NJC Letter

Fluoride ligands exhibit marked departures from the hydrogen bond acceptor behavior of their heavier halogen congeners†

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Received (in New Haven, USA) 5th August 1999

Much shorter hydrogen bonds with unexpected directional properties are formed by fluoride ligands in comparison to their heavier halogen congeners (X = Cl, Br, I). *Ab initio* calculations elucidate the underlying electronic origin of this geometric behavior. The viability of hydrogen bonding is clearly established for all donor–acceptor combinations, D–H···X–M (D = C, N, O; X = F, Cl, Br, I).

The hydrogen bond acceptor capability of halogens has attracted attention in fields as diverse as supramolecular chemistry,[1–3] biochemistry,[4] coordination and organometallic chemistry.[5] Recent studies have examined both the ability[1] and inability[4] of specific halogens to form strong hydrogen bonds depending upon the coordination environment of the halogen. Interest in organometallic chemistry has centered upon the protonation and protonolysis of metal halides.[5b,e] Halide ions and halogen-containing ions have been shown to exhibit a templating effect *via* hydrogen bonding to form cavities[2a,b] or channels[2c] in supramolecular assemblies. Hydrogen bonding has been used strategically in the design of receptors for halide ions,[2d] but perhaps most pertinent to the present work are the possibilities of using metal halides in the design of receptors for molecules that can serve as proton donors.[5a] This idea is reinforced by recent work demonstrating the potential utility of D–H···Cl–M hydrogen bonds (D = N, O; M = transition metal) in the self-assembly of tape and sheet structures.[3]

Previously we have shown that metal-bound chlorine is a very good hydrogen bond acceptor in contrast to its organochlorine counterpart.[1a] Comparisons have also been made between the hydrogen bond acceptor capability of the halide ions.[1b,c] Here we focus specifically on intermolecular hydrogen bonds involving terminal, metal-bound halogens and show that the acceptor groups involving fluorine (F–M) exhibit substantially different behavior from that of their heavier halogen counterparts. Much shorter hydrogen bonds are formed and quite different directionality is exhibited by the F–M acceptors, *viz.* angles M–F···H ≫ M–X···H (X = Cl, Br, I). This can be rationalized by consideration of the electronic structure of metal halides as it manifests itself in the electrostatic potential around the halogen.

To compare the relative hydrogen bond acceptor capabilities of the halogens the Cambridge Structural Database[6] has been used to examine the geometries of D–H···X–M hydrogen bonds[7] (D = C, N, O; X = F, Cl, Br, I). The hydrogen bond distances for all donor–acceptor pairs have been put on a common scale by use of the normalized distance function $R_{HX} = d(H\cdots X)/(r_H + r_X)$.[7] This allows a qualitative assessment of the relative strengths[8] of the different hydrogen bond types as summarized in Table 1 (and SUP 57619). The ability to form viable hydrogen bonds is indicated for *all* hydrogen bond donor (D–H) and acceptor (M–X) combinations. The shortest mean R_{HX} arises for the combination of the most polar bonds in the donor and acceptor components, *i.e.* O–H···F–M; the longest R_{HX} arises for C–H···I–M. Hydrogen bonds involving metal fluorides are *markedly* shorter than those of their heavier halogen congeners, for all donor groups considered. The appropriateness of a hydrogen bonding description is confirmed by the clear preference for D–H···X angles approaching 180° at shorter R_{HX} separations for *all donor–acceptor combinations.* Fig. 1 illustrates these observations for the case of N–H···X–M hydrogen bonds. Spatially normalized distance *vs.* angle plots are used to avoid the biases inherent in simple distance *vs.* angle plots.[9] The preference for linearity at short H···X separations is most pronounced for acceptors M–F > M–Cl > M–Br > M–I (Fig. 1) and donors O–H > N–H > C–H (SUP 57619 Fig. S1).

