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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(C-C) = 0.002$ Å
 R factor = 0.021
 wR factor = 0.052
 Data-to-parameter ratio = 21.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1-Ethyl-4-hydroxy-2,6-dimethylpyridinium bromide dihydrate

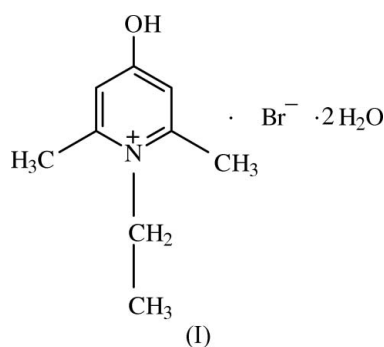
The title compound, $C_9H_{14}NO^+Br^- \cdot 2H_2O$, comprises 1-ethyl-2,6-dimethyl-4-hydroxypyridinium cations and bromide anions, with two solvent water molecules per formula unit. In the crystal structure, the anions, cations and water molecules are linked *via* intermolecular $O-H \cdots Br$ and $O-H \cdots O$ hydrogen bonds, forming layers parallel to the (100) plane.

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Comment

2,6-Dimethyl-4-hydroxypyridinone and 4-hydroxypyridinium salts have attracted much attention in the field of non-linear optics (NLO), since the 4-hydroxypyridinium conjugated electronic system could be an interesting hyperpolarizable chromophore for NLO activity (Manivannan *et al.*, 2004; Dhanuskodi *et al.*, 2006). To achieve self-assembly of organic cations in the manner required to exhibit NLO activity (Tamuly *et al.*, 2005), suitable anions must be identified and used effectively. Halide anions have been reported to improve the physicochemical stability of 1-ethyl-2,6-dimethyl-4-(1*H*)-pyridinones (Dhanuskodi *et al.*, 2006). We report here the crystal structure of 1-ethyl-2,6-dimethyl-4-hydroxypyridinium bromide dihydrate (EDMPBr·2H₂O), (I).



The crystal structure of (I) (Fig. 1) comprises 1-ethyl-2,6-dimethyl-4-hydroxypyridinium cations and bromide anions, with two solvent water molecules per formula unit. The C2–N1–C6 bond angle in the cation [120.71 (16)°] is comparable to that in 2,6-dimethylpyridine (Bond & Davies, 2001) and the 2,6-dimethylpyridine-urea complex (Lee & Wallwork, 1965). The organic cations lie in layers parallel to the (100) plane (Fig. 2). The bromide anions and water molecules lie between these layers, forming hydrogen-bonded sheets *via* $O-H \cdots O$ and $O-H \cdots Br$ interactions (Fig. 3 and Table 1). Two distinct ring motifs exist within these sheets, with graph-set descriptors $R_4^6(12)$ and $R_{10}^6(20)$ (Bernstein *et al.*, 1995). $O-H \cdots O$ hydrogen bonds are formed between atom O1 of the hydroxyl

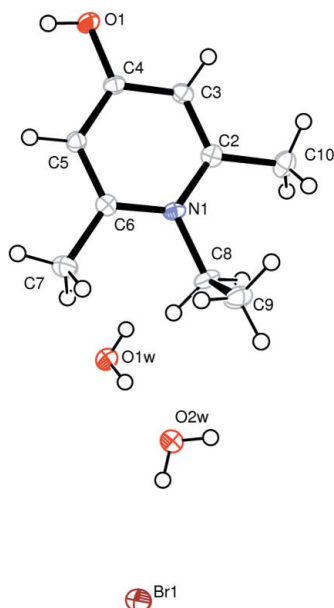


Figure 1
The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level. H atoms are represented by circles of arbitrary radius.

group of the organic cation and one of the solvent water molecules (Fig. 2 and Table 1).

Experimental

The title compound was synthesized by dissolving 1-ethyl-2,6-dimethyl-4(1*H*)-pyridinone trihydrate (EDMP·3H₂O, 1.51 g) with HBr (2.43 g) in distilled water (5 ml). The solution was stirred well at room temperature for 7 h and the solvent was allowed to evaporate at 323 K. The residual crystalline powder was redissolved in distilled water, and single crystals of (I) were obtained by slow evaporation at 303 K.

