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1-[(4-Chlorobenzoyl)methyl]-4-(*N*,*N*-dimethylamino)pyridinium bromide sesquihydrate and 1-[(4-bromobenzoyl)methyl]-4-(*N*,*N*-dimethylamino)pyridinium bromide sesquihydrate

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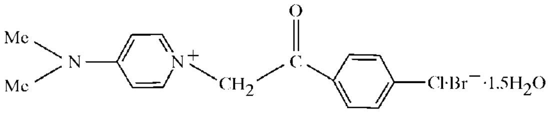
The title compounds, $C_{15}H_{16}ClN_2O^+\cdot Br^-\cdot 1.5H_2O$ and $C_{15}H_{16}BrN_2O^+\cdot Br^-\cdot 1.5H_2O$, are isomorphous. The benzene ring is oriented nearly normal to the pyridine ring in both compounds. The molecular packing is mainly influenced by intermolecular O—H···O and O—H···Br interactions, as well as weak intramolecular C—H···O interactions. The H_2OBr^- units form an extended water–bromide chain, with a bridging water molecule on a twofold axis.

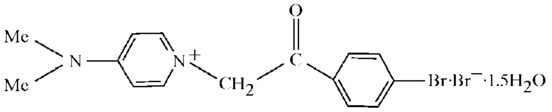
Comment

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, polymerizations and rearrangements (Prabakaran *et al.*, 2001, and references therein). As part of our interest in the identification of bioactive compounds, we report here the structure determination of two of the derivatives of DMAP, *viz*. the title compounds (I) and (II). Compound (II) is isomorphous with (I).

Perspective views of the DMAP moieties of molecules of (I) and (II), with the atomic numbering schemes, are shown in Figs. 1 and 2, respectively. The corresponding bond lengths and angles in (I) and (II) are essentially equivalent and are comparable to those in a related structure (Prabakaran *et al.*, 2001). The dimethylamine N atom is almost coplanar with the plane of the pyridine ring in both (I) and (II) [2.9 (3)° in (I) and 2.6 (4)° in (II)]. The angles between the least-squares planes of the pyridine and benzene rings are 81.01 (11)° in (I) and 78.64 (13)° in (II).



(I)



(II)

An interesting feature of the pyridinium systems is that they have a substantial degree of quinoidal character, since the C2—C3 and C5—C6 bond lengths [1.334 (4) and 1.339 (5) Å in (I), and 1.339 (5) and 1.342 (5) Å in (II)] are significantly shorter than the C3—C4 and C4—C5 bonds [1.406 (4) and 1.413 (4) Å in (I), and 1.407 (5) and 1.412 (5) Å in (II)]. The C4—N2 bond lengths in (I) and (II) are the same within experimental error [1.326 (4) and 1.327 (4) Å] and are intermediate between typical C—N single- and double-bond distances [1.458 (4) and 1.326 (4) Å in (I), and 1.462 (5) and 1.327 (4) Å in (II)], indicating a significant conjugation. The sums of the bond angles at atoms N1 and N2 [359.7 (3) and 360.0 (3)°, and 359.7 (3) and 359.9 (3)°] for (I) and (II) are almost 360° and hence there is little evidence for the presence of an sp^3 lone pair.

Even after the substitution of halide atoms at the *para* position, the general conformation of the molecule is not affected in (I) and (II). In each compound, the asymmetric units contain two water molecules, with the O atom of one of the water molecules lying on a special position [O2*W*; (0, 0.06, 0.25)] on the twofold axis. In addition to hydrogen-bonded clusters in the form of quadrilaterals, as reported for the

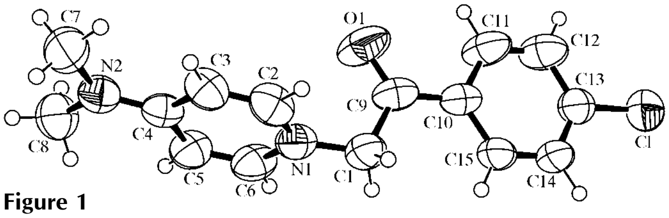


Figure 1
A view of the DMAP moiety of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii. For clarity, atom Br1 and the water molecules have been omitted.

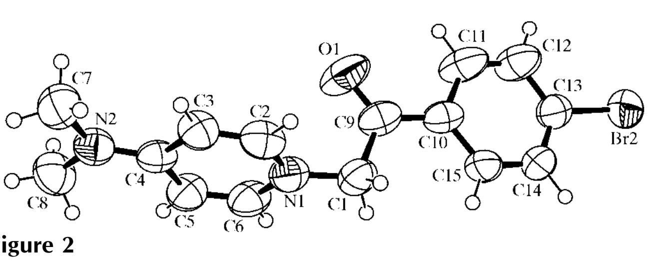


Figure 2
A view of the DMAP moiety of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii. For clarity, atom Br1 and the water molecules have been omitted.

