Hydrogen bonding and halogen–halogen interactions in 4-halopyridinium halides

Matthias Freytag,[a] Peter G. Jones,*[a] Birte Ahrens[a] and Axel K. Fischer[b]

[a] *Institut für Anorganische und Analytische Chemie, Technical University of Braunschweig, Postfach 3329, 38023 Braunschweig, Germany*
[b] *Institut für Chemie, University of Magdeburg, Universitätsplatz 2, 37106 Magdeburg, Germany*

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The solid state structures of the 4-halopyridinium halides 4-$XC_5H_4NH^+X^-$ (X = Cl, Br, I) all display chains of the form $[\cdots X–C_5H_4N–H^+\cdots X^-\cdots X–C_5H_4N–H^+\cdots X^-\cdots]$ involving N–H···X^- hydrogen bonds and X···X^- contacts; the former become longer and the latter shorter (relative to the sum of the van der Waals radii) with increasing size of X.

Secondary interactions, those forces determining molecular cohesion in the solid state, are the subject of considerable current interest. The archetypal such interaction is the classical hydrogen bond, but several other types have attracted much recent attention, for example non-classical hydrogen bonds such as C–H···O[1] and C–H···Cl.[2] We ourselves have investigated non-classical hydrogen bonds in complexes of bis(diphenylphosphino)methane and related ligands.[3] Finally, halogen–donor interactions such as C–Cl···O have been shown by a combined database and theoretical study[4] to arise mostly from electrostatic effects, provided first that the chlorine atom is in an electron-withdrawing environment, and secondly that the angle at chlorine is approximately linear (as is generally observed).

It has long been known that X···X contacts (X = halogen, excluding fluorine, throughout this paper) between neutral molecules can be appreciably shorter that the sum of the (isotropic!) van der Waals radii. Desiraju and colleagues have forcefully argued[5] that these contacts represent attractive interactions, whereby polarisation effects become more important for heavier X; however, there have been alternative explanations, such as the packing of elliptical, rather than spherical, Cl atoms (reduced repulsion, rather than increased attraction, in certain directions).[6] It has also been suggested[6] that the apparent prevalence of Cl···Cl contacts in polychlorinated species may simply be a statistical reflection of the preponderance of Cl atoms at the periphery of such molecules. The role of X···X contacts, whatever their cause, in determining supramolecular structure is an important one, and it may be possible to exploit them directly in crystal engineering, the deliberate design of supramolecular aggregates.[7]

Considering the established importance of a positivised chlorine environment for the formation of C–Cl···O contacts,[4] similar effects might be expected to apply to C–Cl···Cl contacts if the first chlorine forms part of a cation and the second is a chloride counteranion; such contacts can be termed *charge-assisted*.[8] Such X···X contacts have been observed, *e.g.* in the linear spoke systems $P^+–X\cdots X^-$ by the groups of McAuliffe and du Mont.[9]

We are interested in systems displaying more than one kind of secondary interaction and have already published an investigation into the competition between hydrogen bonds and aurophilic interactions in amine complexes of gold(I).[10] We turn now to the interplay between halogen–halogen contacts and hydrogen bonds in the series of 4-halopyridinium halides, 4-$XC_5H_4NH^+X^-$ (**1-Cl**, **1-Br**, **1-I**).

The compounds **1-Br** and **1-I** do not crystallise easily, tending to form a polycrystalline mass and at best very small single crystals, which diffract weakly but absorb strongly. However, low-temperature methods and the increased precision of area detector technology have enabled us to obtain suitable data (see Experimental for details).

Compounds **1-Cl** and **1-Br**, which are isostructural, display crystallographic mirror symmetry through the atoms N, H1, C4, Cl1 and Cl2 (Fig. 1); **1-I** (Fig. 2) has no imposed symmetry. The cation dimensions are unremarkable, displaying angles >120° at nitrogen, as is usual for pyridinium systems[11] [**1-Cl**, 122.3(3)°; **1-Br**, 124.1(5)°; **1-I**, 122.9(4)°].