Crystal data

C ₉ H ₁₄ NO ⁺ Br ⁻ ·2H ₂ O	$Z = 4$
$M_r = 268.15$	$D_x = 1.476 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.5747 (3) \text{ \AA}$	$\mu = 3.39 \text{ mm}^{-1}$
$b = 8.0382 (1) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 15.0377 (4) \text{ \AA}$	Block, colourless
$\beta = 109.298 (1)^\circ$	$0.54 \times 0.48 \times 0.12 \text{ mm}$
$V = 1206.41 (5) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	15899 measured reflections
φ and ω scans	2768 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2455 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.176$, $T_{\max} = 0.666$	$R_{\text{int}} = 0.033$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.702P]$
$R[F^2 > 2\sigma(F^2)] = 0.021$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
2768 reflections	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$
131 parameters	Extinction correction: <i>SHELXL</i>
H-atom parameters constrained	Extinction coefficient: 0.0104 (6)

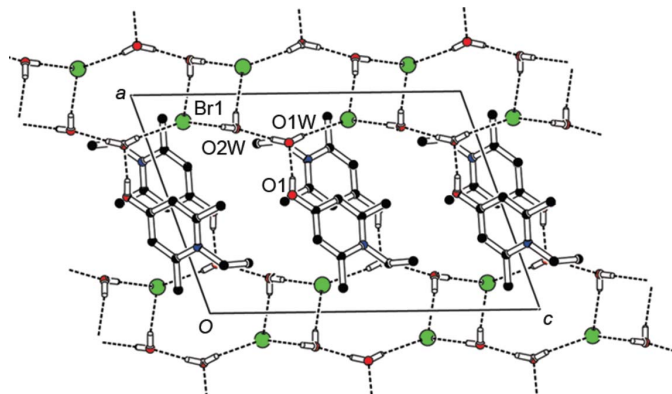


Figure 2
View of (I) along b , showing layers of organic cations lying parallel to the (100) plane, with Br⁻ anions and water molecules lying between them. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

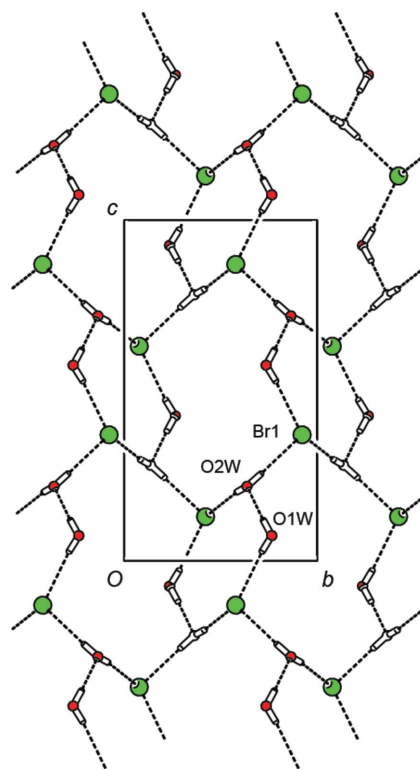


Figure 3
A single Br⁻/H₂O sheet viewed along the a -axis direction, showing O—H...O and O—H...Br hydrogen bonds (dashed lines).

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O1W ⁱ	0.80	1.78	2.5720 (16)	173
O1W—H11...O2W	0.82	1.90	2.7135 (16)	175
O1W—H12...Br1 ⁱⁱ	0.76	2.50	3.2610 (12)	172
O2W—H21...Br1	0.81	2.52	3.3332 (12)	178
O2W—H22...Br1 ⁱⁱⁱ	0.79	2.52	3.3061 (12)	173

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

H atoms, except those of the water molecules, were positioned geometrically with C–H = 0.93 (CH), 0.96 (CH₃) or 0.97 Å (CH₂), and with O–H = 0.80 Å. They were then refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,O})$ or $1.5U_{\text{eq}}(\text{methyl C})$. H atoms of the water molecules were found in difference Fourier maps and refined initially with a restrained geometry. In the final cycles of refinement, they were made to ride on their parent O atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli 1995).

