

Hydrogen-Bond Distances to Halide Ions in Organic and Organometallic Crystal Structures: Up-to-date Database Study

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Abstract

Geometrical data on hydrogen bonds to halide ions are compiled from the currently available crystal structures. Hydrogen bonds from 25 donor types to fluoride, chloride, bromide and iodide ions are considered. Compared with earlier compilations, the increased data volume allows a finer subdivision of O–H and N–H donors, and the donors C–H, S–H and P–H can be included. For a given donor type, the hydrogen-bond distance typically increases by over 0.5 Å from fluoride to chloride, 0.15 Å from chloride to bromide and 0.25 Å from bromide to iodide acceptors. The strongest of the C–H donors considered, chloroform, forms hydrogen bonds with chloride ions with an average H···Cl separation of only 2.39 Å and an average C···Cl separation of 3.42 Å. The lengthening of the N–H covalent bond in hydrogen bonds to chloride ions is quantified from neutron diffraction data.

1. Introduction

Many organic and organometallic crystal structures contain halide ions Hal^- . If the cation is capable of donating hydrogen bonds, $X\text{--H}\cdots\text{Hal}^-$ hydrogen bonds are normally formed and constitute one of the largest contributors to crystal stability. However, the focus of the structural studies is in almost all cases on the organic or organometallic cations and the halides are only considered as necessary counterions. Therefore, even in major texts on hydrogen bonding, $X\text{--H}\cdots\text{Hal}^-$ interactions are devoted only short sections and detailed reference data are not easy to find.

Since the volume of structural data has enormously increased in the last few years, it is of interest to compile geometrical data on $X\text{--H}\cdots\text{Hal}^-$ hydrogen bonds from the currently available crystal structures. Compared with earlier compilations (Pimentel & McClellan, 1971; Jeffrey & Saenger, 1991, and references therein), the data volume allows a finer subdivision of O–H and N–H hydrogen-bond donors and some new donor types can be included (C–H, S–H, $\text{P}^+\text{--H}$). Furthermore, a sufficient bulk of data on fluoride and iodide ions is now

available for a description of some statistical significance.

The main part of the study considers only roughly linear hydrogen bonds, whereas those with strongly bent geometries and minor components of bifurcated (three-centered) hydrogen bonds are excluded. Some information on hydrogen-bond angles and on multi-center hydrogen bonds is given in Appendix A. Some results on X–H bond lengthening are given in Appendix B.

2. Database analysis

The study is based on ordered and error-free organic and organometallic crystal structures with R values < 0.06 archived in the Cambridge Structural Database (CSD, June 1997 update with 167 797 entries; Allen & Kennard, 1993). $X\text{--H}$ vectors were normalized to bond distances of 0.983 Å for O–H (CSD default), 1.009 Å for N–H (CSD default), 1.083 Å for C–H (CSD default), 1.338 Å for S–H (the only neutron-determined S–H bond distance available; Takusagawa *et al.*, 1981) and 1.42 Å for P–H (gas phase value for PH_3 ; Callomon *et al.*, 1976). For justification of the normalization procedure, see Allen (1986) and Jeffrey & Saenger (1991).

Retrieved were crystal structures with $X\text{--H}\cdots Y$ contacts to halide ions with $H_{\text{norm}}\cdots Y$ distances < 3.0 Å and $X\text{--}H_{\text{norm}}\cdots Y$ angles $> 140^\circ$ (for I^- the distance limit was extended to 3.2 Å). The distance cutoff is selected such that the long-distance end of the distributions shown below is included. The angle cutoff is selected such that hydrogen bonds to nearest neighbors are included, whereas such to second- and third-nearest neighbors are typically excluded. Further discussion on the selected cutoff criteria is given in Appendix A.

Some of the distributions contain one or a few severe outliers. Since they do in some cases influence the mean values significantly, in particular for sets with small data quantities, all data with $H\cdots Y$ distances falling outside $\pm 4\sigma$ of the mean values of $H\cdots Y$ were excluded. For some general information on the 4σ cutoff strategy see Allen *et al.* (1992), where it is also used.

Table 1. $D-H \cdots X^-$ hydrogen bonds to halide ions with angles at $H > 140^\circ$

Given are: mean $H \cdots X^-$, mean $D \cdots X^-$ distances (Å) and number of hydrogen bonds [n]. Standard errors of the mean values are given in parentheses (except for $n < 4$, where this quantity is meaningless). Data for normalized H-atom positions.