The crystal packing of **1-X** (Figs. 3–6) reveals the result of the cooperation between classical hydrogen bonds and charge-assisted halogen–halogen interactions; in all three compounds, infinite chains of the type

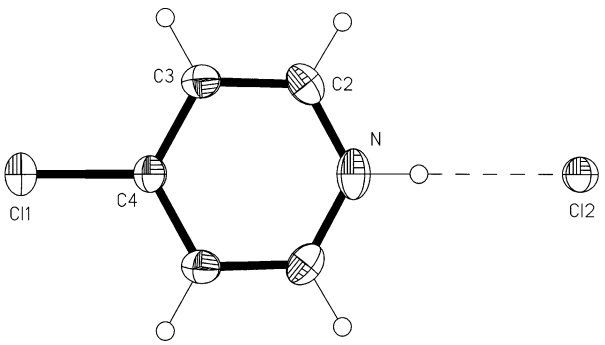

Fig. 1 Structure of the formula unit of compound **1-Cl** in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary. Compound **1-Br** is isostructural and labelled in an exactly analogous fashion.

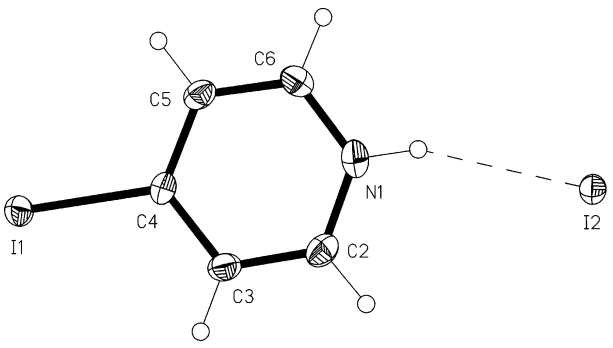

Fig. 2 Structure of the formula unit of compound **1-I** in the crystal. Ellipsoids represent 50% probability levels. Hydrogen radii are arbitrary.

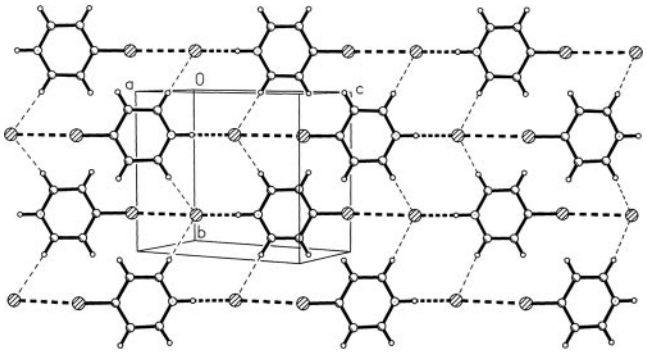

Fig. 3 Packing diagram of compound **1-Cl**. Key to secondary bond types: thick dashed bonds, classical H bonds and Cl···Cl interactions; thin dashed bonds, C–H···Cl interactions. Compound **1-Br** is isostructural.

[···X–C_5H_4N–H^+···X^-···X–C_5H_4N–H^+···X^-···] are observed. The chains are essentially linear for **1-Cl** (Cl^-···Cl–C 162°, H···Cl^-···Cl 163°) and **1-Br** (Br^-···Br–C 167°, H···Br^-···Br 163°) but more angled at the iodide anion for **1-I** (I^-···I–C 176°, H···I^-···I 126°). It is noteworthy that an exactly linear chain structure is observed for 4-iodopyridine, the only free base of this series for which a structure has been determined;[12] the molecules are connected by very short N···I contacts of 2.988 Å.

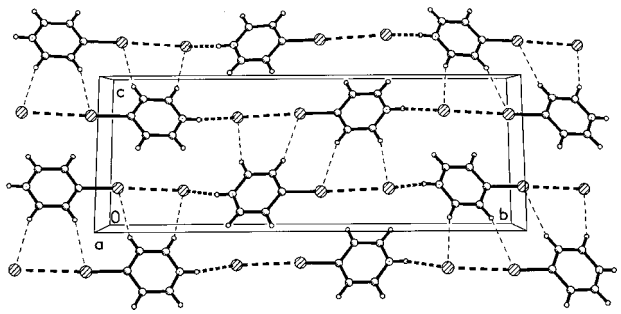

Fig. 4 Packing diagram of compound **1-I**. Key to secondary bond types: thick dashed bonds, classical H bonds and I···I interactions; thin dashed bonds, C–H···I interactions.

