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6*H*-Dipyrido[1,2-*a*:2′,1′-*d*][1,3,5]triazin-5-ium bromide monohydrate

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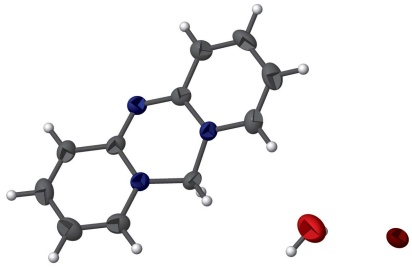
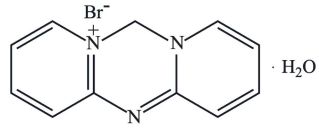
Structural data: full structural data are available from iucrdata.iucr.org

In the cation of the title compound, $C_{11}H_{10}N_3^+\cdot Br^-\cdot H_2O$, the central 1,3,5-triazinium ring has a flattened boat conformation and the outer heterocyclic rings are nearly planar [maximum deviations = 0.010 (4) and 0.009 (4) Å] and twisted with respect to each other with a dihedral angle of 22.87 (19)°. In the crystal, classical O—H···Br hydrogen bonds and weak C—H···Br and C—H···O hydrogen bonds link the cations, bromide anions and water molecules of crystallization into a three-dimensional supramolecular network.

3D view



Chemical scheme



Structure description

N-Heterocyclic carbene ligands (NHC) have been shown to have wide applicability in co ordination chemistry and catalysis (Lee *et al.*, 2004). The preparation of chelating bis(-NHC) ligands is also receiving much attention, since they can provide additional air and moisture stability for the metal centers (Lee & Cheng, 2010). Knowledge of the crystal structure of such benzoicacid derivatives gives us not only information about nuclearity of the complex molecule, but is important in understanding the behaviour of these compounds with respect to the mechanisms of pharmacological activities and physiological activities (Niu *et al.*, 2008). Therefore, we have synthesized the title compound, (I), and report its crystal structure here.

The molecular structure of (I) is shown in Fig. 1, the compound crystallized with a structural configuration in which the pyridine ring (C1–C5/N3) is twisted by a dihedral angle of 10.92 (4)° with respect to a plane defined by the azacyanine ring (N1–C5–N3–C6–N2–C7). In the crystal, classical O—H···Br hydrogen bonds and weak C—H···Br and C—H···O hydrogen bonds (Table 1 link the cations, bromide anions and water molecules of crystallization into a three-dimensional supramolecular network.

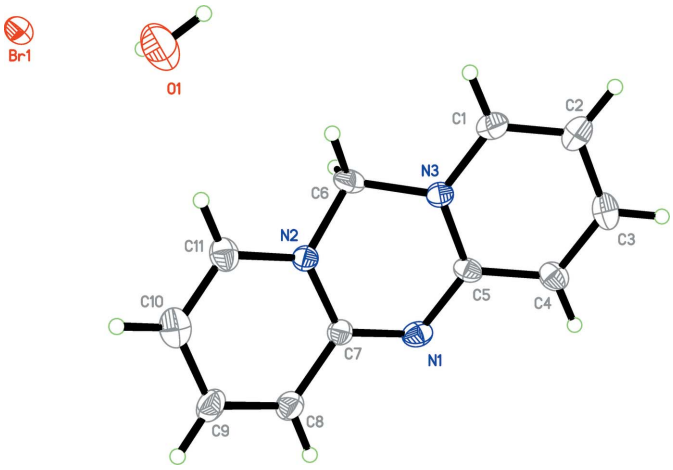


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 30% probability level.

Synthesis and crystallization

A mixture of 2-aminopyridine (1.0 g, 0.01 mol) and dibromomethane (15 ml, 0.2 mol) was added to a flask (100 ml) and was stirred at 366 K in an oil bath for 3 h. The progress of the reaction was monitored by detecting NH_3 released from the reaction system using wet pH paper. The reaction mixture was treated by reduced pressure distillation to remove the unreacted dibromomethane. The resulting pale-yellow powder was washed with 30 ml of propanone.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1W···Br1	0.85 (5)	2.67 (4)	3.423 (4)	147 (4)
O1—H2W···Br1^{i}	0.84 (3)	2.52 (3)	3.346 (4)	169 (3)
C1—H1···Br1^{i}	0.93	2.81	3.704 (4)	161
C3—H3···Br1^{ii}	0.93	2.89	3.714 (4)	149
C10—H10···O1^{iii}	0.93	2.57	3.353 (6)	143
C11—H11···O1	0.93	2.46	3.326 (7)	155

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{10}N_3^+\cdot Br^-\cdot H_2O$
M_r	282.14
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	5.4965 (5), 11.9528 (10), 17.7702 (18)
β (°)	95.354 (3)
V (Å^3)	1162.38 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.52
Crystal size (mm)	0.22 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.465, 0.532
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12145, 1995, 1446
R_{int}	0.131
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.589
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.088, 1.02
No. of reflections	1990
No. of parameters	153
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.35

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *XPREP* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *XCIF* (Sheldrick, 2008).

