

Hydrogen-bonded (H₂O·X)₂ [X=Cl⁻, Br⁻] clusters in 1-phenacyl-4-(dimethylamino)pyridinium halide monohydrates[†]

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The synthesis, and X-ray crystal and molecular structures, of 1-phenacyl-4-(dimethylamino)pyridinium chloride and bromide monohydrates are described.

Keywords: crystal structure, hydrogen bonding, aminopyridinium salts

Aminopyridines are key intermediates for the synthesis of important pharmaceuticals and agrochemicals. 4-Dimethylaminopyridine (DMAP) is an excellent catalyst for a variety of synthetic transformations under mild conditions such as alkylations, acylations, silylations, esterifications, polymerisations and rearrangements.¹ The crystal structures of only a few organic derivatives² and metal complexes³ of DMAP have been reported in the literature. We are interested in the synthesis and structural chemistry of various derivatives of DMAP in order to identify bioactive compounds. Here, for the first time, we present the synthesis and X-ray structural characterisation of the 4-dimethylamino-1-phenacylpyridinium chloride and bromide monohydrates, C₁₅H₁₇N₂O⁺·X⁻·H₂O [X=Cl, Br], **1-Cl** and **1-Br** respectively.

In the present investigation, both the compounds **1-Cl** and **1-Br** are found to be isomorphous; 4-dimethylaminopyridinium chloride and bromide have recently been shown to possess strikingly different structures.⁴ The ORTEP diagrams of **1-Cl** and **1-Br** with atomic numbering schemes are depicted in Fig. 1. The pyridine ring systems in **1-Cl** and **1-Br** are almost planar, with values of 3.5(2)° and 3.3(2)° deviations from the respective exocyclic C(1)–N(1) bonds, and these values are comparable to that of an 8.9° deviation observed for 1-(bromodifluoromethyl)-4-(dimethylamino)pyridinium bromide.^{2a}

The dihedral angles between the dimethylamino nitrogen moiety, comprising atoms N(2), C(7) and C(8), and the plane determined by atoms C(3), C(4) and C(5) in the pyridine ring are 9.1(5)° for **1-Cl** and 9.4(5)° for **1-Br**. These dihedral angles are comparable to those values of 10.6° observed for *N*-(bromodifluoromethyl)-4-(dimethylamino)pyridinium bromide^{2a} and 14.4(5)° for (4-dimethylaminopyridine)-tris(2,2,6,6-tetramethylheptane-3,5-dionato)terbium(III),^{3d} but significantly larger than those values of 0.3(6)° and 3.5° in the chloride^{4b} and 2,5-dihydroxybenzoquinone^{2e} adducts of DMAP, respectively. This indicates that the dimethylamino nitrogen is nearly coplanar with the pyridine ring of DMAP structures in free or adduct forms only, and such planarity is affected by substitution or metal chelation.

An interesting feature of the pyridinium systems is that they have a substantial degree of quinoidal character, since the bond lengths C(2)–C(3) and C(5)–C(6) in **1-Cl** and **1-Br** [1.347(4), 1.349(5) and 1.357(4), 1.348(5) Å] are significantly

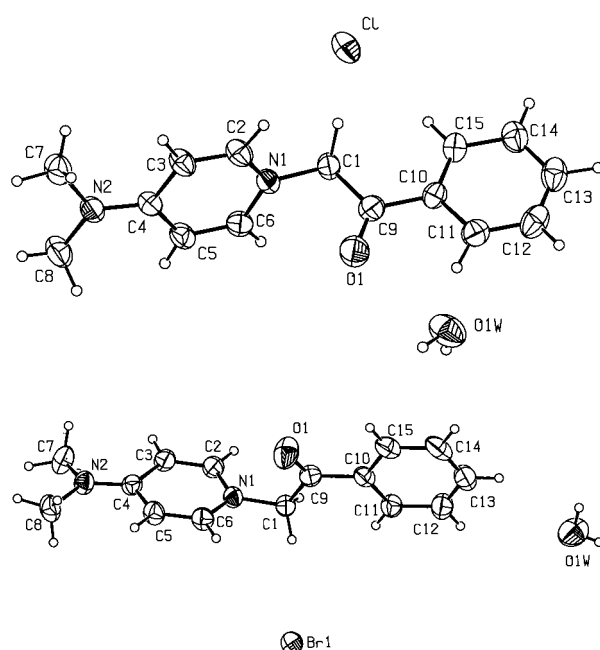


Fig. 1 Crystal structures of **1-Cl** and **1-Br**. The thermal ellipsoids are scaled to the 30% probability level.

