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2,2′-Bipyridinium bis(perchlorate)

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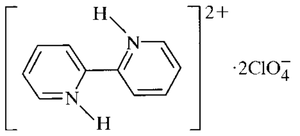
The title compound, $[H_2bipy](ClO_4)_2$ or $C_{10}H_{10}N_2^{2+}\cdot 2ClO_4^-$, was obtained at the interface between an organic (2,2′-bipyridine in methanol) and an aqueous phase (perchloric acid in water). The compound crystallizes in space group $P\overline{1}$ and comprises discrete diprotonated *trans*-bipyridinium cations, $[H_2bipy]^{2+}$, and ClO_4^- anions. The cations and anions are connected through N—H···O and C—H···O hydrogen bonds [distances N···O 2.817 (4) and 2.852 (4) Å, and C···O 3.225 (6)–3.412 (5)Å]. The C—C bond distance between the two rings is 1.452 (5) Å. The bipyridinium cation has a *trans* conformation and the N—C—C—N torsion angle is 152.0 (3)°.

Comment

The conformations of 2,2′-bipyridine (bipy) and its protonated species constitute an important aspect in the understanding of the properties of this popular ligand in coordination chemistry. The 2,2′-bipyridine molecule is a nitrogen-donor ligand to metal ions (McWhinnie & Miller, 1969). It behaves as a weak base, often forming monoprotonated species. The stability constants are $\log K_1 = 4.43$ and $\log K_1 = K_2 = -0.5$ (estimated) for the mono- and diprotonated species, respectively (McWhinnie & Miller, 1969; Reddy *et al.*, 1984). Hence, the $[Hbipy]^+$ cation is more stable than the $[H_2bipy]^{2+}$ dication in aqueous solution.

Recently, bipy and related bipyridines have attracted considerable attention (Howard, 1996; Lenstra *et al.*, 1994). For bipy, the *trans* conformer is more stable than the *cis*, but the energy difference between the conformations is small (about 6 kJ mol^{-1}) and the *cis*/*trans* equilibrium can be shifted by the solvent and/or pH of the solution (Nakamoto, 1960). In the monoprotonated cation, *i.e.* $[Hbipy]^+$, the *cis* conformer is more stable than the *trans* and the barrier for the *trans*/*cis* interconversion has been estimated to be about 14 kJ mol^{-1} (Howard, 1996). In coordination compounds with metal ions, the *cis* conformer is usually found. 2,2′-Bipyridine exists in a *trans* conformation both in the solid state and in organic solvents (Cheng *et al.*, 1972). The *cis* form of 2,2′-pyridylpyridinium can be found in 2,2′-bipyridine acidic solution. A weak N1···H—N2 hydrogen bond has been assumed to stabilize the *cis* conformation in the 2,2′-pyridylpyridinium cation, according to *ab initio* self consistent-field (SCF) calculations (Howard, 1996).

The crystal structures of 2,2′-bipyridine (Merritt & Schroeder, 1956; Felix *et al.*, 1965) and 2,2′-pyridylpyridinium, $[Hbipy](ClO_4)$ (Lipkowski *et al.*, 1976), have been studied previously. Two crystal structure determinations of the diprotonated cation, *i.e.* $[H_2bipy]^{2+}$, have been published with bromide (Nakatsu *et al.*, 1972) and chloride (Troyanov *et al.*, 1989). Usually, in coordination chemistry studies in aqueous solution, counter-anions are used which do not coordinate to the metal ion so that the equilibrium between the metal ion and the studied ligand (here bipy) is not disturbed. Therefore, in the present study, the structure of the diprotonated cation as its perchlorate salt, (I), has been determined.



(I)

A crystal of 2,2′-bipyridinium diperchlorate, $[H_2bipy](ClO_4)_2$, (I), was obtained at the interface of a methanol and an aqueous solution. The C—C bond distance between the

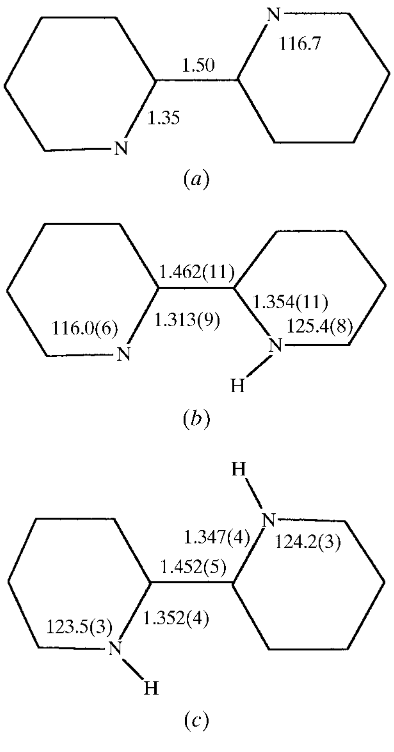


Figure 1
Experimental bond lengths (Å) and angles (°) for the bipyridine species in (*a*) solid 2,2′-bipyridine (Merritt & Schroeder, 1956; s.u.'s not given), (*b*) the 2,2′-pyridylpyridinium cation (Lipkowski *et al.*, 1976) and (*c*) the 2,2′-bipyridinium dication (present work).