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full crystallographic data

IUCrData (2016). **1**, x160180 [https://doi.org/10.1107/S2414314616001802]

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Crystal data

$C_{11}H_{10}N_3^+\cdot Br^-\cdot H_2O$
M_r = 282.14
Monoclinic, $P2_1/c$
a = 5.4965 (5) Å
b = 11.9528 (10) Å
c = 17.7702 (18) Å
β = 95.354 (3)°
V = 1162.38 (19) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.612 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2457 reflections
θ = 2.3–23.1°
μ = 3.52 mm^{-1}
T = 296 K
Block, yellow
0.22 × 0.20 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.465, T_{max} = 0.532
12145 measured reflections
1995 independent reflections
1446 reflections with $I > 2\sigma(I)$
R_{int} = 0.131
θ_{max} = 24.7°, θ_{min} = 2.3°
h = −6→6
k = −14→13
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.088
S = 1.02
1990 reflections
153 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.0521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.93554 (8)	0.66573 (3)	0.26282 (2)	0.04207 (17)
C1	0.5912 (8)	0.0190 (3)	0.3352 (2)	0.0397 (11)
H1	0.7233	0.0375	0.3085	0.048*
C2	0.4882 (8)	−0.0834 (3)	0.3270 (3)	0.0473 (12)
H2	0.5507	−0.1368	0.2960	0.057*
C3	0.2855 (8)	−0.1071 (3)	0.3663 (3)	0.0444 (11)
H3	0.2094	−0.1764	0.3600	0.053*
C4	0.1982 (7)	−0.0316 (3)	0.4131 (2)	0.0369 (10)
H4	0.0655	−0.0500	0.4395	0.044*
C5	0.3060 (7)	0.0751 (3)	0.4225 (2)	0.0303 (9)
C6	0.5855 (8)	0.2109 (3)	0.3795 (2)	0.0353 (10)
H6A	0.7528	0.2125	0.3663	0.042*
H6B	0.4843	0.2518	0.3412	0.042*
C7	0.3739 (7)	0.2364 (3)	0.4914 (2)	0.0302 (9)
C8	0.3438 (8)	0.3013 (3)	0.5566 (2)	0.0370 (10)
H8	0.2089	0.2889	0.5834	0.044*
C9	0.5064 (8)	0.3803 (3)	0.5803 (3)	0.0427 (11)
H9	0.4842	0.4212	0.6236	0.051*
C10	0.7098 (8)	0.4018 (3)	0.5402 (3)	0.0456 (11)
H10	0.8238	0.4559	0.5571	0.055*
C11	0.7370 (8)	0.3432 (3)	0.4771 (3)	0.0391 (10)
H11	0.8696	0.3576	0.4496	0.047*
H1W	0.978 (11)	0.454 (3)	0.311 (3)	0.14 (3)*
H2W	1.068 (9)	0.351 (2)	0.305 (2)	0.067 (17)*
N1	0.2284 (6)	0.1499 (3)	0.47091 (19)	0.0346 (8)
N2	0.5713 (5)	0.2625 (2)	0.45281 (19)	0.0288 (8)
N3	0.5015 (5)	0.0957 (2)	0.38257 (18)	0.0291 (8)
O1	1.0672 (10)	0.4049 (3)	0.3351 (2)	0.0842 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0455 (3)	0.0433 (3)	0.0378 (3)	−0.0017 (2)	0.00566 (19)	−0.0088 (2)
C1	0.037 (2)	0.046 (3)	0.038 (3)	0.003 (2)	0.010 (2)	−0.002 (2)
C2	0.050 (3)	0.043 (3)	0.050 (3)	0.009 (2)	0.006 (2)	−0.010 (2)
C3	0.046 (3)	0.031 (2)	0.054 (3)	−0.004 (2)	−0.006 (2)	0.003 (2)
C4	0.031 (2)	0.038 (2)	0.042 (3)	−0.0063 (19)	0.004 (2)	0.0038 (19)
C5	0.025 (2)	0.038 (2)	0.028 (2)	−0.0028 (17)	0.0021 (18)	0.0053 (18)
C6	0.038 (2)	0.038 (2)	0.031 (2)	−0.0105 (19)	0.010 (2)	0.0017 (18)
C7	0.028 (2)	0.033 (2)	0.030 (2)	0.0051 (18)	0.0036 (18)	0.0027 (17)

C8	0.035 (2)	0.038 (2)	0.037 (3)	0.0067 (19)	0.004 (2)	−0.0009 (18)
C9	0.053 (3)	0.037 (2)	0.037 (3)	0.010 (2)	−0.001 (2)	−0.012 (2)
C10	0.047 (3)	0.036 (2)	0.051 (3)	−0.005 (2)	−0.012 (2)	−0.004 (2)
C11	0.037 (2)	0.032 (2)	0.048 (3)	−0.005 (2)	0.002 (2)	0.003 (2)
N1	0.0292 (18)	0.0397 (19)	0.036 (2)	−0.0064 (15)	0.0086 (16)	−0.0057 (16)
N2	0.0267 (18)	0.0277 (16)	0.033 (2)	−0.0011 (14)	0.0062 (15)	0.0006 (14)
N3	0.0251 (17)	0.0322 (18)	0.0305 (19)	−0.0007 (14)	0.0043 (15)	−0.0003 (14)
O1	0.146 (4)	0.051 (2)	0.055 (3)	−0.005 (3)	0.008 (3)	−0.005 (2)