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supporting information

Acta Cryst. (2007). E63, o599–o601 [https://doi.org/10.1107/S1600536807000232]

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(I)

Crystal data

$C_9H_{14}NO^+Br^- \cdot 2H_2O$

$M_r = 268.15$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 10.5747$ (3) Å

$b = 8.0382$ (1) Å

$c = 15.0377$ (4) Å

$\beta = 109.298$ (1)°

$V = 1206.41$ (5) Å³

$Z = 4$

$F(000) = 552$

$D_x = 1.476$ Mg m⁻³

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

Cell parameters from 2935 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 3.39$ mm⁻¹

$T = 120$ K

Block, colourless

$0.54 \times 0.48 \times 0.12$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: Bruker Nonius FR591
rotating anode

10 cm confocal mirrors monochromator
 φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)

$T_{\min} = 0.176$, $T_{\max} = 0.666$

15899 measured reflections

2768 independent reflections

2455 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

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

$h = -13 \rightarrow 13$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.052$

$S = 1.04$

2768 reflections

131 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.702P]$

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

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

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.52$ e Å⁻³

Extinction correction: SHELXL,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0104 (6)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.53552 (11)	0.11597 (15)	-0.12166 (8)	0.0210 (3)
H1	0.6082	0.1578	-0.1037	0.025*
N1	0.30377 (13)	0.25353 (16)	0.03692 (9)	0.0151 (3)
C2	0.25160 (15)	0.15705 (19)	-0.04183 (11)	0.0164 (3)
C3	0.33045 (16)	0.11197 (19)	-0.09427 (11)	0.0167 (3)
H3	0.2949	0.0458	-0.1474	0.020*
C4	0.46300 (16)	0.16421 (19)	-0.06866 (11)	0.0159 (3)
C5	0.51367 (15)	0.26305 (19)	0.01139 (11)	0.0162 (3)
H5	0.6019	0.2999	0.0295	0.019*
C6	0.43404 (15)	0.30649 (19)	0.06379 (11)	0.0162 (3)
C7	0.49030 (18)	0.4105 (2)	0.15046 (13)	0.0242 (4)
H7A	0.5830	0.4336	0.1602	0.036*
H7B	0.4825	0.3515	0.2039	0.036*
H7C	0.4415	0.5132	0.1428	0.036*
C8	0.21871 (17)	0.2994 (2)	0.09484 (12)	0.0203 (3)
H8A	0.1264	0.3101	0.0541	0.024*
H8B	0.2474	0.4065	0.1243	0.024*
C9	0.22680 (19)	0.1707 (2)	0.17072 (13)	0.0252 (4)
H9A	0.2006	0.0639	0.1419	0.038*
H9B	0.1678	0.2021	0.2046	0.038*
H9C	0.3171	0.1648	0.2135	0.038*
C10	0.10880 (16)	0.1013 (2)	-0.07030 (13)	0.0241 (4)
H1A	0.0942	0.0425	-0.0190	0.036*
H1B	0.0897	0.0292	-0.1240	0.036*
H1C	0.0509	0.1966	-0.0861	0.036*
O1W	0.22566 (12)	0.76473 (15)	0.07413 (9)	0.0252 (3)
H11	0.2091	0.7218	0.1186	0.030*
H12	0.1964	0.7154	0.0286	0.030*
O2W	0.15723 (11)	0.63640 (15)	0.21883 (8)	0.0221 (3)
H21	0.1498	0.7078	0.2552	0.027*
H22	0.0903	0.5849	0.2026	0.027*
Br1	0.123005 (16)	0.92168 (2)	0.370123 (12)	0.02309 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0193 (6)	0.0291 (6)	0.0176 (6)	-0.0035 (5)	0.0102 (5)	-0.0053 (5)
N1	0.0185 (6)	0.0149 (6)	0.0138 (7)	0.0036 (5)	0.0079 (5)	0.0023 (5)
C2	0.0168 (7)	0.0171 (7)	0.0136 (8)	0.0022 (6)	0.0029 (6)	0.0045 (6)
C3	0.0193 (8)	0.0177 (7)	0.0121 (8)	-0.0003 (6)	0.0038 (6)	0.0002 (6)
C4	0.0189 (8)	0.0164 (7)	0.0137 (8)	0.0025 (6)	0.0072 (6)	0.0024 (6)
C5	0.0164 (7)	0.0182 (8)	0.0141 (8)	-0.0018 (6)	0.0051 (6)	0.0009 (6)
C6	0.0191 (8)	0.0141 (7)	0.0149 (8)	0.0008 (6)	0.0048 (6)	0.0021 (6)
C7	0.0297 (9)	0.0252 (9)	0.0193 (9)	-0.0042 (7)	0.0100 (7)	-0.0056 (7)
C8	0.0238 (8)	0.0200 (8)	0.0225 (9)	0.0047 (7)	0.0148 (7)	0.0013 (7)
C9	0.0330 (10)	0.0243 (9)	0.0243 (10)	0.0016 (7)	0.0177 (8)	0.0025 (7)
C10	0.0166 (8)	0.0306 (9)	0.0245 (10)	-0.0001 (7)	0.0060 (7)	0.0021 (7)
O1W	0.0263 (6)	0.0302 (6)	0.0224 (7)	-0.0068 (5)	0.0125 (5)	-0.0044 (5)
O2W	0.0223 (6)	0.0229 (6)	0.0212 (6)	-0.0018 (5)	0.0071 (5)	-0.0026 (5)
Br1	0.02279 (10)	0.02429 (11)	0.02064 (11)	0.00401 (7)	0.00508 (7)	-0.00067 (7)