The most remarkable aspect of the behavior of transition metal fluoride acceptors is in the directionality of approach of the donor groups to the fluoride. Considering N–H···X–M hydrogen bonds, for example, H···X–M angles in the range 90–130° account for 66.0% (Cl), 62.3% (Br), and 75.4% (I) of observations, but only 32.4% where X = F.[10] Rather, for N–H···F–M 64.1% of the hydrogen bonds adopt larger H···F–M angles in the range 130–160°. These angular preferences are illustrated in the histograms of Fig. 2; more detailed spatially normalized distance *vs.* angle plots are also provided in SUP 57619 (Fig. S2). Qualitatively similar trends in H···X–M angles are seen for O–H···X–M hydrogen bonds, whereas C–H···X–M hydrogen bonds exhibit no discernible directional preference for approach of the C–H donor to the X–M acceptor.

Table 1 Mean R_{HX} distances from H···X contacts[7] with $(R_{HX})^3 \leqslant 1.150$ (*ca.* $R_{HX} < 1.048$)

	Mean normalized distance, R_{HX} (number of observations)		
	C–H···X–M	N–H···X–M	O–H···X–M
X = F	0.943 (374)	0.776 (73)	0.703 (37)
X = Cl	0.975 (7943)	0.853 (1341)	0.799 (416)
X = Br	0.982 (3269)	0.879 (205)	0.820 (30)
X = I	0.997 (2429)	0.923 (83)	0.868 (8)

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† *Supplementary material available:* model geometries used in *ab initio* calculations; $(R_{HX})^3$ *vs.* $1 - \cos(180 - (D\text{–}H\cdots X))$ plots; $(R_{HX})^3$ *vs.* $1 - \cos(180 - H\cdots X\text{–}M)$ plots; calculated electrostatic potentials. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/965/, otherwise available from BLDSC (No. SUP 57619, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

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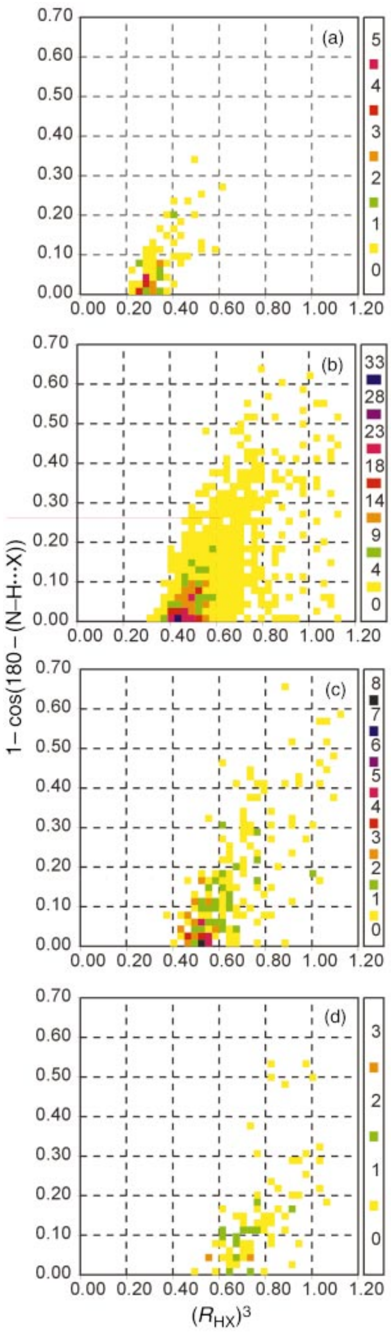


Fig. 1 Spatially normalized plots[9] of hydrogen bond distances (represented as $(R_{HX})^3$) against angle at the hydrogen {represented as 1 − cos(180 − (N–H···X))} for hydrogen bonded N–H···X–M, X = F (a), Cl (b), Br (c), I (d).

