CHEMISTRY
A EUROPEAN JOURNAL

Ab Initio Study of the Complexes of Halogen-Containing Molecules RX (X = Cl, Br, and I) and NH_3: Towards Understanding the Nature of Halogen Bonding and the Electron-Accepting Propensities of Covalently Bonded Halogen Atoms

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Abstract: Ab initio calculations have been performed on a series of complexes formed between halogen-containing molecules and ammonia to gain a deeper insight into the nature of halogen bonding. It appears that the dihalogen molecules form the strongest halogen-bonded complexes with ammonia, followed by HOX; the charge-transfer-type contribution has been demonstrated to dominate the halogen bonding in these complexes. For the complexes involving carbon-bound halogen molecules, our calculations clearly indicate that electrostatic interactions are mainly responsible for their binding energies. Whereas the halogen-bond strength is significantly enhanced by progressive fluorine substitution, the substitution of a hydrogen atom by a methyl group in the $CH_3X{\cdots}NH_3$ complex weakened the halogen bonding. Moreover, remote substituent effects have also been noted in the complexes of halobenzenes with different *para* substituents. The influence of the hybridization state of the carbon atom bonded to the halogen atom has also been examined and the results reveal that halogen-bond strengths decrease in the order $HC{\equiv}CX > H_2C{=}CHX \approx O{=}CHX \approx C_6H_5X > CH_3X$. In addition, several excellent linear correlations have been established between the interaction energies and both the amount of charge transfer and the electrostatic potentials corresponding to an electron density of 0.002 au along the R−X axis; these correlations provide good models with which to evaluate the electron-accepting abilities of the covalently bonded halogen atoms. Finally, some positively charged halogen-bonded systems have been investigated and the effect of the charge has been discussed.

Keywords: ab initio calculations · charge transfer · electrostatic potential · halogen bonds · molecular complexes

Introduction

Intermolecular noncovalent interactions between halogen atoms and lone-pair-possessing atoms (frequently N and O) have elicited much interest during the last decade due to their importance in the fields of molecular recognition,[1] crystal engineering,[2] and possibly in biological systems.[3] It has been shown that the behavior of halogen atoms, which act as electron-acceptor sites with respect to an electron-donor molecule, closely resembles the behavior of heteroatom-bound hydrogen atoms (i.e., hydrogen-bond donors) in many aspects, and the term "halogen bonding" has been suggested to stress its similarity with hydrogen bonding.[1a,4]

Halogen bonding in dihalogen systems has been extensively studied.[4a,5,6] Legon and co-workers[4a,5] have successfully characterized a number of prereactive complexes formed between dihalogen molecules and electron-donor molecules by using Fourier transform microwave spectroscopy with the aid of a pulsed nozzle. Theoretical investigations into the charge-transfer and electron donor–acceptor interactions of halogen-bonded complexes[6] have usually been performed by using methods proposed by Mulliken and Person.[7] More recently, interactions between carbon-bound halogen atoms and electron donors have been perceived and proven to be an essential driving force for crystal engineering and supramolecular self-assembly.[1,2] Moreover, it has been demonstrated that some carbon-bound halogen

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DOI: 10.1002/chem.200400504

atoms, when interacting with appropriate electron-donor molecules, can yield stabilization effects whose strengths are comparable to, or even larger than, those of competitive hydrogen bonds.[1b,8] However, theoretical studies of halogen bonding in systems other than those involving dihalogen molecules have been limited. To reveal the nature of the short contacts observed in the database of crystal structures (e.g., Cl···Cl and halogen···electronegative (N and O) atom), Price et al.[9] and Allen and co-workers[10] have performed some intermolecular perturbation theory calculations on the complexes formed between chlorine-containing molecules and electron-donating ones. Meille and co-workers[11] conducted a theoretical calculation on the halogen-bonded complexes formed between fluoroalkyl halides and ammonia and examined the effect of increasing fluorine substitution on the halogen bonding. More recently , Romaniello and Lelj[12] analyzed the halogen bond between CF_3I adducts and several electron donors; to explore the solvent effect on the NMR spectra, Glaser et al.[13] examined theoretically the halogen bonding between some haloarenes and DMSO; Wong and co-workers[14] have devoted themselves to elucidating the blue-shifting properties of halogen bonding. These theoretical calculations have revealed that the most important contribution to the intermolecular interactions of halogen atoms is electrostatic, whereas the contribution from charge-transfer-type interactions is minor and even negligible in some cases. In addition, to provide a qualitative understanding of the electron-accepting nature of carbon-bound halogen atoms, the molecular-surface electrostatic potentials (ESP) of some halogen-containing molecules have been reported.[15–17] The results clearly reveal that there is a positive cap at the end regions of the halogen atoms along the C–X (X = Cl, Br, and I) bond vectors.

