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Partial transfer of bridging atom in halogen-bonded complexes

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ABSTRACT

Ab initio calculations assess the displacement of the bridging atom within halogen-bonded complexes and comparison is made with proton transfers within H-bonds. Lewis acid units considered include C—X, F—X, N—X, and O—X bonds within the context of F_3CX, FX, F_2NX, FOX, and F_2NOX where X = Cl, Br, and I, and H in the corresponding H-bonded complexes. NMe_3 and NCl_3. were both taken as bases due to their widely differing nucleophilicity. The degree of transfer is small even when a strong acid is combined with a strong base. This reluctance to transfer is due in part to the fact that such a transfer would lead to a high-energy ion pair. Cl shifts its position the most within most of these complexes, followed by Br and then I; the proton is more resistant to transfer.

1. Introduction

There are many diverse aspects of the H-bond that have generated a good deal of study over the years [1–4]. The H-bond is a directional phenomenon in that the proton prefers a location close to the axis between the proton donor and acceptor atoms. Angular deviations from this configuration are energetically costly, and have direct implications on the properties of the bond. The effect of H-bond formation upon the IR and NMR spectra of the constituent subunits has served as a crucial signpost of the presence of H-bonds, and their strength. The dynamic formation, breakage, and rescrambling of H-bonds is an integral component of solvation.

One of the more interesting issues concerned with H-bond formation is the position adopted by the bridging proton. It is almost a universal observation that the A-H covalent bond is stretched upon complexation with a base B to form the AH···B H-bond (with some exceptions that have come to be called blue-shifting H-bonds [5–9]). But the degree of this stretch is quite variable. In certain cases, the proton can adopt a position roughly midway between the A and B subunits in what is alternately called a low-barrier or very strong H-bond [10–13]. Other acid/base combinations can lead to a double-well proton transfer potential where not only the AH···B but also the A···HB configuration represents a minimum [14–23]. These two configurations will generally have different energies from one another, and the latter structure is the result of a proton transfer within the confines of the H-bond. If the energy barrier separating these two minima is sufficiently low, the situation can best be represented as a dynamic and rapid equilibrium between the two minima, where the transition between them is assisted by quantum mechanical tunneling [24–26]. The study of the proton transfer process has generated a rich and complex body of knowledge with relevance to chemistry and biology that continues to this day.

Recent years have witnessed the rediscovery of the halogen bond, which in many ways parallels the H-bond except that the bridging H of the Lewis acid unit is replaced by Cl, Br, or I [27–38]. The continuing exploration of the properties of the halogen bond has reiterated its similarity to the H-bond, including directionality and substituent effects, as well as the similarity of the fundamental forces of which they are both comprised.

Given these parallels it is perhaps not surprising that certain elements of the proton transfer of H-bonds have begun to emerge within the framework of halogen bonds as well. Whether X refers to H or a halogen atom, interaction with a Lewis base leads to stretching of the A—X bond, which can be quite substantial in certain instances [34,39–46], consistent with the idea of at least a partial transfer.

Previous calculations by this group [47] have elucidated the governing principles of halogen transfer in the context of a cationic system where the X^+ is shifting between a pair of neutral molecules, and found strong similarities with proton transfer. These symmetric transfer potentials are of single-well character when the halogen bond is short, but evolve to double wells for longer intermolecular separation.

The earlier work, however, left unsolved the situation when the entire system is neutral. The transfer of a X^+ within the AX···B system would generate a $A^-\cdots X^+B$ ion pair. Many years of study of the H-bond have led to some basic understanding of what it might take for a proton

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to transfer within the context of a neutral system. It would be of fundamental interest to determine how such criteria might be modified in the parallel case of the halogen bond. Does the larger size of the halogen as compared to a proton, and its greater diffusion of positive charge, permit an easier transfer? Can such a transition to an ion pair occur within the gas phase, or is a solvent or crystal environment required? Elucidation of the rules for halogen transfer would have far-reaching implications for such fields as pharmaceuticals, many of which participate in halogen bonds in certain environments.