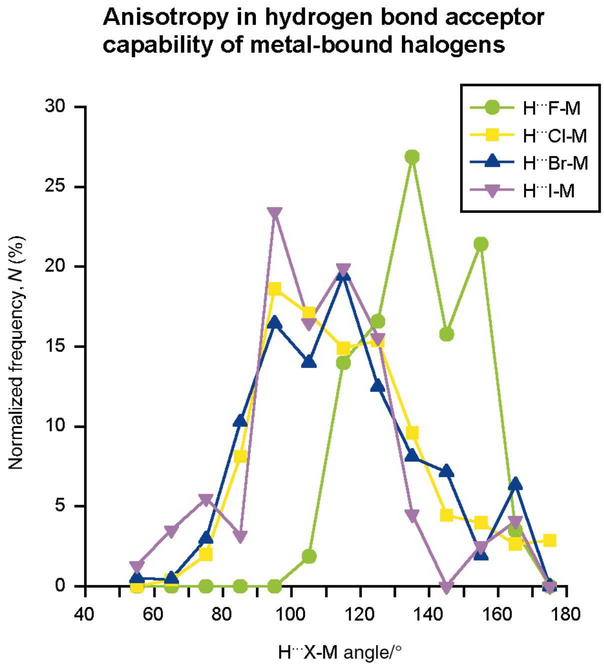


Fig. 2 Normalized distribution of H···X–M angles[10] expressed as percentages of total number of observed N–H···X–M hydrogen bonds.

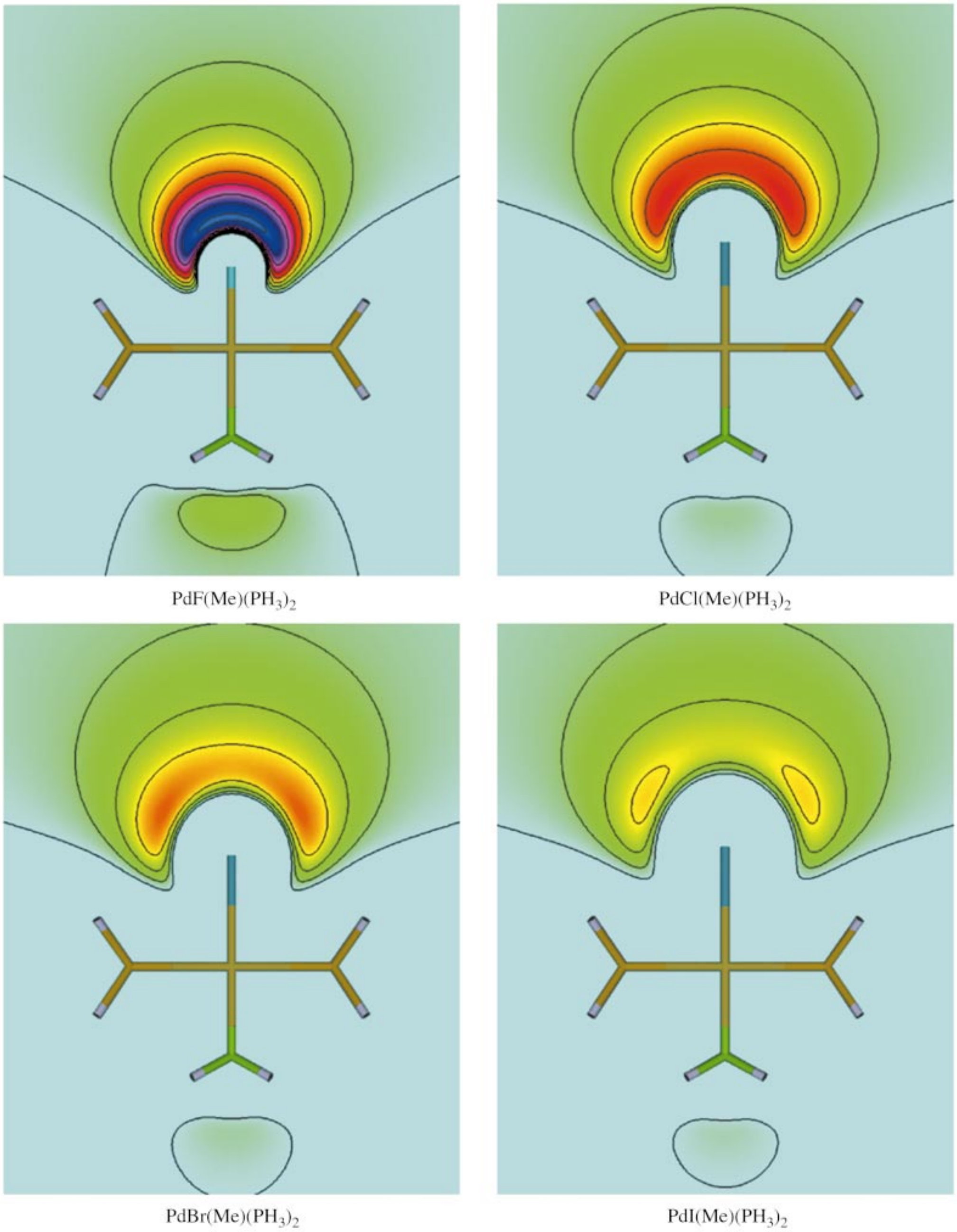
The difference between the angular behavior of the fluoride acceptors and those of the other halogens could in principle be electronic in origin or merely the effect of greater steric repulsions due to *cis* ligands being in closer proximity to the smaller fluoride ligand. As the electrostatic attraction between donors and acceptors is typically the largest contributor to hydrogen bond energies, the possible electronic origin of the geometric trend was investigated by calculating the electrostatic potentials of model compounds *trans*-$PdX(Me)(PH_3)_2$ using *ab initio* methods.[11] These potentials are shown in Fig. 3. The angle subtended at the halogens by the points of potential energy minimum should indicate the preferred angle of approach of a hydrogen bond donor assuming the electrostatic contribution to the hydrogen bond energy is the dominant one.[5c] The angles are in excellent agreement with the database results. (Compare Table 2 with Fig. 3.) The depths of the potential minima (Table 2) also illustrate why the fluoride acceptors form much stronger hydrogen bonds than the other halogens.