| Acceptor | F^- | | | Cl^- | | | Br^- | | | I^- | | |
|------------------------------------|----------|----------|------|-----------|-----------|-------|-----------|-----------|-------|----------|----------|------|
| <i>O-H donors</i> | | | | | | | | | | | | |
| H-O-H | 1.71 (2) | 2.68 (2) | [14] | 2.237 (3) | 3.190 (3) | [799] | 2.400 (8) | 3.339 (7) | [148] | 2.66 (1) | 3.60 (1) | [47] |
| Si-O-H | — | — | — | 2.15 | 3.13 | [2] | — | — | — | — | — | — |
| Csp^3 -O-H | 1.58 | 2.57 | [1] | 2.150 (5) | 3.100 (4) | [299] | 2.310 (9) | 3.254 (8) | [90] | 2.55 (2) | 3.48 (1) | [27] |
| Ph-O-H | — | — | — | 2.109 (9) | 3.066 (8) | [76] | 2.31 (1) | 3.25 (1) | [52] | 2.54 (2) | 3.47 (1) | [8] |
| $=N-O-H$ | — | — | — | 2.07 (1) | 3.03 (1) | [34] | 2.10 | 3.08 | [1] | 2.46 | 3.43 | [2] |
| $O=C-O-H$ | 1.50 (1) | 2.47 (1) | [5] | 2.044 (8) | 2.997 (6) | [65] | 2.20 (2) | 3.14 (1) | [16] | 2.42 | 3.38 | [1] |
| As-O-H | — | — | — | 2.01 (2) | 2.95 (2) | [9] | — | — | — | — | — | — |
| P-O-H | — | — | — | 1.97 (2) | 2.94 (2) | [13] | — | — | — | — | — | — |
| N^+-O-H | — | — | — | 1.96 (2) | 2.93 (2) | [6] | — | — | — | — | — | — |
| $C=O^+-H$ | — | — | — | 1.91 (2) | 2.89 (1) | [4] | — | — | — | — | — | — |
| <i>N-H donors</i> | | | | | | | | | | | | |
| $-Nsp^2H_2$ | 1.74 | 2.73 | [2] | 2.350 (7) | 3.299 (6) | [314] | 2.52 (2) | 3.46 (1) | [77] | 2.79 (2) | 3.66 (1) | [30] |
| $-N^+H_3$ | 1.67 | 2.65 | [3] | 2.247 (5) | 3.207 (4) | [467] | 2.49 (2) | 3.44 (1) | [88] | 2.72 (2) | 3.68 (2) | [29] |
| $>Nsp^2-H$ | 1.64 (1) | 2.64 (1) | [5] | 2.221 (7) | 3.181 (6) | [256] | 2.39 (1) | 3.35 (1) | [40] | 2.69 (2) | 3.65 (2) | [20] |
| $>N^+H_2$ | 1.69 | 2.69 | [1] | 2.162 (5) | 3.130 (4) | [312] | 2.34 (1) | 3.295 (9) | [63] | 2.76 | 3.61 | [1] |
| $(CC)N^+-H$ | 1.56 | 2.55 | [2] | 2.126 (6) | 3.095 (5) | [174] | 2.29 (1) | 3.26 (1) | [39] | 2.63 | 3.58 | [3] |
| $(CCC)N^+-H$ | — | — | — | 2.079 (4) | 3.059 (3) | [232] | 2.29 (1) | 3.247 (7) | [90] | 2.54 (4) | 3.50 (3) | [5] |
| <i>C-H donors</i> | | | | | | | | | | | | |
| Cl_3C-H | — | — | — | 2.39 (3) | 3.42 (2) | [14] | 2.62 | 3.56 | [1] | 2.84 (2) | 3.86 (4) | [4] |
| Cl_2CH_2 | — | — | — | 2.53 (3) | 3.57 (3) | [17] | 2.73 | 3.74 | [2] | 2.85 (3) | 3.88 (2) | [12] |
| $C\equiv C-H$ | — | — | — | 2.56 (4) | 3.58 (4) | [8] | 2.70 (6) | 3.72 (5) | [5] | — | — | — |
| $(NN)Csp^2-H$ | — | — | — | 2.54 (2) | 3.57 (2) | [48] | 2.73 (4) | 3.72 (4) | [7] | 2.90 | 3.85 | [3] |
| $(NC)Csp^2-H$ | 2.18 | 3.21 | [1] | 2.64 (1) | 3.66 (1) | [110] | 2.74 (2) | 3.75 (2) | [56] | 2.99 (2) | 4.00 (2) | [44] |
| <i>Other donors</i> | | | | | | | | | | | | |
| F-H, Cl-H | — | — | — | — | — | — | — | — | — | — | — | — |
| S-H | — | — | — | 2.23 (7) | 3.54 (8) | [4] | 2.77 | 4.03 | [1] | — | — | — |
| P^+-H | — | — | — | 2.52 | 3.93 | [3] | 2.40 | 3.75 | [2] | — | — | — |
| <i>Sample standard deviations†</i> | | | | | | | | | | | | |
| for O/N-H | 0.06 | 0.04 | — | 0.08 | 0.07 | — | 0.10 | 0.08 | — | 0.10 | 0.08 | — |
| for C-H | — | — | — | 0.10 | 0.10 | — | 0.12 | 0.12 | — | 0.12 | 0.12 | — |

† Approximate values. Within the O-H, N-H and C-H categories given, sample standard deviations σ are similar for all donors; ~95% of the data are within $\pm 2\sigma$ of the given mean values.