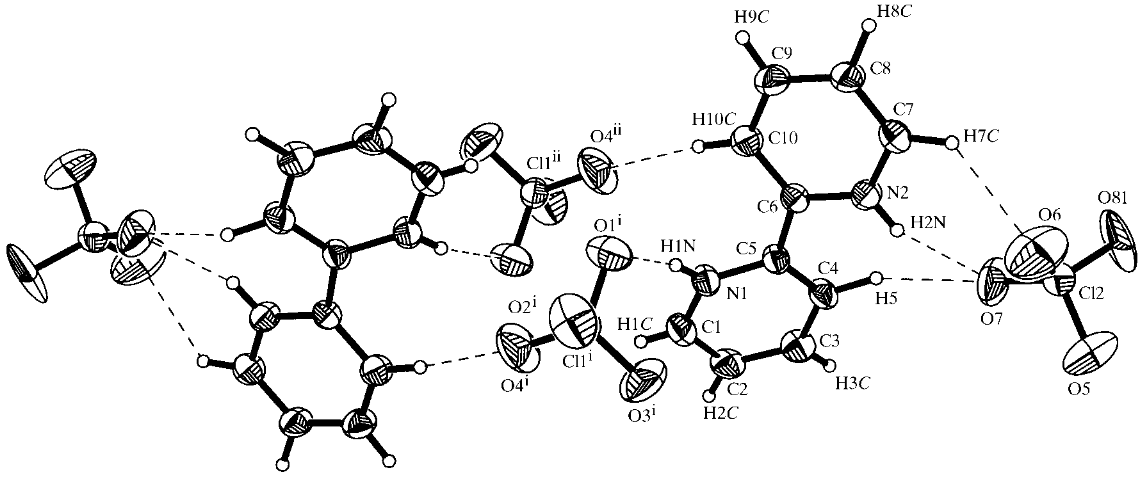


Figure 2

*ORTEP*II (Johnson, 1976) drawing of a selected fragment of the structure of (I) (displacement ellipsoids are plotted at the 50% probability level). One of the disordered O82 atoms has been omitted. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y, 1+z$.]

two rings is 1.452 (5) Å. The corresponding distance is 1.50 Å in 2,2′-bipyridine and 1.462 Å in the 2,2′-pyridylpyridinium ion (see Fig. 1). The C—N—C angle increases by 7–9° on protonation from pyridyl to pyridinium (*cf.* Fig. 1). The C—N—C angles in the two rings of the 2,2′-bipyridinium cation increase by 7.1 and 7.6° compared with those in 2,2′-bipyridine. This is in good agreement with previous studies (Gillespie & Nyholm, 1957; Merritt & Schroeder, 1956; Bi-Cheng & Cordes, 1970). The N—C—C—N torsion angles are 152.2 and −14.7° for (I) and [Hbipy](ClO_4) (Lipkowski *et al.*, 1976), respectively. These values are also in good agreement with those found in [H_2bipy]Cl_2 (Troyanov *et al.*, 1989) and [Hbipy](PF_6) (Milani *et al.*, 1997) of −160.5 and −18.2°, respectively. The difference between the conformations of [H_2bipy]$^{2+}$ and [Hbipy]$^+$ is probably caused by the existence of an intramolecular N—H···N hydrogen bond in the [Hbipy]$^+$ cation and repulsion of H^+ in [H_2bipy]$^{2+}$. Five hydrogen bonds (types N—H···O and C—H···O) bind the two [H_2bipy]$^{2+}$ cations and four ClO_4^- anions present in the unit cell of (I) (Fig. 2). The (C)H···*Y* bond distances (*Y* = O, N, Cl) are much shorter than the sum of the corresponding van der Waals radii, which can be considered as weak hydrogen bonding [for a discussion of the existence of C—H···O hydrogen bonds, *cf.* Berkovitch-Yellin & Leiserovitz (1984), Yanliang *et al.* (1999) and Taylor & Kennard (1982)]. The C—H···O hydrogen-bond distances in (I) are of the same order of magnitude as those reported previously (Taylor & Kennard, 1982; Berkovitch-Yellin *et al.*, 1984).

Experimental

2,2′-Bipyridine (0.09 g, 0.6 mmol) was dissolved in methanol (1 ml) and the solution was placed in a thin tube (5 mm diameter). $HClO_4$ (1 ml, 1.0 mol l^{-1}) was added slowly to the tube through its inside wall. White block-shaped crystals grew at the interface after a few hours.

Crystal data

$C_{10}H_{10}N_2^{2+}\cdot 2ClO_4^-$
$M_r = 357.10$
Triclinic, $P\overline{1}$
$a = 7.6042$ (8) Å
$b = 9.0007$ (11) Å
$c = 10.8647$ (16) Å
$\alpha = 97.974$ (19)°
$\beta = 98.50$ (2)°
$\gamma = 108.63$ (2)°
$V = 683.07$ (15) Å^3
$Z = 2$
$D_x = 1.736$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 13.7$–16.0°
$\mu = 0.520$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2696 measured reflections
2696 independent reflections
1811 reflections with $I > 2\sigma(I)$
$\theta_{max} = 26.00°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: −3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.148$
$S = 1.014$
2696 reflections
248 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0914P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^i	0.78 (4)	2.13 (4)	2.862 (4)	157 (4)
N2—H6···O7	0.90 (4)	1.96 (4)	2.817 (4)	158 (4)
C4—H5···O7	1.06 (3)	2.45 (3)	3.412 (5)	151 (2)
C7—H7···O6	1.02 (4)	2.42 (4)	3.225 (6)	135 (3)
C10—H10···O4^{ii}	0.92 (4)	2.41 (4)	3.313 (5)	168 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y, 1+z$.

One of the O atoms of the ClO_4^- anion is disordered. All H atoms were localized from difference Fourier maps and were refined isotropically [C—H = 0.92 (4)–1.06 (3) Å]

Data collection: *CAD*-4 *VAX*/*PC* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *VAX*/*PC*; data reduction: *JANA*98 (Petricek & Dusek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1046). Services for accessing these data are described at the back of the journal.

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