

The Crystal Structures of Pyridinium Chloride Revisited: Evidence for Extensive C–H⋯Cl Hydrogen-Bond Interactions

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A reinvestigation of the previously determined structures of two polymorphs of pyridinium chloride shows that both polymorphs contain several aromatic C–H⋯Cl hydrogen-bond interactions. These hydrogen bonds, hitherto unrecognized, may play a significant structural role, both in solution and in the solid-state.

Introduction

Although there is now an increasing recognition of the existence of C–H⋯X (X = F, Cl, Br or I) hydrogen bonds in neutral organic molecules [1, 2], there have been surprisingly few studies of C–H⋯X[−] interactions in organic salts. We have recently demonstrated the existence of extensive hydrogen bonding between aromatic C–H groups and halide ions, C–H⋯X[−], within a series of imidazolium salts [3–5]. It is our contention that such hydrogen bonds are present in a wide range of compounds containing cationic heterocyclic aromatic systems. Although these interactions are, energetically, relatively weak, it is important to be aware of their existence, as they may have a deterministic part to play, both in solution (precipitation/nucleation processes), and in the solid state (geometry and packing of ions). In order to investigate this hypothesis, we decided to reexamine two recent crystal structures of two polymorphs of pyridinium chloride, in order to find possible crystallographic evidence for aromatic C–H⋯Cl hydrogen bonds. Neither of the original investigations explored the possibilities of such interactions being present.

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Data

The crystallographic data for two polymorphs of pyridinium chloride, monoclinic [6], and triclinic [7], were obtained from the Cambridge Crystallographic Database. As the original studies were carried out using single crystal X-ray diffraction, the accuracy of hydrogen-atom positions are affected by the intrinsic uncertainties associated with X-ray diffraction. In the original structure determination of the monoclinic polymorph [3], the hydrogen atoms were not located and, hence, for the purpose of this study, the hydrogen atoms of this polymorph were fixed in the plane of the ring, at $r(\text{C–H})$ 1.09 Å.

Analysis

The classification of C–H⋯X hydrogen bonds was based upon standard geometrical criteria [8]. A hydrogen bond is thought to exist if the distance between the proton and the acceptor atom is less than their combined van der Waals' radii. Furthermore, only contacts with $\sphericalangle \text{C–H}\cdots\text{Cl} > 100^\circ$ were considered. The following van der Waals' radii were used: C, 1.75; H, 1.20; N, 1.55; Cl, 1.75 Å [9]. However, since the hydrogen atom positions were calculated for the monoclinic structure, no H⋯Cl interactions larger than 2.8 Å were accepted, in order to allow for possible inaccuracies resulting from the theoretically evaluated hydrogen atom positions.

Results and Discussion

The result of the analysis of nearest-neighbour contacts for both polymorphs involving C–H hydrogen-bond donors is summarized in Table I. The relevant N–H⋯Cl interactions are listed in Table II.

The anion of the triclinic polymorph is involved in one N–H⋯Cl and two short C–H⋯Cl interactions, $r(\text{H}\cdots\text{Cl})$ 2.665 and 2.682 Å. This creates a pyramidal configuration around the chloride anion, Fig. 1, with $\sphericalangle(\text{H}\cdots\text{Cl}\cdots\text{H})$ angles in the range

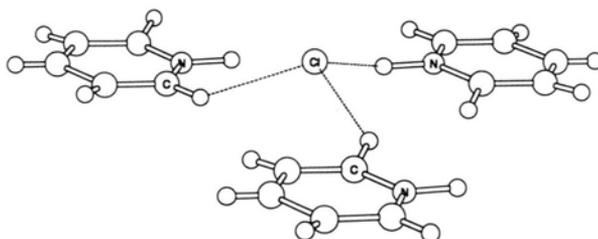


Fig. 1. The pyramidal arrangement of hydrogen-bonded pyridinium cations around the chloride anion in the triclinic polymorph of [pyH]Cl.



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Polymorph	<i>n</i>	<i>r</i> [C–H]/Å	Bond lengths and angles		
			<i>r</i> [H···X]/Å	<i>r</i> [C···X]/Å	∠(C–H···X)/°
Triclinic	2	0.98	2.665	3.492	142
	2	1.02	2.682	3.513	139
Monoclinic Cl(1)	2	1.09	2.53	3.49	146
	2	1.09	2.53	3.41	136
	3	1.09	2.542	3.55	154
Cl(2)	3	1.09	2.60	3.65	161
	4	1.09	2.57	3.63	164
	2	1.09	2.351	3.36	152
	3	1.09	2.63	3.545	141

Table I. Hydrogen bond interactions, C–H(*n*)···X, displayed by [pyH]Cl.