3. Results

3.1. General

The mean $H \cdots Hal^-$ and $X \cdots Hal^-$ distances are compiled in Table 1 for roughly linear hydrogen bonds from the donors O-H, N-H, acidic C-H, S-H and P^+-H to the acceptors F^- , Cl^- , Br^- and I^- , respectively (angle at H $> 140^\circ$). The numbers of hydrogen bonds for each type are given in parentheses. Since in an $X-H \cdots Y$ hydrogen bond $H \cdots Y$ is the chemically more relevant parameter than $X \cdots Y$, further discussion is focussed mainly on the $H \cdots Hal^-$ distances.

The typical shape and location of the $H \cdots Hal^-$ distributions is shown for the example of the water donor in Fig. 1. The distributions are relatively narrow and have a well defined peak, allowing meaningful characterization even for moderate data quantities. The analogous distributions for O-H \cdots O and N-H \cdots O hydrogen bonds are significantly broader (and are also sample-dependent; Jeffrey & Saenger, 1991). Presum-

ably this is because the spherical and mobile halide ions can move more easily to positions of lowest energy than any other hydrogen-bonding moiety (Jeffrey & Saenger, 1991).

The shapes and widths of the $H \cdots Hal^-$ distributions are surprisingly similar for the different donor types. Typically, the standard deviations of the distributions are around $\sigma = 0.06$ Å for F^- , 0.08 Å for Cl^- and 0.10 Å for Br^- and I^- acceptors. This means that roughly 95% of the data fall into ranges of approximately ± 0.12 Å around the mean value for F^- , ± 0.16 Å for Cl^- and ± 0.20 Å for Br^- and I^- acceptors. Only for the weak S-H and C-H donors are the distributions broader with standard deviations larger by several 0.01 Å; unfortunately, this is difficult to characterize because of the small data numbers available for these donors.

The average $H \cdots Hal^-$ distances increase by ~ 0.15 Å from Cl^- to Br^- for most donor types and a further 0.25 Å from Br^- to I^- . This is only a moderate increase. The difference between the F^- and Cl^- acceptors is

much larger: typically, the mean $\text{H}\cdots\text{F}^-$ distance is shorter by 0.5 Å or more compared with the corresponding value for Cl^- .

3.2. O—H donors

The O—H donors can be subdivided into a considerable number of sets with significantly different mean $\text{H}\cdots\text{Hal}^-$ distances. In Table 1, these sets are listed in the sequence of decreasing average $\text{H}\cdots\text{Hal}^-$ separations. Clearly weakest is the water donor, C—OH is stronger, and strongest are O—H donors which are bonded to the atoms N, P and As. A positive charge on that atom further increases the O—H donor strength. This sequence is perfectly in line with the data given by Jeffrey & Saenger (1991). Unfortunately, no relevant crystal structures with O—O—H, S—O—H and Se—O—H donors could (yet) be found in the CSD.

The set of water molecules in Table 1 is composed of molecules that coordinate to metal atoms and those that

do not. With chloride acceptors, subsets were formed for water molecules bonded to transition metal atoms [$n = 59$, mean $\text{H}\cdots\text{Cl}^- = 2.182$ (8) Å], coordinated to group IA and IIA cations [$n = 38$, mean $\text{H}\cdots\text{Cl}^- = 2.24$ (1) Å] and without clear metal contacts [$n = 662$, mean $\text{H}\cdots\text{Cl}^- = 2.242$ (3) Å]. These are only minor variations in average $\text{H}\cdots\text{Cl}^-$ distances. For the other acceptors the corresponding differences were statistically insignificant.

The C—OH donors can be subdivided into carboxylic acids, phenols and hydroxyl groups, which have significantly different average hydrogen-bond distances to halides. For the example of the Cl^- acceptor this is illustrated in Fig. 2. A further subdivision of Csp^3 —OH into primary, secondary and tertiary hydroxyl groups did not result in markedly different average $\text{H}\cdots\text{Hal}^-$ distances [for Cl^- : mean $\text{H}\cdots\text{Cl}^- = 2.14$ (1), 2.16 (1) and 2.16 (2) Å for primary, secondary and tertiary hydroxyl groups, respectively, and $n = 137$, 136 and 26, respectively].

For the N—OH donors the data quantity allows a subdivision into the types $=\text{N}-\text{OH}$ and N^+-OH , with