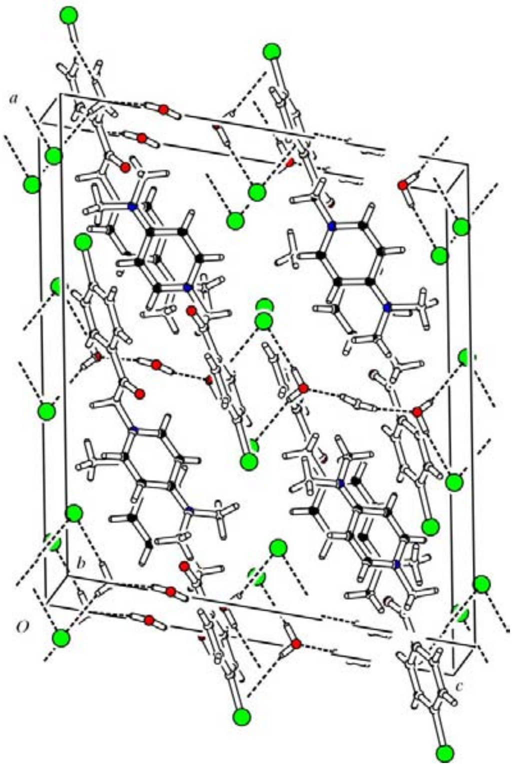


Figure 3
A crystal packing diagram for (II), showing the presence of hydrogen-bonded $(H_2OBr)_2$ clusters.

related structure by Prabakaran *et al.* (2001), we observe additional hydrogen bonds connecting two quadrilaterals through the water molecule in the special position, running along the *c* axis as an infinite continuous chain. The $(H_2OBr)_2$ clusters in (I) and (II) are sandwiched between organic molecules by C—H$\cdots$Br$^-$ hydrogen bonds, as illustrated in Fig. 3 for (II). The hydrogen-bonding geometry is given in Tables 1 and 2 for (I) and (II), respectively.

Experimental

DMAP (0.5 g, 41 mmol) was added to a solution of *p*-chlorophenacyl bromide (0.85 g, 4 mmol) in dry acetone. The mixture was refluxed for 30 min. After cooling, the resulting solid product was filtered off and washed with dry acetone to give (I) (m.p. 472–474 K), which was dried in a vacuum and recrystallized from ethanol. Compound (II) was prepared in an identical fashion but with *p*-bromophenacyl bromide (0.85 g, 4 mmol) in dry acetone as the starting material (m.p. 501–504 K). The resulting solid, (II), was dried in a vacuum and recrystallized from ethanol.

Compound (I)

Crystal data

$C_{15}H_{16}ClN_2O^+\cdot Br^-\cdot 1.5H_2O$
$M_r = 382.68$
Monoclinic, $C2/c$
$a = 20.661$ (9) Å
$b = 9.795$ (4) Å
$c = 17.249$ (7) Å
$\beta = 99.182$ (12)°
$V = 3446$ (2) Å^3
$Z = 8$

$D_x = 1.475$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 873 reflections
$\theta = 2.2$–28.9°
$\mu = 2.55$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
$T_{min} = 0.515$, $T_{max} = 0.630$
13 764 measured reflections

3632 independent reflections
2396 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.1°$
$h = -25 \rightarrow 25$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.107$
$S = 1.01$
3632 reflections
209 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 2.1711P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2W—H20$W\cdots$O3W^{i}	0.82 (3)	1.96 (4)	2.764 (4)	166 (4)
O3W—H30$W\cdots$Br1^{ii}	0.84 (6)	2.54 (6)	3.360 (4)	167 (4)
O3W—H31$W\cdots$Br1^{iii}	0.73 (4)	2.63 (4)	3.353 (4)	168 (5)
C8—H8$A\cdots$Cl^{iv}	0.96	2.87	3.707 (4)	147
C1—H1$A\cdots$O2W^{v}	0.97	2.44	3.351 (4)	157
C6—H6$\cdots$O2W^{v}	0.93	2.56	3.394 (4)	149

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

Compound (II)

Crystal data

$C_{15}H_{16}BrN_2O^+\cdot Br^-\cdot 1.5H_2O$
$M_r = 427.14$
Monoclinic, $C2/c$
$a = 20.403$ (6) Å
$b = 10.022$ (3) Å
$c = 17.386$ (4) Å
$\beta = 100.182$ (8)°
$V = 3499.0$ (17) Å^3
$Z = 8$

$D_x = 1.622$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 873 reflections
$\theta = 2.3$–27.4°
$\mu = 4.64$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.40 × 0.30 × 0.30 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
$T_{min} = 0.258$, $T_{max} = 0.337$
20 471 measured reflections

3587 independent reflections
2391 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 26.4°$
$h = -25 \rightarrow 25$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.111$
$S = 1.02$
3587 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 3.7037P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00162 (14)

Since the two title compounds are isomorphous, (II) was refined with the coordinates of the dimethylaminopyridinium moiety of (I). The positions of the Br atoms and water molecules were determined

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Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H20W···O3W^{vi}	0.85 (4)	1.95 (4)	2.784 (5)	167 (5)
O3W—H30W···Br1$^{\text{vii}}$	0.74 (5)	2.65 (5)	3.369 (4)	168 (5)
O3W—H31W···Br1$^{\text{viii}}$	0.89 (6)	2.48 (6)	3.360 (4)	174 (5)
C8—H8A···Br2$^{\text{iv}}$	0.96	2.92	3.732 (5)	143
C1—H1A···O2W^{v}	0.97	2.46	3.373 (5)	156
C6—H6···O2W^{v}	0.93	2.55	3.394 (5)	151

Symmetry codes: (iv) $1 - x, y, \frac{3}{2} - z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (viii) $\frac{1}{2} + x, y - \frac{1}{2}, z$.

from a difference Fourier map. The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å), with U_{iso}(H) values of $1.5U_{\text{eq}}$(C). All remaining H atoms were placed in idealized positions (C—H = 0.93–0.97 Å) and were constrained to ride on their parent non-H atoms, with U_{iso}(H) values of $1.2U_{\text{eq}}$(C).

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1711). Services for accessing these data are described at the back of the journal.

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