The current work attempts to address this issue in a systematic fashion to answer the following questions. Are there any acid/base pairs where the halogen would spontaneously transfer across to the base? And for what sort of pair might the ion pair represent even a metastable equilibrium? How does formation of the complex alter the position of the bridging halogen? How are the halogen transfer properties related to other aspects of the complex, e.g. the binding energy or the native halogen acidity and basicity of the partner monomers? In order to address these questions, a full range of acids and bases are considered. The acids place the halogen on a C, N, F or O atom for purposes of comparison, and two different bases are considered with substantially different strength. The Cl, Br, and I halogen atoms are all considered as bridging halogen atom, and the results are compared with those obtained with the parallel H-bonds.

2. Systems and methods

A diverse set of Lewis acid molecules was chosen so as to present a wide spectrum in the data set. The halogen/hydrogen atom was bonded to C in F_3CX where X refers to either H, Cl, Br, or I. The three F substituents provide maximal acidity to this C-acid. At the opposite end of the continuum, FX places the bridging atom on F. N is used as the X donor atom in F_2NX, and O-acids are represented by FOX and F_2NOX. As bases, NMe_3 is a strong neutral nucleophile due in part to the three electron-releasing methyl group substituents. Electron-withdrawing Cl makes NCl_3 a much weaker base.

Ab initio calculations were run in the framework of the Gaussian 09 set of programs [48]. All geometries were fully optimized and minima verified as containing all real frequencies. The aug-cc-pVDZ basis set applied here includes polarization and diffuse functions, and its reliability has been documented in numerous prior studies [49–52]. Relativistic effects related to I were included by use of the aug-cc-pVDZ-PP pseudopotential [53] for this fourth-row atom. Electron correlation was incorporated through the MP2 protocol. The binding energy, E_b, was computed as the difference in energy between the dimer and the sum of the energies of monomers in their fully optimized structure, and is reported here as a positive quantity.

3. Results

The intrinsic force with which the various units hold onto the X^+ (where X refers to either H or a halogen) may be encapsulated by the energy required to separate the latter from the unit which will be left behind. In the case of the neutral Lewis acids, this quantity refers to the deprotonation energy, or its analogue for any of the other halonium ions:

$$RX \rightarrow R^- + X^+ \quad (1)$$

while the amine (Am) cations revert to a neutral molecule upon losing X^+.

$$AmX^+ \rightarrow Am + X^+ \quad (2)$$

These deprotonation energies and their analogous halogen quantities (all denoted here generically as dehalogenation energies) are listed in Table 1 where several trends are in evidence. Regarding the proton, removal from the C atom is most difficult, requiring 383 kcal/mol, followed by F, N and then O. Replacing the F substituent of FOH by the NF_2 group of F_2NOH eases the proton loss by some 76 kcal/mol, making F_2NOH the most acidic of molecules considered here.

Table 1
Energy (kcal/mol) required to remove X^+ from indicated subunit (see Reactions (1) and (2)).

	H^+	Cl^+	Br^+	I^+
F_3CX	383.02	391.01	347.94	297.49
FX	370.13	320.09	293.71	263.36
F_2NX	367.61	355.99	319.00	275.28
FOX	365.61	334.30	302.72	265.74
F_2NOX	289.53	257.13	222.93	188.23
Me_3NX^+	233.64	214.67	181.20	141.75
Cl_3NX^+	175.68	151.21	120.09	85.80

Replacement of the bridging H by a halogen atom leaves most of these trends intact with one exception. The dehalogenation of FX is considerably easier than either F_2NX or FOX, in contrast to the relatively high deprotonation energy of FH. Removal of X^+ becomes progressively less endothermic as the halogen atom grows in size: Cl > Br > I. The lowest dehalogenation energy of 188 kcal/mol is associated with F_2NOI. The deprotonation energies are larger than the analogous quantities for removal of the halogens, with the single exception of F_3CX. This trend may be due in part to the high energy required to remove all electrons from H, leaving only a bare proton in the gas phase. There is a second factor dealing with the intrinsic bond enthalpies. For example, the average bond enthalpy of a O—H bond is twice that of a O—Cl bond, and likewise for N—H vs N—Cl.

The last two rows of Table 1 refer to the two amine bases. Due to the electron-withdrawing capacity of Cl, it is much easier for Cl_3N to accommodate the excess electron density that accrues upon removal of X^+ as compared to Me_3N, so the values are much smaller in Table 1 for the former. The nature of the X atom plays an important part in the calculated dehalogenation energies of the bases. Just as in the case of the acids, the Cl → Br → I replacements cause a progressive reduction in these quantities for the two amines as well.