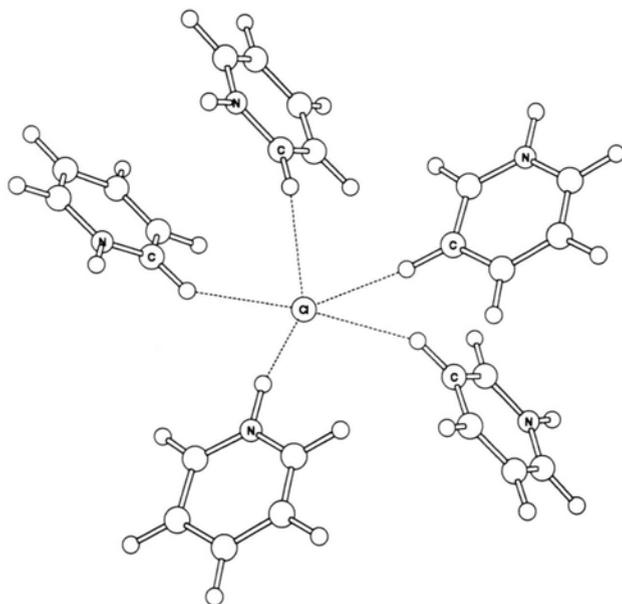
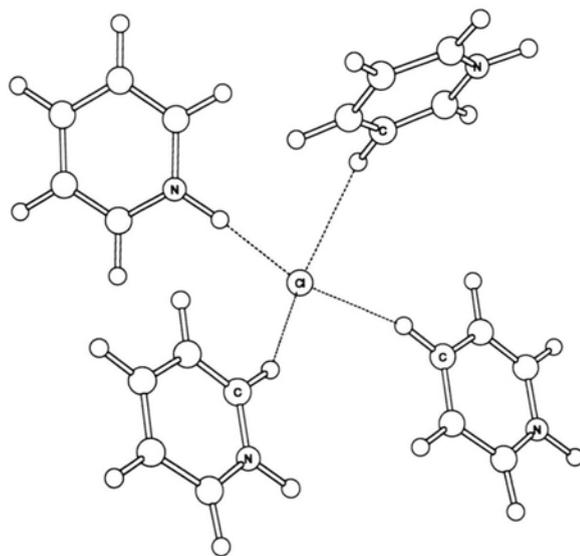
Polymorph	<i>r</i> [N–H]/Å	Bond lengths and angles		
		<i>r</i> [H···X]/Å	<i>r</i> [N···X]/Å	∠(N–H···X)
Triclinic	1.14	1.92	3.01	159
Monoclinic	1.09	2.037	3.110(8)	168
	1.09	1.99	3.068(7)	168

Table II. Hydrogen bond interactions, N–H···X, displayed by [pyH]Cl.

105–114°. Neither of the two CHCl angles is unreasonably narrow, at 142° and 139°.

Since the chloride ion is spherical, it would not be easily forced into specific sites within the crystal by steric considerations. Hence, it is very likely that the short C–H···Cl distances observed here are due to hydrogen bonds, mainly of electrostatic origin, and not a result of packing forces.

The two independent anions, Cl(1) and Cl(2), of the monoclinic polymorph are involved in four, and three, C–H···Cl distances, respectively, Fig. 2a–b, where *r*(H···Cl) is less than 2.8 Å. As for the triclinic polymorph, the relevant angles, ∠(CHCl), are in an acceptable range at 136–164°. It is important to notice that, within this crystal structure, a hydrogen atom at every position on a

Fig. 2a. Five hydrogen-bonded cations around the anion, Cl[−](1), in monoclinic [pyH]Cl.Fig. 2b. Four hydrogen-bonded cations around the anion, Cl[−](2), in monoclinic [pyH]Cl.

ring (*ortho*, *meta* and *para*), is involved, at least once, in a C–H...Cl hydrogen bond.

Any concern regarding the validity of using calculated hydrogen atom positions in the monoclinic polymorph can be dispelled by comparing the C...Cl distances between the two structural forms; triclinic, 3.49–3.51 Å; monoclinic, 3.41–3.65 Å. As they are similar, it is highly unlikely that the corresponding H...Cl distances will differ significantly.

The H...Cl interaction which fell closest outside the chosen cut-off distance (and, hence, was not included), 2.84 Å, displays a C...Cl distance of 3.844 Å, which falls significantly outside the range exhibited by the interactions that are considered to be true hydrogen bonds. Furthermore, since no correction has been applied to compensate for the shortening of C–H bond lengths generally observed with X-ray crystallographic techniques, the actual H...Cl bond lengths are likely to be shorter than those reported here.

A similar reinvestigation of several [pyH]·xHCl complexes (structures determined by Mootz and Hocken, [7]), also provide evidence for a number of C–H...Cl hydrogen bonds. The existence of aromatic C–H...X hydrogen bonds in ionic compounds containing charged heterocyclic systems is very likely to be a regularly occurring phenomenon which needs to be further analyzed in a systematic and stringent fashion in order to rationalize the structural behaviour displayed by such ions.

In addition, a preliminary study of the crystal structure of [py][HF] (determined by Boenigk and Mootz, [10]), shows that there are a number of short C–H...F interactions present, all of which can be classified as hydrogen bonds. This indicates that the aromatic system involved need not necessarily be cationic, and that hydrogen bonding is also possible in neutral heterocyclic compounds.

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