Herein we report the results of ab initio calculations performed on the halogen-bonded complexes formed by ammonia, a representative electron-donor molecule, and a series of halogen-containing molecules with a general formula RX, where X = Cl, Br, and I, and R represents F, Cl, Br, I, H, HO, H_2N, H_3C, FH_2C, F_2HC, F_3C, MeH_2C, Me_2HC, Me_3C, $CH_2{=}CH$, $HC{\equiv}C$, HC(O), MeC(O), phenyl, 4-NH_2-phenyl, 4-F-phenyl, 4-NO_2-phenyl, and 4-pyridyl. The purpose of this effort was to explore systematically the effect of the chemical environment of the halogen atom on the halogen bonding, and in particular, to provide some quantitative insight into this specific nonbonding intermolecular interaction.

In addition, it is well known that when one of the two partners in a hydrogen-bonded complex bears an electric charge, the resulting hydrogen bond is significantly stronger than that between the two neutral species. This charge-assisted phenomenon, to some degree, supports the electrostatic nature of hydrogen bonding.[18,19] Hence, several halogen-bonded complexes involving chlorine- and bromine-containing cations have also been considered in order to acquire a deeper understanding of halogen bonding.

Computational Details

All computations were performed with the Gaussian 98 suite of programs.[20] The geometries of all the monomers and dimers, including all electrons, were fully optimized by using Moller–Plesset second-order perturbation theory. Dunning's basis set, Aug-cc-PVDZ, was used to study the RX···NH_3 (X = Cl and Br) systems. This level of theory was thought to be adequate for reasonably weak nonbonded interactions, and was used in recent theoretical studies of halogen-bonded complexes formed between dihalogen molecules and H_2O or H_2S.[5a,21–23] Nevertheless, for selected systems, single-point calculations using the MP2(full)/Aug-cc-PVDZ geometries were carried out at the MP2(full)/Aug-cc-PVTZ and CCSD(T)/Aug-cc-PVDZ levels of theory to check the convergence. For the iodine-containing systems, the Lanl2DZ basis set, augmented by one set of six d polarization functions (Lanl2DZ*) with the following exponents, $\alpha_C = \alpha_N = \alpha_O = \alpha_F = 0.80$, $\alpha_{Cl} = 0.75$, $\alpha_{Br} = 0.39$, and $\alpha_I = 0.29$, was used. Recent theoretical calculations which used this modified effective core potential (ECP) basis set have been shown to give reasonably good results for the pyridine–I_2 complex[24] and those of carbonyl compounds with dihalogen molecules.[25–27] The MP2(full)/Lanl2DZ* level of theory was also employed for the calculations on the RBr···NH_3 complexes to ensure that the halogen bonds of these three different donors (RX) are comparable. The halogen bonding energy (ΔE_{HalB}) of each complex was calculated as the difference between the total energy of the complex and the sum of the total energies of the monomers, that is, $\Delta E_{HalB} = E_{RX} + E_{NH3} - E_{RX\cdots NH3}$. The basis set superposition error (BSSE) was incorporated into the calculations in order to obtain the corrected interaction energies by using the counterpoise (CP) technique developed by Boys and Bernardi.[28] Atomic charges were computed by means of natural (NPA) and Mulliken population analyses as well as by the electrostatic potential-fitted method (Chelpg). Finally, electrostatic potentials, and electronic densities if necessary, at some given points were obtained in order to evaluate the electrostatic contribution to the halogen bonds.

Results and Discussion

Geometries: Table 1 shows the optimized equilibrium X···N distances, d(X···N), for all complexes and the variations in the R–X distances upon complex formation, that is, the difference between the R–X distances in the RX···NH_3 complex and that in the isolated RX. As can be seen from Table 1, the internuclear distances d(Cl···N) range from 2.27 to 3.35 Å and d(Br···N) from 2.32 to 3.24 Å at the MP2(full)/Aug-cc-PVDZ level of theory, and values of d(Br···N) range from 2.37 to 3.25 Å and d(I···N) from 2.52 to 3.25 Å at the MP2(full)/Lanl2DZ* level of theory. Although the d(Br···N) and d(I···N) values for all of the complexes are smaller than the sum of the van der Waals (VDW) radii of the halogen and nitrogen atoms, the internuclear distances d(Cl···N) in the complexes $MeCH_2Cl$···NH_3, Me_2CHCl···NH_3, and Me_3CCl···NH_3 are calculated to be 3.313, 3.336, and 3.349 Å, respectively, which are slightly larger than the sum of the VDW radii of the chlorine and nitrogen atoms (3.30 Å). This implies very weak halogen bonding in these three complexes.