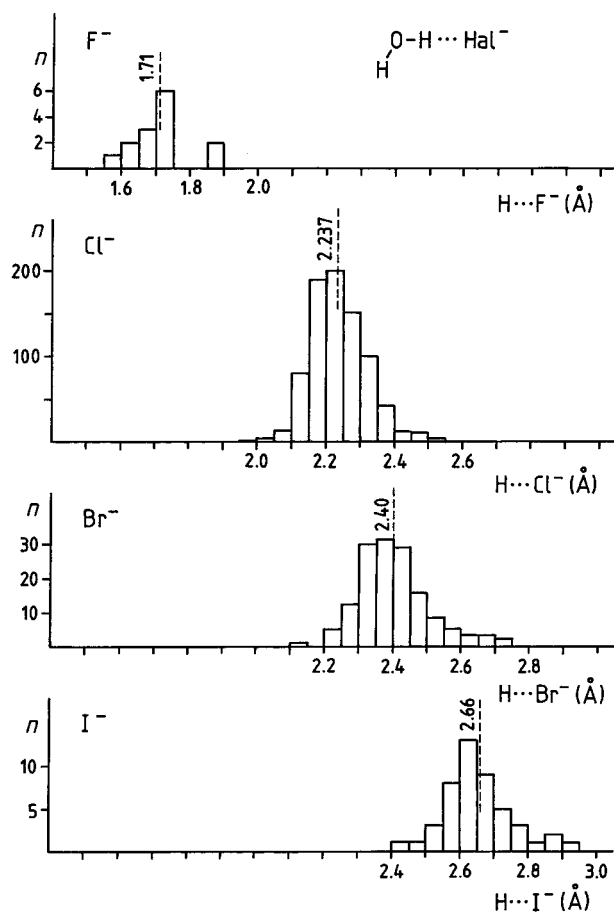


Fig. 1. Hydrogen bonds from water molecules to halide ions with angles at $\text{H} > 140^\circ$. Shown are distributions of $\text{H}\cdots\text{Hal}^-$ separations (for normalized H-atom positions). Mean values are indicated by dashed lines. Note that the n scales are different owing to the different data quantities.

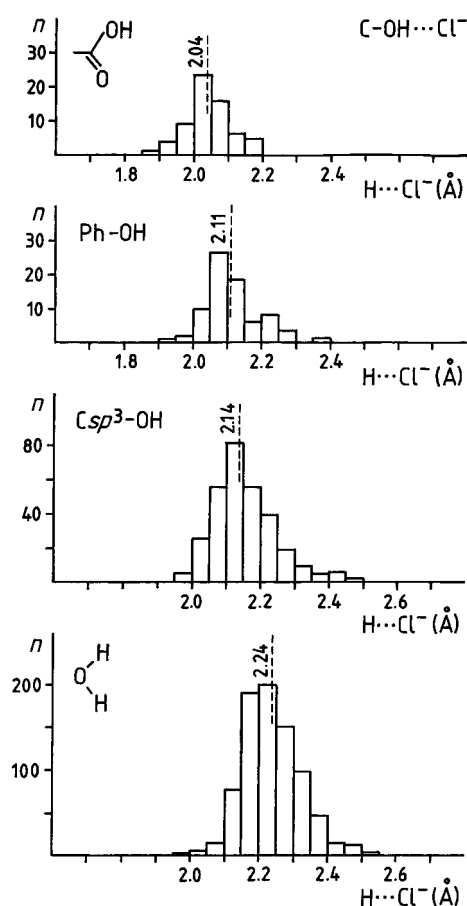


Fig. 2. Hydrogen bonds of three different C—OH types and water molecules to chloride ions (angles at $\text{H} > 140^\circ$). Shown are distributions of $\text{H}\cdots\text{Cl}^-$ separations (for normalized H-atom positions).

the latter having 0.11 Å shorter hydrogen-bond distances to Cl⁻ (Table 1). It is unfortunate that the data quantities do not reasonably allow such a subdivision for the strong As—OH and P—OH donors. For P—OH, there is only a single case of a relevant P⁺—OH group, which notably forms the shortest hydrogen bond to Cl⁻ in the whole data set: hydroxy triphenylphosphonium chloride, (Ph)₃P⁺—OH···Cl⁻, with H···Cl⁻ = 1.76 Å, O···Cl⁻ = 2.747 (2) Å and angle at H = 176.8° (for normalized H-atom position; Haupt *et al.*, 1977). The crystal structure of the arsenic analog (Ph)₃As⁺—OH···Cl⁻ contains two symmetry-independent formula units, one of which forms the second shortest hydrogen bond to Cl⁻ in the data set: H···Cl⁻ = 1.87 Å, O···Cl⁻ = 2.85 Å and angle at H = 171° (Kokorev *et al.*, 1987).

3.3. N—H donors

Different N—H donors have very different mean hydrogen-bond distances to halide ions. The far strongest donor is the tertiary ammonium group (CCC)N⁺H and the weakest in the data set is —Nsp²H₂. The ranking in Table 1 is very similar, as reported previously (Jeffrey & Saenger, 1991). The amines >Nsp³H and —Nsp³H₂ are certainly even weaker donors, but can of course not be crystallized as free bases from hydrohalogenic solutions and do not appear in Table 1.

It is of interest and maybe of some surprise that the primary ammonium group —N⁺H₃ forms on average longer hydrogen bonds to halide ions than the uncharged donor >Nsp²—H. For the latter a subset was formed with the particularly important peptide type N—H, *i.e.* the uncharged O=C—Nsp²(C)—H fragment. For chloride acceptors a mean H···Cl⁻ separation of 2.23 (1) Å was found (*n* = 78), which is not different from the >Nsp²—H set as a whole.

