)
C5	0.0110 (7)	0.0144 (8)	0.0157 (8)	0.0020 (6)	0.0004 (6)	-0.0005 (7)
C6	0.0147 (8)	0.0205 (9)	0.0220 (9)	-0.0043 (7)	0.0054 (7)	0.0003 (7)
C7	0.0199 (9)	0.0166 (9)	0.0288 (10)	-0.0027 (7)	0.0064 (8)	0.0033 (8)
C8	0.028 (1)	0.0254 (10)	0.0170 (8)	0.0006 (8)	0.0064 (7)	0.0000 (8)
N1'	0.0117 (7)	0.0138 (7)	0.0148 (7)	0.0000 (5)	0.0018 (5)	0.0018 (6)
C1'	0.0135 (8)	0.0234 (9)	0.0138 (8)	-0.0030 (7)	0.0005 (6)	0.0008 (7)
C2'	0.0153 (8)	0.0218 (9)	0.0142 (8)	-0.0034 (7)	0.0037 (6)	-0.0048 (7)
C3'	0.0111 (8)	0.0164 (8)	0.0213 (9)	-0.0035 (6)	0.0045 (7)	-0.0017 (7)
C4'	0.0130 (8)	0.0175 (8)	0.0153 (8)	-0.0009 (6)	0.0017 (6)	0.0013 (7)
C5'	0.0110 (7)	0.0151 (8)	0.0143 (8)	-0.0025 (6)	0.0021 (6)	0.0002 (7)
C6'	0.0125 (8)	0.0157 (8)	0.0213 (9)	0.0027 (6)	0.0006 (7)	0.0032 (7)
C7'	0.0164 (8)	0.0184 (9)	0.0246 (9)	0.0016 (7)	0.0044 (7)	0.0068 (7)
C8'	0.0194 (9)	0.0172 (9)	0.0266 (9)	-0.0003 (7)	0.0053 (7)	-0.0036 (8)
O1W	0.0309 (8)	0.0252 (8)	0.0342 (8)	-0.0016 (6)	0.0096 (6)	-0.0014 (7)

Geometric parameters (Å, °)

N1—C1	1.348 (2)	N1'—C1'	1.344 (2)
N1—C5	1.359 (2)	N1'—C5'	1.358 (2)
N1—C6	1.491 (2)	N1'—C6'	1.492 (2)
C1—C2	1.372 (3)	C1'—C2'	1.375 (2)
C1—H1	0.9500	C1'—H1'	0.9500
C2—C3	1.390 (2)	C2'—C3'	1.389 (2)
C2—H2	0.9500	C2'—H2'	0.9500
C3—C4	1.393 (2)	C3'—C4'	1.396 (2)
C3—C8	1.494 (2)	C3'—C8'	1.495 (2)
C4—C5	1.374 (2)	C4'—C5'	1.377 (2)

C4—H4	0.9500	C4'—H4'	0.9500
C5—C5'	1.482 (2)	C6'—C7'	1.523 (2)
C6—C7	1.528 (3)	C6'—H6A'	0.9900
C6—H6A	0.9900	C6'—H6B'	0.9900
C6—H6B	0.9900	C7'—H7A'	0.9900
C7—C7'	1.523 (3)	C7'—H7B'	0.9900
C7—H7B	0.9900	C8'—H8A'	0.9800
C7—H7A	0.9900	C8'—H8B'	0.9800
C8—H8A	0.9800	C8'—H8C'	0.9800
C8—H8B	0.9800	O1W—H1W	0.809 (19)
C8—H8C	0.9800	O1W—H2W	0.807 (19)
C1—N1—C5	119.74 (15)	C1'—N1'—C6'	117.50 (14)
C1—N1—C6	117.59 (15)	C5'—N1'—C6'	122.62 (14)
C5—N1—C6	122.66 (14)	N1'—C1'—C2'	121.64 (16)
N1—C1—C2	121.59 (17)	N1'—C1'—H1'	119.2
N1—C1—H1	119.2	C2'—C1'—H1'	119.2
C2—C1—H1	119.2	C1'—C2'—C3'	120.09 (16)
C1—C2—C3	120.29 (16)	C1'—C2'—H2'	120.0
C1—C2—H2	119.9	C3'—C2'—H2'	120.0
C3—C2—H2	119.9	C2'—C3'—C4'	117.37 (16)
C2—C3—C4	116.94 (16)	C2'—C3'—C8'	121.61 (16)
C2—C3—C8	122.41 (16)	C4'—C3'—C8'	121.00 (16)
C4—C3—C8	120.65 (16)	C5'—C4'—C3'	120.79 (16)
C5—C4—C3	121.45 (16)	C5'—C4'—H4'	119.6
C5—C4—H4	119.3	C3'—C4'—H4'	119.6
C3—C4—H4	119.3	N1'—C5'—C4'	120.31 (15)
N1—C5—C4	119.97 (15)	N1'—C5'—C5	120.15 (15)
N1—C5—C5'	120.37 (15)	C4'—C5'—C5	119.46 (15)
C4—C5—C5'	119.58 (15)	N1'—C6'—C7'	111.60 (14)
N1—C6—C7	111.16 (14)	N1'—C6'—H6A'	109.3
N1—C6—H6A	109.4	C7'—C6'—H6A'	109.3
C7—C6—H6A	109.4	N1'—C6'—H6B'	109.3
N1—C6—H6B	109.4	C7'—C6'—H6B'	109.3
C7—C6—H6B	109.4	H6A'—C6'—H6B'	108.0
H6A—C6—H6B	108.0	C6'—C7'—C7	115.78 (15)
C7'—C7—C6	116.31 (15)	C6'—C7'—H7A'	108.3
C7'—C7—H7B	108.2	C7—C7'—H7A'	108.3
C6—C7—H7B	108.2	C6'—C7'—H7B'	108.3
C7'—C7—H7A	108.2	C7—C7'—H7B'	108.3
C6—C7—H7A	108.2	H7A'—C7'—H7B'	107.4
H7B—C7—H7A	107.4	C3'—C8'—H8A'	109.5
C3—C8—H8A	109.5	C3'—C8'—H8B'	109.5
C3—C8—H8B	109.5	H8A'—C8'—H8B'	109.5
H8A—C8—H8B	109.5	C3'—C8'—H8C'	109.5
C3—C8—H8C	109.5	H8A'—C8'—H8C'	109.5
H8A—C8—H8C	109.5	H8B'—C8'—H8C'	109.5
H8B—C8—H8C	109.5	H1W—O1W—H2W	104 (3)