The competition between the acid and the base for the central X^+ is based in large part on the relative forces with which each hold on to this cation. It is clear from Table 1 that the deprotonation and dehalogenation energies of the Lewis acids are all larger than the energy required to separate X^+ from the base. This distinction is even true for the strongest acid F_2NOX when paired with the base Me_3N with the stronger hold on X^+.

In order to understand the transfer properties of the bridging ion, each of the five Lewis acids in Table 1 was paired with each of the two bases to form an acid-X^+-base complex. Several examples of such complexes are displayed in Fig. 1 for illustrative purposes. The binding energy of each such dimer, relative to the neutral pair RX + NR′3, is reported in Table 2. These quantities are uniformly much larger for NMe_3 as compared to its less basic NCl_3 analogue. The binding energy rises along with halogen atomic size Cl < Br < I, conforming to the diminishing dehalogenation energy of Table 1. This trend is also consonant with the well documented ability of larger halogen atoms to engage in stronger halogen bonds. The largest complexation energy occurs for FX, followed by FOX, F_2NX, and then by F_3CX. With the exception of the proton-bound systems, this same ordering of acids causes a progressive diminution in the dehalogenation energies, again buttressing the idea that stronger acids engage in more tightly held complexes with a base. Overall, the binding strength is enhanced by both stronger acid and stronger base.

Within each of the complexes, the proton/halogen transfer potential contains a single minimum, wherein X adopts a position between the acid and the N atom of the amine base. This equilibrium position is characterized in Table 3 in terms of its stretch away from its bond length within the monomer. In other words, the H atom within F_3C-H–NMe_3 has moved 0.003 Å further from the C than in the isolated F_3CH

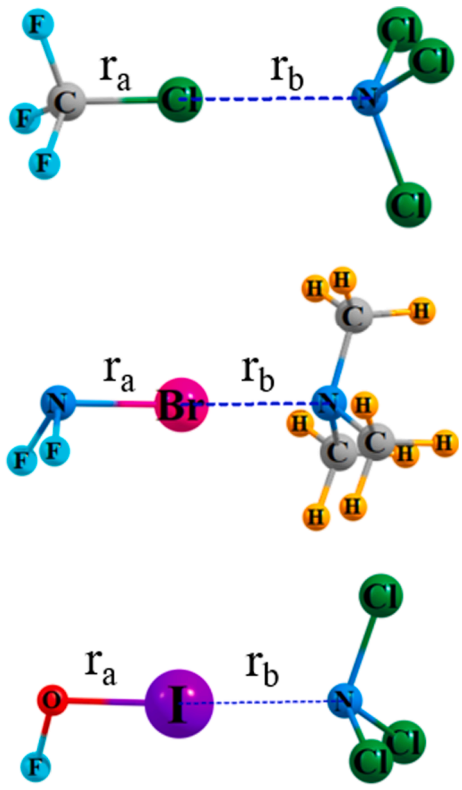

Fig. 1. Geometries of several sample complexes, defining r_a and r_b distances. All geometries were fully optimized with no geometric or symmetry restrictions at the MP2/aug-cc-pVDZ level.

monomer. With respect to the base, the central H is located 1.162 Å further from the N than in Me_3NH^+. That is, the bridging H has stretched only a small amount away from the acid and remains quite a distance from the base. The third row of Table 3 presents the ratio of these two stretches, in this case 0.003/1.162 = 0.0026. This $\Delta r_a/\Delta r_b$ ratio can be taken as a simple measure of the degree of X transfer. A 1:1 ratio of 1.0 would thus refer to what may be considered a half-transfer wherein the bridging X has stretched equal amounts from the acid as from the base.

There are some interesting trends in Table 3. Regarding first the stretches of X^+ away from the acid caused by the NMe_3 base, it is Cl that usually elongates the most, followed by Br and then I (with the exception of F_2NBr where r(N-Br) lengthens the most). The proton moves away from the acid unit by the smallest amount, when compared to the halogens. There is an opposite trend for Δr_b which shrinks as the halogen atom grows larger. When these two trends are combined, the degree of transfer $\Delta r_a/\Delta r_b$ diminishes along the Cl > Br > I ≫ H order, again with the exception of CF_3X. The switching of the NMe_3 nucleophile to its less basic NCl_3 congener strongly reduces Δr_a while enlarging Δr_b. The combined effect is a lowering of the degree of transfer, not surprising in light of the lesser basicity of NCl_3. With regard to comparisons amongst the various acids, there is essentially no transfer at all for the F_3CX acids, with the $\Delta r_a/\Delta r_b$ ratio never exceeding 0.036. On the other end of the spectrum, the FX acid is subject to the highest partial transfer, with $\Delta r_a/\Delta r_b$ reaching up to as high as 0.54. Just below FX on this scale is FOX, followed by F_2NX.