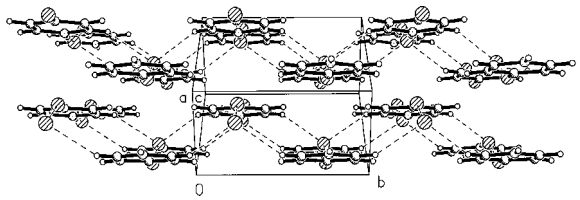

Fig. 5 Two corrugated sheets of **1-Cl** viewed end-on.

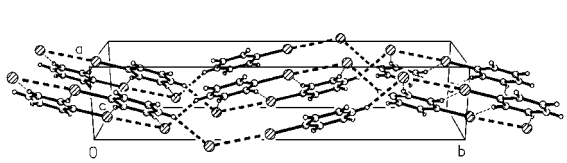

Fig. 6 One corrugated sheet of **1-I** viewed obliquely from the side.

The H···X hydrogen bonding distances and X···X contact distances in **1-X** (Table 1[13]) display the trends one would expect for decreasing electronegativity and increasing polarisability of X; the hydrogen bonds become proportionately longer, and the X···X distances relatively shorter (compared to the sum of the van der Waals radii) as X becomes larger.

The halogen–halogen contacts in the phosphonium species mentioned above are appreciably shorter than those observed for **1-X**: Pr^i_3PCl···Cl, 3.234(1); Ph_3PBr···Br, 3.123(2); Ph_3PI···I, 3.16(2) Å,[9] but it is not clear to what extent these very short interactions may involve significant covalent bonding character.

The chains in compounds **1-X** are linked by non-classical hydrogen bonds of the type C–H···X^- (Table 2[13]) to form corrugated sheets (Figs. 3–6). However, **1-I** is qualitatively different in two respects; both I atoms (not just the iodide anion) are involved, and one C–H···I interaction (last line of Table 2, not shown in the figure) links neighbouring sheets.

We are currently investigating structures of other halogenated pyridinium salts and related systems, which will form the basis of future publications.

Experimental

Preparation of compounds

1-Cl. The compound as purchased was recrystallised by liquid diffusion of diethyl ether into a solution in ethanol.

1-Br. 4-$BrC_5H_4NH^+Cl^-$ was converted to the free base with aqueous KOH and extracted with dichloromethane. Hydrogen bromide was bubbled through the solution to produce a white precipitate, which was dried *in vacuo* and recrystallised by liquid diffusion of petroleum ether into a solution in methanol.

1-I. 4-Iodopyridine free base was dissolved in 57% aqueous HI, after which the product separated. It was recrystallised by diffusion of petroleum ether into a solution in ethanol–methanol (1 : 2).

Elemental analyses and NMR spectra accorded with expectation.

X-Ray structure determinations

Crystals were mounted in inert oil on glass fibres. Data were measured using Mo-Kα radiation on a Siemens (**1-Cl**) or Bruker SMART 1000 CCD diffractometer. Absorption corrections for **1-Cl** were based on a ΔF method (program SHELXA[14]), otherwise on multiple scans (program SADABS of the Bruker system). Structure solution was by direct methods. The structures were refined anisotropically on F^2 using all reflections (program SHELXL-97[14]). The acidic H atom was located and refined for **1-Cl** and **1-Br** (although the latter displayed a very short N–H distance), but had to be geometrically positioned for **1-I**.[14] Other H atoms were included using a riding model.

Table 1 Details of secondary contacts N–H···X and X···X in the compounds **1-X**

Compound	Normalised[13] H···X/Å, [N–H···X/°]	% below vdW sum[a]	X···X/Å	% below vdW sum[a]
1-Cl	1.976 [175]	33	3.3352(14)	5
1-Br	2.174 [180]	29	3.3502(11)	9
1-I	2.579 [152]	19	3.5149(6)	11

[a] The following van der Waals radii were assumed: H 1.2, Cl 1.75, Br 1.85, I 1.98 Å.

Table 2 Details of non-classical hydrogen bonds C–H···X in the compounds **1-X**

Compound	C–H···X system	Normalised[13] H···X/Å	C–H···X/°	Operator for X
1-Cl	C2–H2···Cl2	2.57	152	
1-Br	C2–H2···Br2	2.79	149	
1-I	C2–H2···I2	2.95	164	$x, 0.5 - y, 0.5 + z$
1-I	C3–H3···I1	3.08	158	$1 - x, 1 - y, 1 - z$
1-I	C6–H6···I2	3.03	134	$1 + x, 0.5 - y, -0.5 + z$

1-Cl. $C_5H_5Cl_2N$, $M = 150.00$, monoclinic, $P2_1/m$, $a = 4.5137(12)$, $b = 7.925(2)$, $c = 8.898(2)$ Å, $\beta = 99.173(4)°$, $U = 314.24$ Å^3, $Z = 2$, μ(Mo Kα) = 0.91 mm^{-1}, $T = -100$ °C. Reflections: total 2109 to 2θ 56.7°, unique 829 (R_{int} 0.049). Final *wR*2 0.089, *R*1 0.041.