shorter than those observed for C(3)–C(4) and C(4)–C(5) [1.420(4), 1.414(4) and 1.400(4), 1.421(5) Å]. The bond lengths C(4)–N(2) in **1-Cl** and **1-Br** are the same within experimental error [1.333(3), 1.331(4) Å] and lie between the carbon-nitrogen single and double bond distances (1.47 and 1.24 Å respectively), indicating a significant conjugation. Such conjugation has also been noted for other pyridinium compounds, for example, *N*-(bromodifluoromethyl)-4-(dimethylamino)pyridinium bromide,^{2a} 1,2,4,5-tetrafluoro-3,6-bis(4-dimethylaminopyridinio)benzene,^{2b} 1,2,3,3-tetrakis(4-dimethylaminopyridinio)cyclopropane^{2c} and methyl-3,3-bis(4-dimethylaminopyridinio)propenoate dichloride^{2d}. The sum of the bond angles at N1 and N2 [360.1(3)°, 359.5(3)° and 360.0(3)°, 359.4(3)°] for **1-Cl** and **1-Br** are nearly 360° and hence there is not much evidence for a *sp*³ lone pair. The dihedral angles between pyridine and phenyl rings in **1-Cl** and **1-Br** are 79.1(2)° and 80.4(2)° respectively.

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

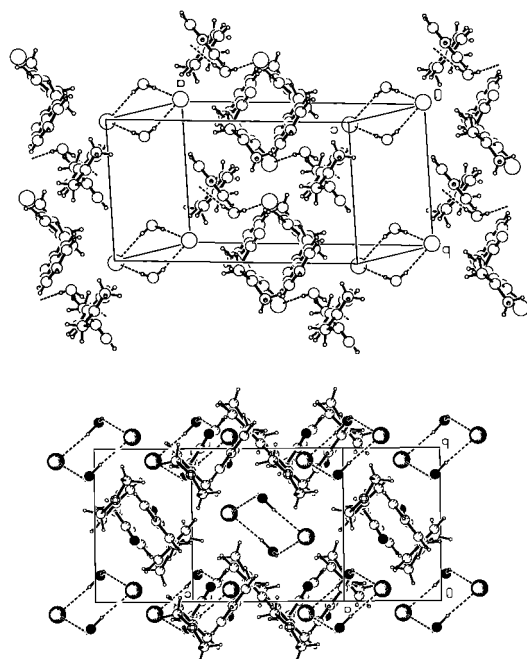


Fig. 2 Crystal packing diagrams for **1-Cl** (top) and **1-Br** (bottom) showing the presence of hydrogen-bonded $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters sandwiched between organic molecules.

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

D-H...A	D-H	H...A	D...A	D-H...A
O(1W)-H(1W)...Cl(i)	0.78(5)	2.48(5)	3.258(4)	171(5)
O(1W)-H(2W)...Cl(ii)	0.95(5)	2.35(5)	3.300(4)	176(4)
O(1W)-H(1W)...Br	0.921(6)	2.47(1)	3.389(5)	174(1)
O(1W)-H(2W)...Br(iii)	0.783(6)	2.88(1)	3.463(4)	133(1)
C(2)-H(2)...Cl(iv)	0.95(3)	2.66(3)	3.585(4)	163(2)
C(13)-H(13)...Cl(v)	1.02(4)	2.71(4)	3.660(4)	156(2)
C(2)-H(2)...Br(i)	0.930(5)	2.86(1)	3.728(4)	155(1)
C(13)-H(13)...Br(vi)	0.930(6)	2.91(1)	3.783(4)	156(1)