For most of the complexes studied, it has been shown that the optimized equilibrium R–X···N contacts are nearly linear. The ∢RXN angles are all greater than 172° except for the MeCOBr···NH_3 complex in which a significant departure from linearity occurs (∢RXN = 160.3°). Moreover, our calculations reveal that in the four complexes formed be-

Table 1. Optimized equilibrium X···N distances, d(X···N), for all complexes and the variations in the R−X distances upon complex formation.[a]

	$RCl\cdots NH_3$ (BS1)[b]		$RBr\cdots NH_3$ (BS1)[b]		$RBr\cdots NH_3$ (BS2)[b]		$RI\cdots NH_3$ (BS2)[b]	
R =	$d(Cl\cdots N)$	$\Delta d(R-Cl)$	$d(Br\cdots N)$	$\Delta d(R-Br)$	$d(Br\cdots N)$	$\Delta d(R-Br)$	$d(I\cdots N)$	$\Delta d(R-I)$
F-	2.2694	0.0729	2.3221	0.0664	2.3751	0.0554	2.5280	0.0460
Cl-	2.5375	0.0479	2.4535	0.0754	2.5369	0.0570	2.6090	0.0576
Br-			2.5062	0.0667	2.5681	0.0546	2.6381	0.0563
I-							2.7070	0.0546
HO-	2.6490	0.0242	2.5816	0.0328	2.6093	0.0314		
H_2N-	2.9607	0.0057	2.8681	0.0110	2.8821	0.0113		
H-	3.2245	0.0015	3.1398	0.0044	3.1458	0.0047	3.1407	0.0100
H_3C-	3.2771	−0.0011	3.1371	0.0009	3.1939	0.0017	3.1744	0.0050
FH_2C-	3.1911	−0.0034	3.0998	−0.0045	3.1298	−0.0039	3.1327	−0.0019
F_2HC-	3.1153	−0.0058	3.0412	−0.0064	3.0443	−0.0065	3.0572	−0.0044
F_3C-	3.0291	−0.0063	2.9560	−0.0019	2.9310	−0.0031	2.9395	0.0038
MeH_2C-	3.3125	−0.0029	3.1660	−0.0016	3.2294	−0.0021	3.2177	0.0013
Me_2HC-	3.3359	−0.0046	3.1794	−0.0039	3.2494	−0.0050	3.2418	−0.0035
Me_3C-	3.3490	−0.0055	3.1797	−0.0055	3.2539	−0.0068	3.2502	−0.0056
$CH_2{=}CH$-	3.2094	−0.0026	3.1049	−0.0000	3.1306	−0.0003	3.1463	0.0039
$HC{\equiv}C$-	3.0181	0.0033	2.9426	0.0096	3.0509	0.0120	2.9475	0.0234
phenyl-	3.1808	−0.0030	3.0846	0.0001	3.1015	0.0003	3.1214	0.0045
4-NH_2-phenyl-	3.2088	−0.0029	3.1013	0.0003	3.1142	0.0000	3.1375	0.0046
4-F-phenyl-	3.1623	−0.0020	3.0659	0.0012	3.0722	0.0012	3.0940	0.0063
4-NO_2-phenyl-	3.1199	−0.0028	3.0366	0.0011	3.0401	0.0008	3.0619	0.0071
4-pyridyl-	3.1383	−0.0034	3.0541	0.0005	3.0586	0.0005		
HC(O)-	3.2196	−0.0111	3.1568	−0.0147	3.1678	−0.0174		
MeC(O)-	3.2757	−0.0098	3.2420	−0.0118	3.2142	−0.0218		

[a] All values are given in Å. [b] BS1: MP2(full)/Aug-cc-PVDZ; BS2: MP2(full)/Lanl2DZ*.