3.4. C—H donors

It has long been known from IR spectroscopic experiments that C—H groups can donate hydrogen bonds to halide anions (Allerhand & Schleyer, 1963). The situation, however, is complicated because the donor strength of C—H groups depends very strongly on their chemical nature (Desiraju, 1996; Steiner, 1997). Alkynes (C≡C—H) and C—H groups bonded to electronegative substituents (as in Cl₃CH, Cl₂CH₂ *etc.*) can donate hydrogen bonds of moderate strengths, whereas the less polarized C—H types are only very weak donors. In principle, one could analyze C—H···Hal⁻ contacts for the whole family of C—H groups, but this is problematic for statistical reasons: the stronger C—H donors exhibit H···Hal⁻ distributions of similar shape as for O/N—H donors (*i.e.* with a clear maximum, *cf.* Figs. 1 and 2) and can be analyzed in the same way as O—H and N—H. As the C—H polarization decreases, the H···Hal⁻ distributions gradually lose this

shape and turn to continuously increasing distributions. Such distributions are troublesome to analyze and certainly should not be directly compared with those for O/N—H. Therefore, only the strongest C—H donor types are included in this study, which have H···Hal⁻ distributions with a clear maximum (Fig. 3).

Of the C—H donors studied, Cl₃CH forms the shortest hydrogen bonds to the halide ions. For Cl₃CH the average H···Cl⁻ distance, 2.39 (3) Å, is only slightly longer than the 2.350 (7) Å for the weakest of the N—H donors, —Nsp²H₂ (Table 1), and only 0.15 Å longer than for water molecules.

3.5. S—H and P⁺—H donors

Only very few data are available for S—H and P—H donors (Table 1). For S—H, examples are found for uncharged S—H, such as in L-cysteine ethyl-ester hydrochloride (H···Cl⁻ = 2.42 Å, S···Cl⁻ = 3.74 Å; Görbitz, 1989) and also for S⁺—H, such as in dimethylsulfide.4HCl (H···Cl⁻ = 2.28 Å, S···Cl⁻ = 3.61 Å; Mootz & Deeg, 1992).

All P—H groups which were found forming short contacts to halide ions are of the type P⁺—H. The archetypical example is triphenylphosphonium bromide, (Ph)₃P⁺—H···Br⁻, with H···Br⁻ = 2.43 Å and P⁺···Br⁻ = 3.81 Å (for a normalized H-atom position; Bricklebank *et al.*, 1993).

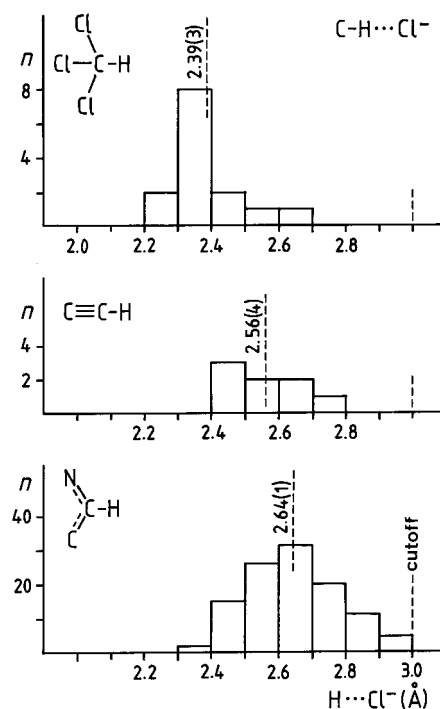


Fig. 3. Hydrogen bonds of three different C—H types to chloride ions (angles at H > 140°). Shown are distributions of H···Cl⁻ separations (for normalized H-atom positions).

Table 2. $F-H\cdots F^-$, $Cl-H\cdots Cl^-$ and $Br-H\cdots Br^-$ hydrogen bonds

Given are mean $X\cdots X^-$ distances (Å) and numbers of $X\cdots X^-$ contacts [n]. $m(X-H)\cdots X^-$ indicates that m $X-H$ molecules hydrogen bond to one X^- ion simultaneously.

| | $F-H\cdots F^-$ | $Cl-H\cdots Cl^-$ | $Br-H\cdots Br^-$ |
|--------------------|-----------------|-------------------|-------------------|
| $X-H\cdots X^-$ | 2.30 (4) [5] | 3.13 (2) [10] | 3.38 [1] |
| $2(X-H)\cdots X^-$ | 2.33 (1) [4] | 3.39 (3) [4] | |
| $3(X-H)\cdots X^-$ | 2.37 [2] | 3.37 (3) [3] | |
| $4(X-H)\cdots X^-$ | | 3.46 (1) [8] | |
| $5(X-H)\cdots X^-$ | | 3.520 (6) [5] | |

3.6. $Hal-H\cdots Hal^-$ hydrogen bonds

For $Hal-H\cdots Hal^-$ hydrogen bonds, well refined data are available in the CSD only for the cases $F-H\cdots F^-$ and $Cl-H\cdots Cl^-$, and a single example for $Br-H\cdots Br^-$, Table 2. Since for these, $X-H$ distances are not reasonably well known, only distances between non-H atoms are given in Table 2. For hydrogen bonds between one $F-H$ molecule and a fluoride ion, the so-called bifluoride ions $[F-H\cdots F]^-$, the mean $F\cdots F^-$ separation is 2.39 (4) Å, for bichloride ions $[Cl-H\cdots Cl]^-$ the mean $Cl\cdots Cl^-$ separation is 3.13 (2) Å, and for the single dibromide ion the $Br\cdots Br^-$ separation is 3.38 Å. Similar to $O/N-H\cdots Hal^-$ hydrogen bonds, the distance increases dramatically from fluoride to chloride and only slightly further to bromide.