Some of these patterns can be reconciled with the data in Table 1. The reluctance of F_3CX to shift its X is consistent with its large deprotonation/dehalogenation energies in Table 1. Likewise, the ability of FX to shift its X toward the base is consistent with its small dehalogenation energies. The difficulty in generating much proton transfer in the complexes compares favorably with the higher deprotonation energies. The particularly small dehalogenation energies of F_2NOX cannot be realized in the X transfer as this molecule decomposes upon addition of NMe_3.

Table 2
Binding Energies of Complexes (kcal/mol).

	NMe_3				NCl_3			
	H^+	Cl^+	Br^+	I^+	H^+	Cl^+	Br^+	I^+
F_3CX	7.05	5.35	9.08	13.28	3.79	3.18	4.58	5.53
FX	16.41	25.42	29.98	31.22	6.02	7.20	9.93	11.05
F_2NX	12.57	9.79	15.91	20.11	5.34	4.16	5.82	6.85
FOX	15.30	16.81	22.88	26.11	6.00	5.37	7.59	8.90
F_2NOX	a	a	a	39.20	10.23	6.30	13.53	15.24

[a]F_2NOX molecule breaks apart during optimization in complex.

Table 3
Differences (Å) between the distance of the X^+ from the acid A and base B in the complex as compared to the isolated AX and BH^+ monomers.

	NMe_3	H^+	Cl^+	Br^+	I^+	NCl_3	H^+	Cl^+	Br^+	I^+
F_3CX	Δr_a(X—CF_3)	0.003	−0.001	0.007	0.020	Δr_a(X—CF_3)	−0.001	−0.001	0.000	0.000
	Δr_b	1.162	1.057	0.800	0.552	Δr_b	1.382	1.166	0.992	0.832
	$\Delta r_a/\Delta r_b$	0.003	−0.001	0.009	0.036	$\Delta r_a/\Delta r_b$	−0.001	−0.001	0.000	0.000
FX	Δr_a (X—F)	0.059	0.153	0.113	0.083	Δr_a (X—F)	0.014	0.028	0.031	0.026
	Δr_b	0.543	0.281	0.246	0.222	Δr_b	0.785	0.635	0.490	0.416
	$\Delta r_a/\Delta r_b$	0.109	0.544	0.460	0.372	$\Delta r_a/\Delta r_b$	0.018	0.044	0.063	0.063
F_2NX	Δr_a (X—NF_2)	0.024	0.046	0.056	0.034	Δr_a (X—NF_2)	0.003	0.001	0.001	−0.003
	Δr_b	0.782	0.652	0.465	0.362	Δr_b	1.003	0.993	0.817	0.664
	$\Delta r_a/\Delta r_b$	0.031	0.070	0.120	0.093	$\Delta r_a/\Delta r_b$	0.003	0.001	0.002	−0.004
FOX	Δr_a (X—OF)	0.044	0.126	0.093	0.069	Δr_a (X—OF)	0.009	0.013	0.016	0.015
	Δr_b	0.636	0.408	0.337	0.279	Δr_b	0.867	0.837	0.653	0.524
	$\Delta r_a/\Delta r_b$	0.069	0.309	0.278	0.247	$\Delta r_a/\Delta r_b$	0.011	0.015	0.024	0.029
F_2NOX	Δr_a(X—ONF_2)	a	a	a	0.236	Δr_a(X—ONF_2)	0.027	0.024	0.076	0.074
	Δr_b	a	a	a	0.133	Δr_b	0.766	0.725	0.546	0.429
	$\Delta r_a/\Delta r_b$	a	a	a	1.781	$\Delta r_a/\Delta r_b$	0.035	0.033	0.138	0.173

[a]F2NOX molecule breaks apart during optimization in complex.

