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Secondary interactions in the isomorphous compounds 2,6-bis(chloromethyl)pyridinium chloride and 2,6-bis(bromomethyl)pyridinium bromide

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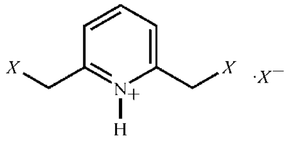
The title compounds, $C_7H_8Cl_2N^+\cdot Cl^-$ and $C_7H_8Br_2N^+\cdot Br^-$, are isomorphous. In the crystal packing, layers parallel to the *ac* plane are formed by a classical $N^+—H\cdots X^-$ hydrogen bond (X = halogen) and two $X\cdots X$ contacts. A third $X\cdots X$ contact links the layers, and a fourth, which is however very long, completes a ladder-like motif of halogen atoms. Hydrogen bonds of the form $C—H\cdots X$ play at best a subordinate role in the packing.

Comment

We are interested in secondary interactions (hydrogen bonds and halogen–halogen contacts) in halides of simple halogenated derivatives of anilines (Gray & Jones, 2002, and references therein) and pyridines [halopyridines (Freytag & Jones, 2001, and references therein) and halomethylpyridines (Jones & Vancea, 2003, and references therein)]. We report here the structures of the isomorphous pair of compounds 2,6-bis(chloromethyl)pyridinium chloride, (I), and 2,6-bis(bromomethyl)pyridinium bromide, (II). It is common for such pairs to be isomorphous, *e.g.* 4-chloropyridinium chloride and its bromine analogue (Freytag *et al.*, 1999).



(I) X=Cl
(II) X=Br

The asymmetric units of (I) and (II) are shown in Figs. 1 and 2, respectively. Bond lengths and angles may be regarded as normal, *e.g.* the widened angles at the ring N atom (Tables 1 and 3). The rings are essentially planar [r.m.s. deviations of 0.006 Å for (I) and (II)], with the substituent C atoms lying slightly outside the plane [in (I): C7 −0.105 (3) Å and C8 0.065 (2) Å; in (II): C7 −0.102 (4) Å and C8 0.063 (3) Å]. The C—X vectors (X = halogen) of the halomethyl groups extend almost perpendicularly from, and to opposite sides of, the ring (for torsion angles see Tables 1 and 3).

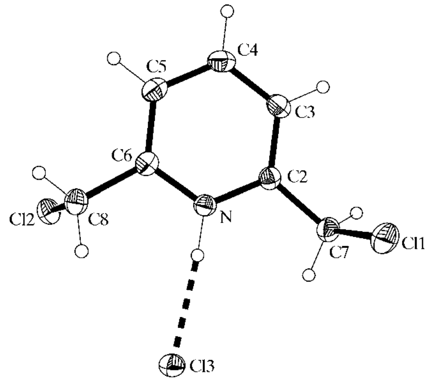


Figure 1
The asymmetric unit of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The classical hydrogen bond is indicated as a broken line.

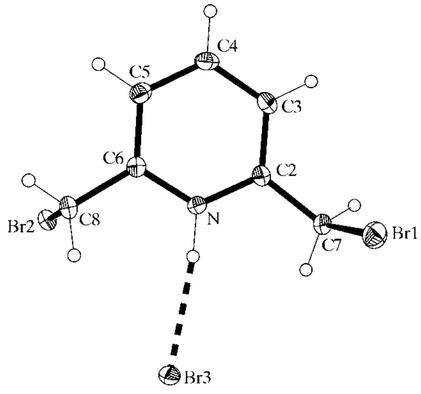


Figure 2
The asymmetric unit of (II) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The classical hydrogen bond is indicated as a broken line.

Both compounds form the expected classical hydrogen bond from the N^+–H group to the halide ion (Tables 2 and 4). Non-classical hydrogen-bond contacts of the form $C—H\cdots X$ are observed, but are all either long (uncorrected $H\cdots X$ > 2.9 Å) and/or markedly non-linear. Three independent halogen–halogen contacts in each structure provide more striking examples of secondary interactions (Table 5). The contact to the anion is, in each case, the shortest (because it is charge-assisted) and essentially linear, as would be expected from the concept of a small positive region in the extension of the C—Cl vector. The other two contacts, between cations, may be classified as type I ($C—X\cdots X$ angles approximately equal) and type II (one $C—X\cdots X$ angle *ca* 90° and the other *ca* 180°) according to the classification of Pedireddi *et al.* (1994).