Geometric parameters (Å, º)

C1—C2	1.351 (6)	C6—H6B	0.9700
C1—N3	1.367 (4)	C7—N1	1.337 (5)
C1—H1	0.9300	C7—N2	1.373 (4)
C2—C3	1.398 (5)	C7—C8	1.416 (5)
C2—H2	0.9300	C8—C9	1.340 (6)
C3—C4	1.345 (5)	C8—H8	0.9300
C3—H3	0.9300	C9—C10	1.404 (6)
C4—C5	1.410 (5)	C9—H9	0.9300
C4—H4	0.9300	C10—C11	1.343 (6)
C5—N1	1.338 (5)	C10—H10	0.9300
C5—N3	1.364 (4)	C11—N2	1.368 (5)
C6—N2	1.450 (5)	C11—H11	0.9300
C6—N3	1.455 (5)	O1—H1W	0.851 (10)
C6—H6A	0.9700	O1—H2W	0.844 (10)
C2—C1—N3	120.1 (4)	N1—C7—C8	122.3 (3)
C2—C1—H1	119.9	N2—C7—C8	116.3 (4)
N3—C1—H1	119.9	C9—C8—C7	121.1 (4)
C1—C2—C3	118.4 (4)	C9—C8—H8	119.4
C1—C2—H2	120.8	C7—C8—H8	119.4
C3—C2—H2	120.8	C8—C9—C10	120.6 (4)
C4—C3—C2	121.3 (4)	C8—C9—H9	119.7
C4—C3—H3	119.4	C10—C9—H9	119.7
C2—C3—H3	119.4	C11—C10—C9	118.9 (4)
C3—C4—C5	120.7 (4)	C11—C10—H10	120.5
C3—C4—H4	119.7	C9—C10—H10	120.5
C5—C4—H4	119.7	C10—C11—N2	120.6 (4)
N1—C5—N3	121.9 (3)	C10—C11—H11	119.7
N1—C5—C4	121.7 (3)	N2—C11—H11	119.7
N3—C5—C4	116.4 (3)	C7—N1—C5	118.3 (3)
N2—C6—N3	109.0 (3)	C11—N2—C7	122.4 (3)
N2—C6—H6A	109.9	C11—N2—C6	119.6 (3)
N3—C6—H6A	109.9	C7—N2—C6	117.6 (3)
N2—C6—H6B	109.9	C5—N3—C1	123.1 (3)
N3—C6—H6B	109.9	C5—N3—C6	117.3 (3)
H6A—C6—H6B	108.3	C1—N3—C6	118.5 (3)
N1—C7—N2	121.3 (3)	H1W—O1—H2W	103.9 (17)

N3—C1—C2—C3	1.8 (7)	C10—C11—N2—C6	171.8 (4)
C1—C2—C3—C4	−2.1 (7)	N1—C7—N2—C11	−173.2 (4)
C2—C3—C4—C5	1.5 (7)	C8—C7—N2—C11	2.8 (5)
C3—C4—C5—N1	−177.3 (4)	N1—C7—N2—C6	14.0 (5)
C3—C4—C5—N3	−0.7 (6)	C8—C7—N2—C6	−170.1 (4)
N1—C7—C8—C9	173.2 (4)	N3—C6—N2—C11	148.2 (3)
N2—C7—C8—C9	−2.7 (6)	N3—C6—N2—C7	−38.8 (5)
C7—C8—C9—C10	0.9 (7)	N1—C5—N3—C1	177.1 (4)
C8—C9—C10—C11	1.0 (7)	C4—C5—N3—C1	0.5 (6)
C9—C10—C11—N2	−1.0 (6)	N1—C5—N3—C6	−15.1 (6)
N2—C7—N1—C5	13.9 (6)	C4—C5—N3—C6	168.3 (4)
C8—C7—N1—C5	−161.9 (4)	C2—C1—N3—C5	−1.1 (7)
N3—C5—N1—C7	−13.3 (6)	C2—C1—N3—C6	−168.7 (4)
C4—C5—N1—C7	163.2 (4)	N2—C6—N3—C5	39.3 (5)
C10—C11—N2—C7	−1.0 (6)	N2—C6—N3—C1	−152.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*W*···Br1	0.85 (5)	2.67 (4)	3.423 (4)	147 (4)
O1—H2*W*···Br1^{i}	0.84 (3)	2.52 (3)	3.346 (4)	169 (3)
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Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+1/2; (ii) *x*−1, *y*−1, *z*; (iii) −*x*+2, −*y*+1, −*z*+1.