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

In the lattice, halide ions and water molecules in **1-Cl** and **1-Br** form remarkable hydrogen-bonded $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters in the form of quadrilaterals [$\text{Cl}^{(i)}\text{-O1W}\text{-Cl}^{(ii)} = 102.6(1)^\circ$ and $\text{O1W}^{(i)}\text{-Cl}\text{-O1W}^{(ii)} = 77.3(1)^\circ$; $\text{Br}\text{-O1W}\text{-Br}^{(iii)} = 81.3(1)^\circ$ and $\text{O1W}\text{-Br}\text{-O1W}^{(iii)} = 96.7(1)^\circ$]. Much attention has been given to characterising water-halide structures in hydrated halide compounds. Particularly, in the case of quaternary ammonium hydrate salts, widely studied by Harmon *et al.*,⁵ fluoride monohydrates always tend to form planar $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters, iodide monohydrates mostly form extended chains, whereas chloride and bromide monohydrates have similar behaviour and contain either $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters or extended water-halide chains. The present work and also our recent report⁶ confirm that chloride and bromide hydrates share common structural features, and they adopt either characteristic hydrogen-bonded $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters or infinite chains. The presence of water-halide $(\text{H}_2\text{O}\cdot\text{X})_2$ clusters in **1-Cl** and **1-Br** are illustrated in Fig. 2. These water-halide clusters are sandwiched between organic molecules by C-H...Cl(Br⁻) hydrogen bonds. The hydrogen-bonding geometry is given in Table 1.

Experimental

Preparation of 1-Cl: A solution of 0.295 g (1.9 mmol) of phenacyl chloride and 0.193 g (0.16 mmol) of 4-dimethylaminopyridine in

30 ml of ethyl acetate was heated under reflux for 2 hours. After cooling, the resulting precipitate was filtered off, washed with ethyl acetate and dried *in vacuo*. The product was recrystallised from a mixture of acetone and methanol (4:1 v/v), yield 0.39 g (84%), m.p. 123–124 $^\circ$ C.

Preparation of 1-Br: A mixture of phenacyl bromide (0.44 g, 2.20 mmol) and DMAP (0.24 g, 2.0 mmol) in ethyl acetate (30 ml) was stirred for 15 minutes at room temperature. The white solid that separated was filtered off, washed with toluene, dried *in vacuo* and recrystallised from acetone-chloroform (1:1 v/v) to give **1-Br**, yield 0.60 g (90%), m.p. 216–218 $^\circ$ C.

Crystal data for 1-Cl: $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{O}\cdot\text{H}_2\text{O}$, $M = 294.77$, Monoclinic, $P2_1/n$, $a = 18.105(2)$, $b = 8.903(3)$, $c = 9.569(2)$ \AA , $\beta = 93.8(1)^\circ$, $V = 1538.9(6)$ \AA^3 , $Z = 4$, $D_c = 1.272$ g cm^{-3} , $T = 293(2)$ K, $\mu(\text{Cu-K}\alpha) = 2.224$ mm^{-1} , $R = 0.0441$, $R_w = 0.1022$ for 2918 data with $F \geq 2\sigma(F)$.

Crystal data for 1-Br: $\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{O}\cdot\text{H}_2\text{O}$, $M = 339.23$, Monoclinic, $P2_1/n$, $a = 9.659(2)$, $b = 8.910(3)$, $c = 18.545(2)$ \AA , $\beta = 93.7(1)^\circ$, $V = 1592.8(7)$ \AA^3 , $Z = 4$, $D_c = 1.415$ g cm^{-3} , $T = 293(2)$ K, $\mu(\text{Cu-K}\alpha) = 3.545$ g mm^{-1} , $R = 0.0446$, $R_w = 0.1347$ for 2995 data with $F \geq 2\sigma(F)$.

Structures were solved by direct methods using SIR97 and refined with SHELXL97. Hydrogen atoms were located from difference Fourier maps and refined for **1-Cl**, and those of **1-Br** were fixed and treated with riding model. PLATON97 was used for computation and graphics.

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