Halide ions can accept hydrogen bonds from more than one hydrogen-halide molecule simultaneously, forming arrangements of the composition $[X(HX)_n]^-$ ('poly-hydrogenhalides'; Mootz & Hocken, 1989; Mootz & Deeg, 1992). The extreme case reported occurs in pyridinium chloride pentakis(hydrochloride), where the chloride ion is hexa-coordinated and accepts hydrogen bonds from five $Cl-H$ molecules and an additional one from the pyridinium N^+-H (Mootz & Hocken, 1989). In these adducts the hydrogen-bond distance systematically increases with increasing number n of participants (Table 2). This is, apparently, more pronounced for the HCl than for the HF species.

Although hetero-bihalide ions are known to exist (Pimentel & McClellan, 1971), no sufficiently convincing case is as yet contained in the CSD to be included in Table 2.

4. Summary

Hydrogen-bond lengths of 25 different donor types to halide ions have been analyzed statistically. The large volume of crystallographic data available allows a fine subdivision of $O-H$, $N-H$ and $C-H$ donors. The data volume is far largest for chloride acceptors, but also the number of crystal structures containing bromide and iodide ions has become appreciable in the last few years. Even for hydrogen bonds donated to fluoride ions, a noticeable bulk of structural data is now available.

The trends of mean hydrogen-bond distances for different types of $O-H$ and $N-H$ groups confirm earlier studies based on much smaller data quantities (Jeffrey & Saenger, 1991) and are now quantified with much better statistical significance. Related trends are also established for different $C-H$ donors. The matrix of donor-acceptor combinations (Table 1) still contains some empty fields and some of the rarer donor types are missing completely; it can be hoped that this will improve in the future.

Hydrogen bonds from $C-H$ groups to halide ions are only rarely discussed in original structure publications (such as those by Davidson *et al.*, 1995; Steiner, 1996; Aakeröy & Seddon, 1993). A look at Table 1 shows that at least for the more acidic $C-H$ types this is not justified. For the less acidic $C-H$ types, in particular for methyl groups, no corresponding statement based on $H\cdots Hal^-$ distributions is made here.

APPENDIX A

Directionality characteristics of $X-H\cdots Hal^-$ hydrogen bonds

Before performing the analyses of mean hydrogen-bond distances shown in this paper, it has been necessary to investigate the distance and directionality characteristics of the interactions under study. This is because the automated data evaluation procedures used require geometrical definitions of hydrogen bonds and these definitions have to be set up in an initial stage.

Distance and directionality characteristics of $X-H\cdots Y$ hydrogen bonds can be conveniently studied in scatterplots of hydrogen-bond angles *versus* the $H\cdots Y$ and/or $X\cdots Y$ distances (Olovsson & Jönsson, 1976). With such scatterplots it can be very useful to extend the angle and distance limits far beyond the hydrogen-bonding region, such as to $H\cdots Y$ distances up to 4 or 5 Å, and to angles 0–180° (Steiner & Saenger, 1992). If all arrangements are included which fall into these extended limits, no matter if they represent hydrogen bonds or not, it can be easily seen if there are more or less well defined geometrical regions of hydrogen bonds or if there is a continuous transition from hydrogen bonds to nonbonding and to random arrangements. Such extended scatterplots were produced for a number of the hydrogen-bond types in Table 1. Since they provide some insights into hydrogen bonding to halide ions as such, three of them are shown below (for chloride acceptors). Owing to the nature of scatterplots, relatively large data quantities are required.

For hydroxyl donors, the simple and clear picture shown in Fig. 4(a) is obtained. There is a well-defined cluster of hydrogen bonds with $H\cdots Cl^-$ distances between ~2.0 and 2.4 Å, and angles at H larger than ~140°. The region to the right of this cluster is almost unpopulated, *i.e.* there are almost no elongated but

linear $Csp^3-OH \cdots Cl^-$ hydrogen bonds. For longer distances, but bent angles, the cluster runs into a weakly populated region representing minor components of

three-center hydrogen bonds (see inset of Fig. 4a). The low population density of this region shows that three-center hydrogen bonds are rare for hydroxyl donors and chloride acceptors (it is noted that three-center hydrogen bonding with chloride acceptors as such is firmly established from neutron diffraction data: Jeffrey & Saenger, 1991). At long distances there is a region of random scatter, which is separate from the hydrogen-bond region and corresponds to hydroxyl groups and chloride ions forming no directional interaction.

For water donors the situation is more complex (Fig. 4b). The cluster of 'normal' hydrogen bonds is very similar to those for hydroxyl donors, only shifted to slightly longer distances (by *ca.* 0.09 Å, Table 1). The region of minor components of three-center hydrogen bonds is more densely populated than in Fig. 4(a), and merges with the region of random scatter and with a new cluster that appears at angles $< 90^\circ$. This new cluster represents the second H atom of hydrogen-bonding water molecules, *i.e.* the H atom that is turned away from the chloride acceptor (see inset). The continuous merging of all regions in Fig. 4(b) resembles the appearance of the related scatterplot for $O-H \cdots O$ hydrogen bonds in carbohydrates (Steiner & Saenger, 1992).