The net effect of the classical hydrogen bond and the two shorter halogen–halogen interactions is to connect the resi-

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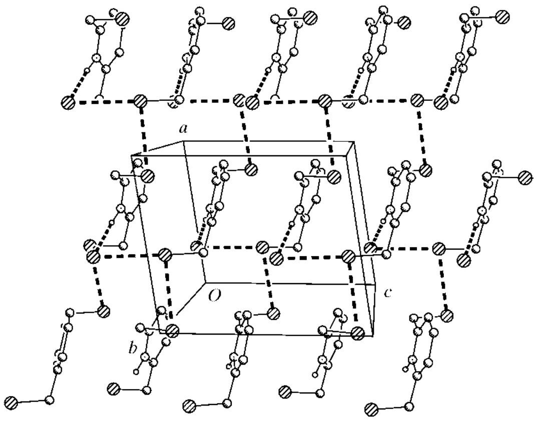

Figure 3
A packing diagram for (I), viewed approximately parallel to the b axis, showing one layer at $b \simeq \frac{1}{4}$. Hydrogen bonds and Cl$\cdots$Cl interactions are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

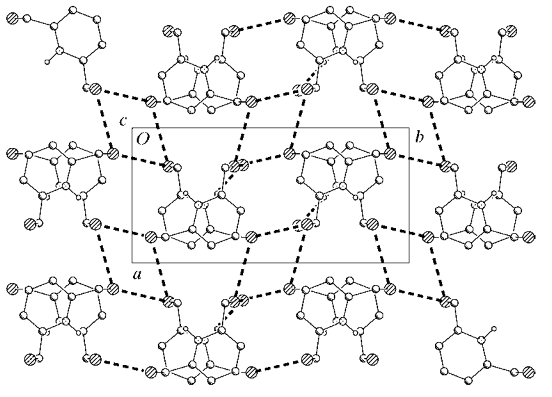

Figure 4
A packing diagram for (I) as a projection parallel to the c axis. Cl$\cdots$Cl interactions are indicated by dashed lines. Note that the chlorine parallelograms (*e.g.* at the left-hand cell margin), which are not an artefact of projection, can themselves be linked *via* Cl atoms (see text).

dues, *via* the glide-plane operators, to form layers parallel to the ac plane at $y \simeq \frac{1}{4}, \frac{3}{4}$. One such layer is shown in Fig. 3. The third and longest halogen–halogen interaction then links the layers, in the process forming halogen parallelograms (Fig. 4), with angles 117.54 (1) and 62.46 (1)° for (I), and 117.39 (1) and 62.61 (1)° for (II). It is noteworthy that the parallelograms are themselves linked into ladder-like tapes *via* further halogen–halogen contacts [3.8840 (6) Å for (I) and 3.9610 (4) Å for (II); symmetry code: $x, \frac{1}{2}-y, \frac{1}{2}+z$], which are much longer than the sum of the van der Waals radii but may still be structurally significant.

Experimental

Compound (I) was obtained as a hygroscopic white solid by bubbling HCl gas through a solution of the corresponding pyridine (0.352 g, 2 mmol) in dichloromethane (10 ml), and was recrystallized from dichloromethane–petroleum ether. Compound (II) was obtained in an analogous fashion, but is insoluble in dichloromethane and was recrystallized from ethanol–diisopropyl ether.

Compound (I)

Crystal data

$C_7H_8Cl_2N^+\cdot Cl^-$
$M_r = 212.49$
Monoclinic, $P2_1/c$
$a = 7.2167 (6)$ Å
$b = 14.6054 (14)$ Å
$c = 8.4990 (8)$ Å
$\beta = 98.716 (5)^\circ$
$V = 885.47 (14)$ Å^3
$Z = 4$
$D_x = 1.594$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4471 reflections
$\theta = 2.8$–30.5°
$\mu = 0.97$ mm^{-1}
$T = 173 (2)$ K
Tapering prism, colourless
$0.38 \times 0.07 \times 0.07$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.722$, $T_{\max} = 0.942$
13 915 measured reflections

2590 independent reflections
1991 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 30.0^\circ$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 0.99$
2590 reflections
104 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (°) for (I).