Geometric parameters (\AA , $^\circ$)

O1—C4	1.3332 (18)	C7—H7C	0.960
O1—H1	0.800	C8—C9	1.522 (2)
N1—C6	1.369 (2)	C8—H8A	0.970
N1—C2	1.370 (2)	C8—H8B	0.970
N1—C8	1.4905 (19)	C9—H9A	0.960
C2—C3	1.372 (2)	C9—H9B	0.960
C2—C10	1.496 (2)	C9—H9C	0.960
C3—C4	1.390 (2)	C10—H1A	0.960
C3—H3	0.930	C10—H1B	0.960
C4—C5	1.393 (2)	C10—H1C	0.960
C5—C6	1.375 (2)	O1W—H11	0.821
C5—H5	0.930	O1W—H12	0.763
C6—C7	1.496 (2)	O2W—H21	0.815
C7—H7A	0.960	O2W—H22	0.786
C7—H7B	0.960		
C4—O1—H1	110.7	H7A—C7—H7C	109.5
C6—N1—C2	120.65 (13)	H7B—C7—H7C	109.5
C6—N1—C8	119.56 (13)	N1—C8—C9	112.01 (13)
C2—N1—C8	119.79 (13)	N1—C8—H8A	109.2
N1—C2—C3	119.91 (14)	C9—C8—H8A	109.2
N1—C2—C10	119.81 (14)	N1—C8—H8B	109.2
C3—C2—C10	120.28 (15)	C9—C8—H8B	109.2
C2—C3—C4	120.64 (15)	H8A—C8—H8B	107.9
C2—C3—H3	119.7	C8—C9—H9A	109.5
C4—C3—H3	119.7	C8—C9—H9B	109.5
O1—C4—C3	118.23 (14)	H9A—C9—H9B	109.5
O1—C4—C5	123.32 (14)	C8—C9—H9C	109.5

C3—C4—C5	118.44 (14)	H9A—C9—H9C	109.5
C6—C5—C4	120.43 (14)	H9B—C9—H9C	109.5
C6—C5—H5	119.8	C2—C10—H1A	109.5
C4—C5—H5	119.8	C2—C10—H1B	109.5
N1—C6—C5	119.93 (14)	H1A—C10—H1B	109.5
N1—C6—C7	120.17 (14)	C2—C10—H1C	109.5
C5—C6—C7	119.90 (14)	H1A—C10—H1C	109.5
C6—C7—H7A	109.5	H1B—C10—H1C	109.5
C6—C7—H7B	109.5	H11—O1W—H12	112.4
H7A—C7—H7B	109.5	H21—O2W—H22	107.6
C6—C7—H7C	109.5		
C6—N1—C2—C3	0.3 (2)	C3—C4—C5—C6	0.4 (2)
C8—N1—C2—C3	-178.74 (14)	C2—N1—C6—C5	0.1 (2)
C6—N1—C2—C10	-179.64 (14)	C8—N1—C6—C5	179.21 (14)
C8—N1—C2—C10	1.3 (2)	C2—N1—C6—C7	-179.43 (14)
N1—C2—C3—C4	-0.4 (2)	C8—N1—C6—C7	-0.4 (2)
C10—C2—C3—C4	179.54 (15)	C4—C5—C6—N1	-0.5 (2)
C2—C3—C4—O1	179.55 (14)	C4—C5—C6—C7	179.06 (15)
C2—C3—C4—C5	0.1 (2)	C6—N1—C8—C9	-90.24 (18)
O1—C4—C5—C6	-179.05 (14)	C2—N1—C8—C9	88.85 (18)

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>
O1—H1...O1W ⁱ	0.80	1.78	2.5720 (16)	173
O1W—H11...O2W	0.82	1.90	2.7135 (16)	175
O1W—H12...Br1 ⁱⁱ	0.76	2.50	3.2610 (12)	172
O2W—H21...Br1	0.81	2.52	3.3332 (12)	178
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