And of course the smaller transfers toward the NCl_3 base are consonant with the much smaller energy required to remove X^+ from NCl_3X^+. On the other hand, reading across a row of Table 1 shows reductions in dehalogenation energy for larger X, leading to an expectation of easier X transfer. But the $\Delta r_a/\Delta r_b$ trends in Table 3 run counter to this expectation, as it is Cl which is generally transferred to the highest degree.

Table 2 had shown that the binding energies are largest for X = I and smallest for X = Cl or H, depending upon specific acid. FX forms the strongest complexes and F_3CX the weakest; NMe_3 is bound more strongly than is NCl_3. There is a rule of thumb proposed several times over the years, that an intermolecular H-bond will strengthen as the proton affinities of the two subunits competing for the bridging proton come closer together. In fact, a near equilibration of these two quantities has been proposed to lead to a single-well transfer potential, with the proton nearly midway between these two subunits, in what has sometimes been called [10–13] a very strong hydrogen bond (VSHB). It was considered intriguing to test out this idea in the more general context of halogen X^+ transfers. Fig. 2 displays the binding energies of the various dimers in terms of the difference in H^+/X^+ affinity between the acid and base groups. While there does appear to be some indication of the interaction strengthening toward the left of the figure as the two affinities approach one another, there is a great deal of spread in the data.

Another idea tested here is whether the degree of H^+/X^+ transfer is related to the affinity difference. These two measures are plotted against one another in Fig. 3. Clearly, the large affinity differences on the right side of Fig. 3 are reflected in only miniscule shifts of the bridging ion position. The transfer measure does increase toward the left as the affinity difference becomes smaller, at least in a general sense. However, this increase is highly scattered with certain systems showing precious little transfer even for small affinity differences. One can conclude then that the trend toward affinity equilibration exerts only a modest, and inconsistent, strengthening of the bond or shift of the central ion.

The clearest correlation arises between the binding energy and degree of transfer. As seen in Fig. 4, strengthening of the intermolecular bond leads to a progressive increase in the transfer, albeit with a fair amount of scatter. The linear relationship between these two quantities is characterized by a modest correlation coefficient R^2 of 0.79. This correlation may be interpreted to suggest that as the force with which the acid pulls in on the base increases, there is a certain reactive force that pulls the central ion toward the base. On the other hand, this overall correlation may be misleading. For most of the acids on an individual level, viz. FX, F_2NX, and FOX, the degree of transfer diminishes in the order Cl > Br > I when complexed with NMe_3, while the binding energies increase in this same order.

Another quantity, and one with particular connection with possible experimental measurements, is the stretching frequency of the A—X bond. In the context of H-bonds, the red shift induced in this band has been of immense value in assessing H-bond strength. The shifts in this

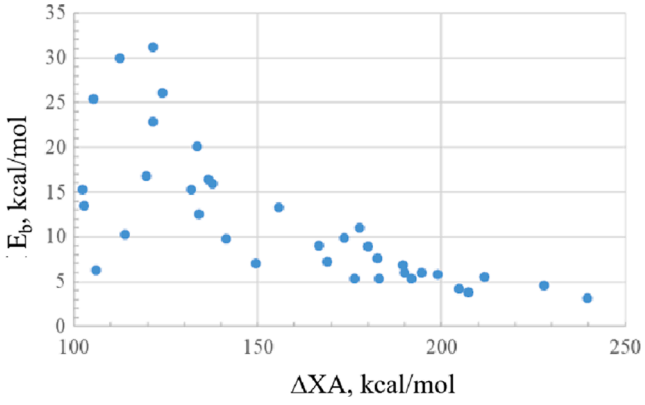

Fig. 2. Comparison of the binding energy of various complexes with the difference in H^+/X^+ affinity ΔXA between the acid and base fragments.

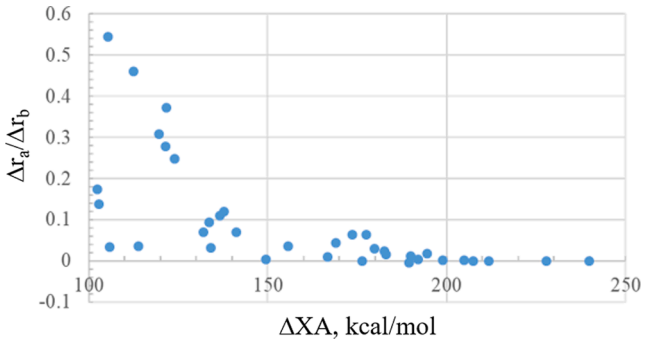

Fig. 3. Comparison of the degree of transfer of the central ion with the difference in H^+/X^+ affinity ΔXA between the acid and base fragments.