C2—N—C6	122.99 (13)		
N—C2—C7—Cl1	−98.77 (14)	N—C6—C8—Cl2	−87.88 (14)
C3—C2—C7—Cl1	78.07 (17)	C5—C6—C8—Cl2	89.62 (16)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H1$\cdots$Cl3	0.95 (2)	2.10 (2)	3.0516 (13)	174.4 (17)
C7—H7$A\cdots$Cl3$^{\rm i}$	0.99	2.99	3.9632 (17)	169
C7—H7$B\cdots$Cl3$^{\rm ii}$	0.99	2.94	3.6572 (16)	130
C8—H8$A\cdots$Cl3$^{\rm iii}$	0.99	2.95	3.6085 (16)	125
C8—H8$B\cdots$Cl3	0.99	2.79	3.5322 (17)	133
C3—H3$\cdots$Cl2$^{\rm iv}$	0.95	2.94	3.7727 (16)	147
C7—H7$A\cdots$Cl2$^{\rm iv}$	0.99	2.98	3.6178 (16)	123
C8—H8$A\cdots$Cl1$^{\rm v}$	0.99	2.72	3.4758 (17)	134

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

Compound (II)

Crystal data

$C_7H_8Br_2N^+\cdot Br^-$
$M_r = 345.87$
Monoclinic, $P2_1/c$
$a = 7.4633 (6)$ Å
$b = 15.0136 (12)$ Å
$c = 8.7377 (6)$ Å
$\beta = 99.146 (4)^\circ$
$V = 966.62 (13)$ Å^3
$Z = 4$
$D_x = 2.377$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4337 reflections
$\theta = 2.7$–30.5°
$\mu = 12.46$ mm^{-1}
$T = 133 (2)$ K
Plate, colourless
$0.26 \times 0.18 \times 0.04$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.282$, $T_{\max} = 0.608$
17 828 measured reflections
2825 independent reflections
2503 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 30.0°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 21$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.057$
$S = 1.02$
2825 reflections
104 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.6042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

Table 3
Selected geometric parameters (°) for (II).

C2—N—C6	123.49 (18)		
N—C2—C7—Br1	−96.15 (19)	N—C6—C8—Br2	−87.12 (19)
C3—C2—C7—Br1	81.1 (2)	C5—C6—C8—Br2	90.7 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N—H1⋯Br3	0.88 (3)	2.37 (3)	3.2417 (17)	174 (2)
C7—H7*A*⋯Br3$^{\rm i}$	0.99	3.08	4.056 (2)	167
C7—H7*B*⋯Br3$^{\rm ii}$	0.99	3.07	3.768 (2)	129
C8—H8*A*⋯Br3$^{\rm iii}$	0.99	2.99	3.694 (2)	129
C8—H8*B*⋯Br3	0.99	2.92	3.677 (2)	134
C3—H3⋯Br2$^{\rm iv}$	0.95	3.10	3.935 (2)	147
C7—H7*A*⋯Br2$^{\rm iv}$	0.99	3.09	3.753 (2)	126
C8—H8*A*⋯Br1$^{\rm v}$	0.99	2.86	3.599 (2)	132

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

Table 5
Cl⋯Cl contacts for (I) and Br⋯Br contacts for (II) (Å, °).

C—*X*⋯*X*—C†	*X*⋯*X*	C—*X*⋯*X*	*X*⋯*X*—C
C8—Cl2⋯Cl3$^{\rm vi}$	3.3085 (6)	173.02 (6)	
C7—Cl1⋯Cl2$^{\rm iv}$—C8$^{\rm iv}$	3.5695 (6)	77.01 (5)	88.82 (5)
C7—Cl1⋯Cl2$^{\rm vii}$—C8$^{\rm vii}$	3.5886 (6)	147.05 (5)	71.80 (5)
C8—Br2⋯Br3$^{\rm vi}$	3.3550 (4)	174.19 (6)	
C7—Br1⋯Br2$^{\rm iv}$—C8$^{\rm iv}$	3.7482 (4)	75.06 (7)	89.16 (6)
C7—Br1⋯Br2$^{\rm vii}$—C8$^{\rm vii}$	3.6959 (4)	149.72 (6)	71.68 (6)

† Final C atom not applicable for chloride and bromide acceptors. Symmetry codes: (iv) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (vii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Crystals of compound (I) cracked badly at 133 K, presumably because of a phase transition, and were therefore measured at the slightly higher temperature of 173 K. The N-bound H atoms were refined freely. Other H atoms were introduced at geometrically calculated positions and refined using a riding model, with fixed C—H distances of 0.95 (sp^2 C—H) or 0.99 Å (methylene H), and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1577). Services for accessing these data are described at the back of the journal.

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