The calculations clearly support an electronic rather than steric rationale for the observed geometries. Examination of the molecular orbitals for the model systems indicates the source of angular discrimination at the halogen. Involvement of the halogen p-orbitals in M–X σ-bonding will reduce the

Table 2 Data for calculated electrostatic potential in the vicinity of the halogen for *trans*-$PdX(Me)(PH_3)_2$ model systems

	In molecular plane (*cf.* Fig. 3)			In orthogonal plane through C–Pd–X (*cf.* Fig. S3)		
	Potential minimum/ kcal mol^{-1}	$R(X\cdots min)^a$	Pd–X···min/° [b]	Potential minimum/ kcal mol^{-1}	$R(X\cdots min)^a$	Pd–X···min/°
X = F	−81.3	0.77	162 (140–180)[c]	−82.9	0.77	137 (120–155)[c]
X = Cl	−47.6	0.94	124	−51.7	0.94	110
X = Br	−39.9	1.02	124	−44.3	1.03	109
X = I	−32.3	1.09	122	−35.5	1.11	106

[a] $R(X\cdots min) = d(X\cdots min)/r_{vdW}(X)$ (*i.e.* distance of potential minimum from halogen nucleus as a fraction of halogen van der Waals radius). [b] The larger angles in the molecular plane arise from overlap of the positive potential of the PH_3 ligands *cis* to the halogen with the negative potential generated by the halogen. [c] Potential well is flat-bottomed, and varies by less than 1 kcal mol^{-1} over this angular range.



PdF(Me)(PH$_3$)$_2$ PdCl(Me)(PH$_3$)$_2$

PdBr(Me)(PH$_3$)$_2$ PdI(Me)(PH$_3$)$_2$

Fig. 3 Calculated electrostatic potential in the metal coordination plane of the model compounds *trans*-PdX(Me)(PH$_3$)$_2$; X = F, Cl, Br, I. Electrostatic potential represented with color gradation and contoured at 10 kcal mol^{-1} intervals. Only negative and zero contours shown; atoms that lie below the coordination plane are not shown.

p-orbital contribution to the lone pair *trans* to the metal,[12] depleting the charge density in this direction relative to that of a spherical halide ion[13] and favoring approaches towards the p-orbital lone-pairs orthogonal to the M–X bond. This effect is much more pronounced for X = Cl, Br, and I than for X = F, due to the smaller p-orbital contribution to M–F bonding.