For the primary ammonium donor (Fig. 4c) the picture is related to the water donor, but the cluster of linear hydrogen bonds is more diffuse, and also the other regions are less distinct. Three-center hydrogen bonding is a frequently occurring phenomenon for this donor.

When comparing Figs. 4(a), 4(b) and 4(c), it becomes clear that defining geometric hydrogen-bond criteria is problematic. One question is whether one should consider or disconsider minor components of three-center hydrogen bonds. In principle, these are relevant interactions that must not simply be ignored. It is obvious, however, that they have different geometries (in particular, longer distances) than hydrogen bonds to nearest-neighbor acceptors. Since they occur with different frequencies for different donor types, and samples cannot be compared if they contain different constituents in different ratios, it seems best to regard for each donor only the close to linear hydrogen bonds (irrespective of if there are additional bent hydrogens or not). This means that all data obtained are then valid *only* for roughly linear hydrogen bonds.

In practice this means that from pictures such as Figs. 4(a)–4(c), the prominent cluster at short distances and linear angles is cut out and used for analysis, whereas the rest of the figure is ignored. To obtain data that can be compared for different donors the same criteria must obviously be used for them all. As the clusters are not really equally shaped for all donor types (they become more diffuse as the donors become weaker), this requires compromises. As the focus of the study is on classifying the stronger donor types, criteria are adapted

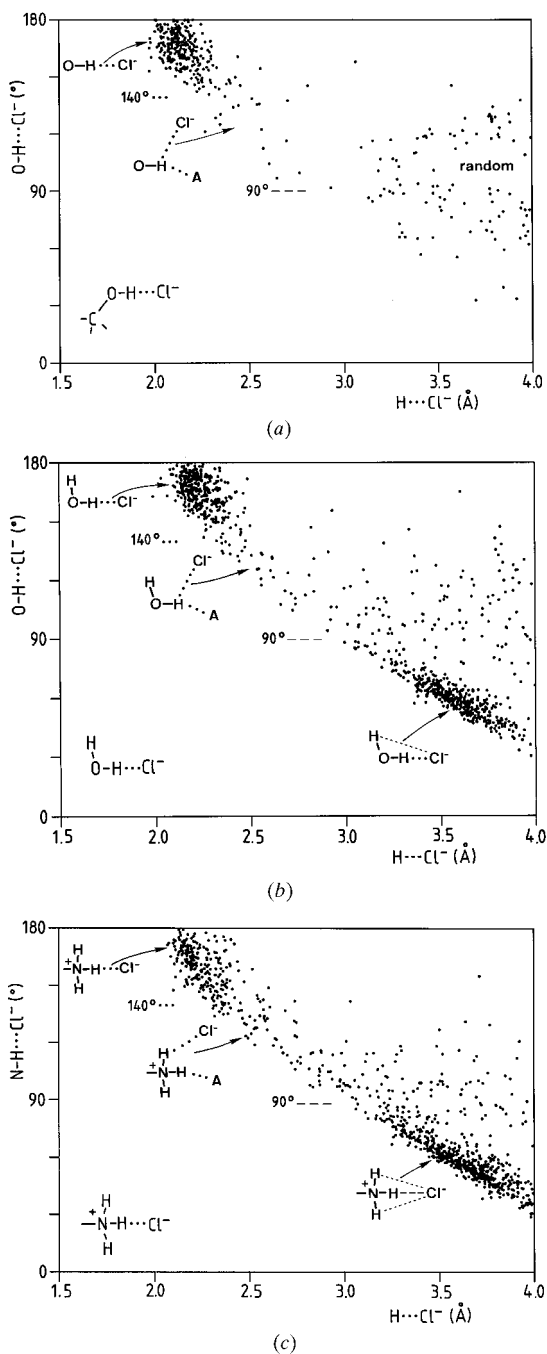


Fig. 4. Scatterplots of $X-H \cdots Cl^-$ angles against $H \cdots Cl^-$ distances (for normalized H-atom positions). Angles are shown in the full range $0-180^\circ$ and distances in the range $1.5-4.0$ Å, irrespective of whether the corresponding arrangement represents a hydrogen bond or not. The angle cutoff used in the main part of the study (140°) is indicated by a dashed line. (a) Hydroxyl donors; (b) water donors; (c) primary ammonium donors.