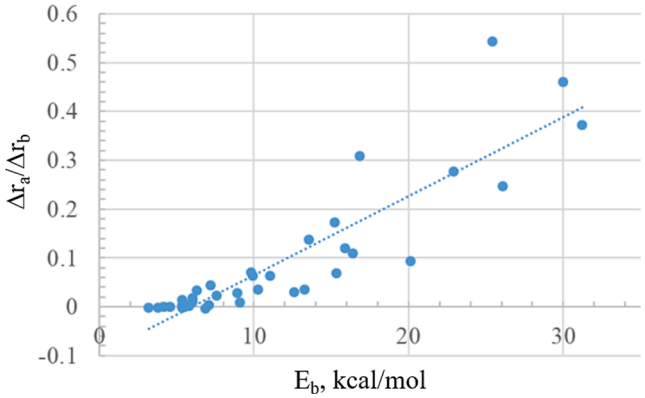

Fig. 4. Correlation between the degree of transfer of the central ion with the binding energy of the individual complex.

frequency are reported in Table 4 where several trends are in evidence. Most of these quantities are negative, consistent with a red shift. The principal exceptions involve the C—X bonds of the F_3CX acids where a small blue shift occurs. Such a blue shift has been seen on numerous occasions [5–8] in connection with CH H-bonds, particularly with sp^3 hybridization of the C [54] which is the case here. The shifts in Table 4 are much larger for the H-bonds, which is due in part to the much smaller mass of the H nucleus. Indeed, the magnitude of these red shifts declines along with increasing X mass: H ≫ Cl > Br > I. With respect to the individual Lewis acids, the red shifts diminish in the order FX > FOX > F_2NX. This is the same order as that observed in Table 3 for degree of proton transfer, as well as the complexation energies in Table 2. Note finally that the frequency shifts are much larger for the stronger NMe_3 base than for NCl_3.

The results described above highlight the difficulty of transferring a proton or halogen ion within the respective noncovalent bonds. Recent calculations have shown that this process can be aided by cooperativity in the form of other noncovalent interactions. Formation of an external tetrel bond, for example, can push a proton along an internal H-bond [55] between N and O, or between two O atoms [56], where the transfer would otherwise not occur.

4. Conclusions

Enlarging the halogen atom from Cl to Br to I progressively lowers the dehalogenation energy of the A—X acid, and also reduces that of the BX^+ base. Whether X = H or halogen, it is difficult to stretch the A—X bond by very much toward a base in the context of an incipient transfer, as such a transfer would lead to an energetically disfavored ion pair. Cl undergoes the highest degree of transfer within most of these complexes, followed by Br and then I; the proton is more resistant to transfer. Higher

Table 4
Shifts of ν(A—X) stretching frequency (cm^{-1}) upon formation of complex.

	NMe_3				NCl_3			
	H^+	Cl^+	Br^+	I^+	H^+	Cl^+	Br^+	I^+
F_3CX	−56.1	9.5	14.7	23.5	10.7	1.6	3.8	6.8
FX	−1296.7	−249.1	−162.7	−105.0	−354.1	−79.3	−57.5	−41.0
F_2NX	−392.7	−61.1	−49.0	−21.9	−56.5	−4.0	−2.6	2.8
FOX	−882.7	−165.6	−95.1	−59.3	−203.4	−29.0	−20.8	−13.7
F_2NOX	a	a	a	−392.9	−521.0	−355.7	−274.6	−279.8

[a]F_2NOX molecule breaks apart during optimization in complex.

degrees of partial transfer are generally favored by lowering the affinity of the anionic acid unit toward the bridging ion, and raising the affinity of the base, although this is not always the case. This transfer is also enhanced by a stronger interaction energy between the acid and the base within the complex in the general case, but this rule is violated for a constant acid unit. The A-I molecule engages in the strongest halogen bonds with a base, followed by Br and then Cl, with H roughly comparable to Cl. The shifts in the frequency of the A—X bond stretch also conform closely to the patterns of proton transfer and bond strength.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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