In summary, the overall order of hydrogen bond strength is D–H···F–M $\gg$ D–H···Cl–M $\geqslant$ D–H···Br–M > D–H···I–M, as implied by the H···X distance distributions and the magnitude of the halogen potential minima from the model complex calculations. The observations agree remarkably well with the trend in intramolecular N–H···X–Ir bond strengths determined experimentally using NMR methods by Crabtree, Eisenstein and coworkers for *mer*-[IrH$_2$X(pyNH$_2$)(PPh$_3$)$_2$] (*viz*., X = F, 5.2; X = Cl, 2.1; X = Br, 1.8; X = 1, <1.3 kcal mol^{-1}).[14] The marked difference in angular preference for the approach of hydrogen bond donors to the terminal halogens can be attributed to the greater contribution to M–X bonding of the halogen axial p-orbital exhibited by the heavier halogens.

We are presently completing similar studies of D–H···X–C and D–H···X$^-$ hydrogen bonds, as well as comparing simple and bifurcated hydrogen bonds, in an effort to provide a comprehensive analysis of the hydrogen bond acceptor behavior of halogens.

Acknowledgements

L.B. and E.A.B. are grateful to Karl Kedrovsky for programming assistance, and the University of Missouri-St. Louis for financial support. L.B. and P.S. thank NATO for support of their collaboration (grant CRG-920164).

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8 (*a*) While inferring a correlation between hydrogen bond length and strength is inappropriate for individual crystal structures, large populations of geometric data allow a qualitative assessment of bond strengths to be made. It is recognized that the relative values of mean normalized distances will be affected by the proportion of neutral and charge-assisted (*i.e.*, interionic) hydrogen bonds in each sample population.[8b] However, it is anticipated that these effects will be similar for each donor–acceptor pair studied. (*b*) D. Braga and F. Grepioni, *New. J. Chem.*, 1998, **22**, 1159.

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10 Histograms of the H···X–M angles were plotted in 10° intervals and corrected for the geometric error in the frequency of observations that naturally arises in sampling such angle data from crystal structures, which depends upon the sine of the angle; see J. Kroon and J. A. Kanters, *Nature* (*London*), 1974, **248**, 667.

11 (*a*) Electrostatic potentials were calculated at the Hartree–Fock level using the GAMESS-UK[11b] package, employing a CEP (compact effective potential) basis set for Pd[11c,e] and pVTZ (polarized valence triple-zeta)[11d,e] basis sets on all other atoms. Details of the model geometries used are provided in SUP 57619; (*b*) GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel and P. Sherwood, with contributions from R. D. Amos, R. J. Buenker, H. J. J. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R. J. Harrison, A. P. Rendell, V. R. Saunders, A. J. Stone and A. H. de Vries. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendoloski, NRCC Software Catalog, 1980, vol. 1, Program No. QG01 (GAMESS), Lawrence Berkely Laboratory, University of California, Berkeley; (*c*) W. J. Stevens, M. Krauss, H. Basch and P. G. Jasien, *Can. J. Chem.*, 1992, **70**, 612; (*d*) A. J. Sadlej, *Theor. Chim. Acta*, 1992, **81**, 45 and refs. therein; (*e*) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

12 This explanation is related to a previously proposed orbital model for N–H···Cl–M hydrogen bonds that considered the relative basicities of sp-hydrid orbital and p-orbital lone pairs on the chloride ligands, though trends with respect to the series of halogens were not considered. See: G. P. A. Yap, A. L. Rheingold, P. Das and R. H. Crabtree, *Inorg. Chem.*, 1995, **34**, 3474.

13 The depopulation (electrons) of the halogen p-orbital *trans* to the metal relative to the average of the two orthogonal halogen p-orbitals is calculated to be: F (0.093 e), Cl (0.226 e), Br (0.270 e), I(0.305 e) using the Lowdin population analysis.[11b]

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