Table 3. Lengthening of the N—H covalent bond in N—H···Cl[−] hydrogen bonds: neutron diffraction data for —NH₃⁺ and —Nsp²H₂ donors

| H···Cl [−] range (Å) | <i>n</i> | Mean H···Cl [−] (Å) | Mean N—H (Å) |
|---|----------|------------------------------|--------------|
| —NH ₃ ⁺ donors | | | |
| Whole range | 23 | 2.22 (2) | 1.032 (2) |
| —Nsp ² H ₂ donors | | | |
| Whole range | 6 | 2.32 (3) | 1.021 (2) |
| —NH ₃ ⁺ and —Nsp ² H ₂ donors | | | |
| 2.10–2.20 | 12 | 2.14 (1) | 1.039 (2) |
| 2.20–2.30 | 10 | 2.264 (4) | 1.027 (2) |
| 2.30–2.40 | 5 | 2.34 (1) | 1.020 (4) |
| 2.40–2.50 | 2 | 2.46 | 1.015 |
| Whole range | 29 | 2.24 (2) | 1.030 (2) |

mainly to fit O—H donors such as those shown in Figs. 4(a) and 4(b). In this sense a cutoff angle of 140° is used for defining 'roughly linear' hydrogen bonds for all donor types, although this may be somewhat restrictive for the weak types of N—H donors and, in particular, for C—H donors (Fig. 3). The distance cutoff is less problematic because there are almost no long linear hydrogen bonds. The distance limit of 3.0 Å for H···Hal[−] (3.2 Å for H···I[−]) could also have been selected more restrictively.

APPENDIX B

Lengthening of the covalent N—H bond in N—H···Cl[−] hydrogen bonds

In X—H···Y hydrogen bonds the covalent X—H bond is lengthened due to the H···Y interaction. Correlations of X—H and H···Y distances can be derived reliably only from neutron diffraction data (see *e.g.* Jeffrey & Saenger, 1991). Such correlations have been published for several hydrogen-bond types: O—H···O (Olovsson & Jönsson, 1976; Chiari & Ferraris, 1982; Steiner & Saenger, 1994), N—H···O (Olovsson & Jönsson, 1976), N—H···N (Steiner, 1995a), C—H···O (Steiner, 1995b). For hydrogen bonds to halide ions, related correlations have not yet been established. The current study is taken as an occasion to look into this matter.

For the hydrogen-bond types in Table 1, quantities of accurate neutron diffraction data are inconsiderable for all types except O—H···Cl[−] and N—H···Cl[−]. The data for O—H···Cl[−] interactions is dominated by structures with water donors, and of these, so many have such unrealistically short O_w—H bonds that the sample is more or less unsuitable for quantitative analysis. Fortunately, at least the neutron diffraction data for N—H···Cl[−] hydrogen bonds is sufficient in quantity and quality for further analysis.

Ordered and error-free neutron crystal structures with *R* < 0.07 containing N—H···Cl[−] interactions with H···Cl[−] distances < 2.6 Å were extracted from the CSD. N—H bonds with standard deviations ≥ 0.01 Å were

excluded. Only for the donor types —NH₃⁺ and —Nsp²H₂ were appreciable data quantities obtained (23 and 6 hydrogen bonds to Cl[−], respectively). For these, the correlation plot of N—H against H···Cl[−] is shown in Fig. 5 and numerical data are given in Table 3. It is obvious that the N—H bond length is actually correlated with the H···Cl[−] separation.

It appears from Fig. 5 that the data for the two donor types populate different H···Cl[−] regions, but are still scattered around a common regression function. The primary ammonium donors form on average shorter hydrogen bonds [mean H···Cl[−] = 2.22 (2) Å] than the weaker —Nsp²H₂ donors [mean H···Cl[−] = 2.32 (2) Å] and they have on average longer N—H bonds [1.032 (2) Å compared with 1.021 (1) Å]. However, it can be seen in the long-distance region of Fig. 5 that if an ammonium N—H bond forms only a long hydrogen bond, it has the same N—H bond length as —Nsp²H₂. This means that the typically longer N—H bonds of the ammonium group are *not* an inherent property of the group, but are just a consequence of the shorter hydrogen bonds formed by the stronger donor. This

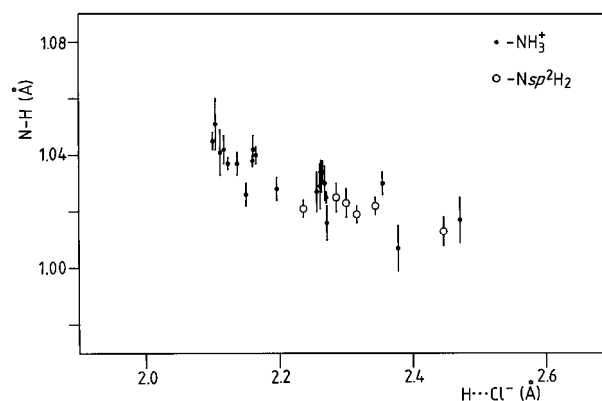


Fig. 5. Lengthening of the covalent N—H bond in N—H···Cl[−] hydrogen bonds. Shown is neutron diffraction data with standard deviations of N—H bond lengths < 0.01 Å. Standard deviations of N—H are indicated by vertical bars. Owing to the different scale on the horizontal axis, standard deviations of H···Cl[−] appear much smaller and are therefore not indicated.

observation is exactly in line with studies on O—H···O and N—H···N hydrogen bonds, where it is also found that donors of different strengths populate different regions of common regression functions (Steiner & Saenger, 1994; Steiner, 1995a; Bertolasi *et al.*, 1996).

Note added in proof. After submission of this paper a study was published which is related to the results in §3.1, §3.2 and §3.3: Mascial, M. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 1999–2001.

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