tween acyl chloride or acyl bromide and NH_3, the angles between the X···N internuclear line and the local C_{3v} axis of NH_3 ($\measuredangle XNH_c$, where H_c is the center of mass of the three hydrogen atoms of ammonia) are 146.0 (HCOCl), 124.5 (MeCOCl), 168.9 (HCOBr), and 120.7° (MeCOBr), whereas for the other complexes, they are all larger than 170°. This structural feature may be ascribed to the effect of the strong polarity of the carbonyl group on the electrostatic distribution of the halogen atom: on one hand, the site with the most positive electrostatic potential on the surface of the halogen atom might deviate from the C−X axis; on the other hand, secondary interactions (i.e., the weak N−H···X hydrogen bond) might become non-negligible because of the change in the electrostatic distribution. Interestingly, for the $HCOBr\cdots NH_3$ and $MeCOBr\cdots NH_3$ complexes, the results of the calculations at the MP2/Lanl2dz* level indicate that both the C−Br−N and the Br−N−H_c atomic arrangements are highly linear. This can be explained by the fact that the weak secondary interactions are underestimated by the relatively small basis set. Nevertheless, it has been found that the d(Br···N) values obtained by these two different methods correlate well with each other; the correlation coefficient is 0.991 and the average absolute error is only 0.036 Å, which demonstrates the applicability of the Lanl2dz* basis set, especially for larger systems for which high-level calculations become prohibitively expensive.

From the data in Table 1, it can be seen that the intermolecular distances are significantly affected by the chemical environment of the halogen atoms. Because there is consistency between the variations in the intermolecular distances and interaction energies, the pertinent discussion will be incorporated into the next section.

The variation in the X−H bond length in the X−H···Y system upon complex formation is another important structural feature of the hydrogen bond. For most hydrogen-bonded systems, the X−H bond is elongated when binding to a hydrogen acceptor;[29] however, in a rather limited number of cases, in which the hydrogen bonds are known as improper and blue-shifting hydrogen bonds,[19] they exhibit opposite behavior. Recently, the nature of the X−H bond contraction (and blue shift) has elicited great interest for theoretical chemists. In the most recent work, Wong and coworkers[14] investigated the blue-shifting nature of the halogen bond as a result of the remarkable parallels in the properties of XH···B and YX···B systems. Actually, several halogen-containing molecules, such as CF_3Cl and CF_3Br, were predicted to have reduced C−X bond lengths when interacting with an electron donor (e.g., NH_3, H_2O). Here, our calculated results (see Table 1) for these two complexes, $CF_3Cl\cdots NH_3$ and $CF_3Br\cdots NH_3$, are in agreement with those given in reference [14]. However, for the analogous CF_3I system, the C−I bond length is shown to increase by 3.8 mÅ upon complexation with NH_3. Furthermore, we found that there are many cases (nearly half the systems investigated) in which the R−X bond is observed to shrink, that is, the blue-shifting phenomenon for halogen-bonded complexes is more frequent than one might expect. In addition, some systems even exhibit opposite behavior on changing the halogen atom X. Hence, the nature of the blue-shifting halogen bond and the discrepancy between this and the blue-shifting hydrogen bond require further study. This is beyond the scope of the present work.

Interaction energies: We have tested the MP2/Aug-cc-PVDZ level of theory by performing single-point calculations on selected RBr···NH$_3$ complexes with a larger basis set (Aug-cc-PVTZ) and with a higher-level correlation method [CCSD(T)]. The interaction energies calculated without (ΔE_{HalB}) and with BSSE corrections (ΔE_{HalB}+BSSE) are listed in Table 2. A comparison of the ΔE_{HalB} values calculated by the MP2/Aug-cc-PVDZ method and those calculated by the MP2/Aug-cc-PVTZ method shows that the interaction energies are insensitive to the basis set. With the exception of FBr···NH$_3$ and HOBr···NH$_3$, for which ΔE_{HalB} values vary by 1.47 and 0.47 kcal mol^{-1}, respectively, with increasing basis set, all the RBr···NH$_3$ complexes considered show little variation in the interaction energies obtained by the two methods (less than 0.23 kcal mol^{-1}). When the BSSE term is incorporated, the maximal change is 0.62 kcal mol^{-1} (FBr···NH$_3$), and the average absolute difference between the ΔE_{HalB}+BSSE values obtained at the two levels is only 0.25 kal mol^{-1}. Similar results were found when comparing the ΔE_{HalB} values calculated at the MP2/Aug-cc-PVDZ and CCSD(T)/Aug-cc-PVDZ levels of theory, although the differences are somewhat larger for the relatively strong dihalogen and HOBr complexes. These results, together with those of previous studies[5a,21–23] on halogen-bonded complexes, have led us to believe that the MP2/Aug-cc-PVDZ level should be adequate, and for relatively large systems, this level may be a good compromise between accuracy and calculation cost. Furthermore, we found that the values of ΔE_{HalB} and ΔE_{HalB}+BSSE calculated at the MP2/Aug-cc-PVDZ level correlate very well with the corresponding values calculated at the MP2/Aug-cc-PVTZ and CCSD(T)/Aug-cc-PVDZ levels (the correlation coefficients are all larger than 0.997), which indicates further the reasonability of the MP2/Aug-cc-PVDZ method, especially in describing the relative halogen-bond strength.