C1'—N1'—C5'	119.79 (15)		
C5—N1—C1—C2	-1.2 (3)	C1'—C2'—C3'—C4'	-0.8 (2)
C6—N1—C1—C2	177.51 (16)	C1'—C2'—C3'—C8'	177.56 (16)
N1—C1—C2—C3	0.0 (3)	C2'—C3'—C4'—C5'	0.2 (2)
C1—C2—C3—C4	1.3 (2)	C8'—C3'—C4'—C5'	-178.18 (16)
C1—C2—C3—C8	-178.70 (17)	C1'—N1'—C5'—C4'	0.4 (2)
C2—C3—C4—C5	-1.5 (2)	C6'—N1'—C5'—C4'	-176.07 (15)
C8—C3—C4—C5	178.50 (16)	C1'—N1'—C5'—C5	177.22 (15)
C1—N1—C5—C4	1.0 (2)	C6'—N1'—C5'—C5	0.8 (2)
C6—N1—C5—C4	-177.65 (15)	C3'—C4'—C5'—N1'	0.0 (2)
C1—N1—C5—C5'	177.79 (15)	C3'—C4'—C5'—C5	-176.85 (15)
C6—N1—C5—C5'	-0.8 (2)	N1—C5—C5'—N1'	66.1 (2)
C3—C4—C5—N1	0.4 (3)	C4—C5—C5'—N1'	-117.12 (18)
C3—C4—C5—C5'	-176.45 (15)	N1—C5—C5'—C4'	-117.09 (18)
C1—N1—C6—C7	87.25 (19)	C4—C5—C5'—C4'	59.7 (2)
C5—N1—C6—C7	-94.09 (19)	C1'—N1'—C6'—C7'	88.23 (18)
N1—C6—C7—C7'	83.16 (19)	C5'—N1'—C6'—C7'	-95.23 (19)
C5'—N1'—C1'—C2'	-1.0 (2)	N1'—C6'—C7'—C7	82.48 (19)
C6'—N1'—C1'—C2'	175.61 (15)	C6—C7—C7'—C6'	-52.2 (2)
N1'—C1'—C2'—C3'	1.3 (3)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots Br2 ⁱ	0.95	2.68	3.5929 (18)	161
C2—H2 \cdots Br1 ⁱⁱ	0.95	2.86	3.7762 (18)	161
C7—H7B \cdots Br1 ⁱ	0.99	2.96	3.7700 (19)	139
C1'—H1' \cdots Br2 ⁱⁱⁱ	0.95	2.64	3.5765 (17)	170
C2'—H2' \cdots Br1 ^{iv}	0.95	2.82	3.6285 (17)	143
C4'—H4' \cdots Br1	0.95	2.74	3.6735 (17)	167
C7'—H7B' \cdots Br1 ^v	0.99	3.04	3.6581 (18)	122
O1W—H1W \cdots Br1	0.81 (2)	2.58 (2)	3.3856 (15)	177 (3)
O1W—H2W \cdots Br2	0.81 (2)	2.56 (2)	3.3670 (15)	175 (3)

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