1-Br. $C_5H_5Br_2N$, $M = 238.92$, monoclinic, $P2_1/m$, $a = 4.4705(12)$, $b = 8.253(2)$, $c = 9.398(2)$ Å, $\beta = 98.945(6)°$, $U = 342.49$ Å^3, $Z = 2$, μ(Mo Kα) = 11.7 mm^{-1}, $T = -130$ °C. Reflections: total 3795 to 2θ 60°, unique 1057 (R_{int} 0.050). Final *wR*2 0.071, *R*1 0.030.

1-I. $C_5H_5NI_2$, $M = 332.90$, monoclinic, $P2_1/c$, $a = 4.5303(6)$, $b = 21.784(3)$, $c = 8.0761(12)$ Å, $\beta = 102.729(4)°$, $U = 777.42$ Å^3, $Z = 4$, μ(Mo Kα) = 8.00 mm^{-1}, $T = -130$ °C. Reflections: total 9068 to 2θ 60°, unique 2259 (R_{int} 0.061). Final *wR*2 0.068, *R*1 0.031.

CCDC reference number 440/144. See http://www.rsc.org/suppdata/nj/1999/1137/ for crystallographic files in .cif format.

Acknowledgements

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Notes and references

1 T. Steiner, *New J. Chem.*, 1998, **22**, 1099.
2 C. B. Aakeröy, T. A. Evans, K. R. Seddon and I. Pálinkó, *New J. Chem.*, 1999, **23**, 145; O. Navon, J. Bernstein and V. Khodorkhovsky, *Angew. Chem.*, 1997, **109**, 640.
3 P. G. Jones and B. Ahrens, *Chem. Commun.*, 1998, 2307.
4 J. P. M. Lommerse, A. J. Stone, R. Taylor and F. H. Allen, *J. Am. Chem. Soc.*, 1996, **118**, 3108.
5 V. R. Pedireddi, D. S. Reddy, B. S. Goud, D. C. Craig, A. D. Rae and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2353; G. R. Desiraju and R. Parthasarathy, *J. Am. Chem. Soc.*, 1989, **111**, 8725.
6 S. L. Price, A. J. Stone, J. Lucas, R. S. Rowland and A. Thornley, *J. Am. Chem. Soc.*, 1994, **116**, 4910.
7 A. Nangia and G. Desiraju, *Acta Crystallogr., Sect. A*, 1998, **54**, 934; J. A. R. P. Sarma and G. R. Desiraju, *Acc. Chem. Res.*, 1986, **19**, 222; C. B. Aakeröy, *Acta Crystallogr., Sect. B*, 1997, **53**, 569.
8 D. Braga and F. Grepioni, *New J. Chem.*, 1998, **22**, 1159.
9 S. M. Godfrey, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, C. A. McAuliffe, A. G. Mackie and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355; F. Ruthe, W.-W. du Mont and P. G. Jones, *Chem. Commun.*, 1997, 1947.
10 P. G. Jones and B. Ahrens, *New J. Chem.*, 1998, **22**, 1041; B. Ahrens, P. G. Jones and A. K. Fischer, *Eur. J. Inorg. Chem.*, 1999, 1103.
11 We have recently presented a brief summary of general trends in the structures of pyridines and pyridones: K. Wijaya, O. Moers, A. Blaschette and P. G. Jones, *Z. Naturforsch., Teil B*, 1999, **54**, 643.
12 B. Ahrens and P. G. Jones, *Acta Crystallogr., Sect. C*, 1999, **55**, 1308.
13 Following T. Steiner [*Acta Crystallogr., Sect. B*, 1998, **54**, 456] and others, we used idealised N–H and C–H distances of 1.009 and 1.080 Å, respectively, to calculate normalised hydrogen bonding parameters.
14 G. M. Sheldrick, *SHELXL-97, a Program for Refining Crystal Structure*, University of Göttingen, Germany, 1997.

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