For comparison, the MP2(full)/Lanl2DZ* calculations were also employed for the RBr···NH$_3$ complexes. It appears that the MP2/Lanl2DZ* method always yields lower ΔE_{HalB} values than the MP2/Aug-cc-PVDZ method except with BrF, CF$_3$Br, and 4-nitrobromobenzene, for which the MP2/Lanl2DZ*-calculated ΔE_{HalB} values are slightly larger. The MP2/Lanl2DZ* calculations systematically give lower interaction energies because the relatively small basis set often poorly describes the polarization and dispersion terms of the weak interactions. For this reason, for the RBr···NH$_3$ complexes, all the calculated results will hereafter refer to the values obtained with the higher-level (MP2/Aug-cc-PVDZ) calculations unless otherwise specified. In spite of this, a good linear correlation has been obtained between the interaction energies determined by these two different approaches, with or without the BSSE correction; the correlation coefficients for the uncorrected and corrected ΔE_{HalB} values are 0.997 and 0.996, and the mean absolute errors are

Table 2. Calculated interaction energies without (ΔE_{HalB}) and with BSSE corrections (ΔE_{HalB}+BSSE).[a]

	RBr···NH$_3$							RCl···NH$_3$		RI···NH$_3$	
	MP2/BS1[b]		MP2/BS2[b]		CCSD(T)[c]	MP2/BS3[b]		(MP2/BS1)[b]		(MP2/BS3)[b]	
R =	ΔE_{HalB}	ΔE_{HalB} +BSSE	ΔE_{HalB}	ΔE_{HalB} +BSSE	ΔE_{HalB}	ΔE_{HalB}	ΔE_{HalB} +BSSE	ΔE_{HalB}	ΔE_{HalB} +BSSE	ΔE_{HalB}	ΔE_{HalB} +BSSE
F-	17.20	14.16	18.67	14.78	15.07	17.49	14.11	12.46	11.75	19.44	16.02
Cl-	11.74	8.69	11.59	8.21	10.01	11.01	8.53	6.81	6.07	14.85	12.03
Br-	10.08	6.94	9.98	6.50	8.53	9.54	7.19			13.35	10.61
I-										10.67	8.43
HO-	9.16	6.83	9.63	7.19	7.79	9.08	6.95	5.43	4.05		
H_2N-	4.80	3.02	4.88	3.30	4.10	4.28	2.98	2.29	1.45		
H-	2.84	1.67	3.00	1.85	2.60	2.32	1.53	1.20	0.69	4.29	3.35
H_3C-	2.17	0.92	2.25	1.10	1.88	1.31	0.51	0.52	0.07	3.19	2.22
FH_2C-	2.98	1.65	3.03	1.78	2.70	2.35	1.48	1.50	0.92	4.14	3.11
F_2HC-	3.89	2.43	3.86	2.48	3.63	3.60	2.59	2.19	1.52	5.47	4.29
F_3C-	5.21	3.53	5.13	3.55	4.93	5.38	4.16	3.19	2.37	7.70	6.25
MeH_2C-	1.88	0.66	1.89	0.87	1.62	1.02	0.23	0.38	−0.09	2.69	1.75
Me_2HC-	1.68	0.48				0.81	0.00	0.27	−0.23	2.36	1.41
Me_3C-	1.54	0.36				0.70	−0.15	0.26	−0.26	2.18	1.20
$CH_2{=}CH$-	2.83	1.46	2.61	1.63	2.52	2.18	1.27	1.18	0.61	3.93	2.90
$HC{\equiv}C$-	5.42	3.64	5.34	3.76	5.01	5.42	4.17	3.20	2.34	6.22	4.83
phenyl-	2.98	1.56				2.32	1.31	1.36	0.66	4.07	2.94
4-NH_2-phenyl-	2.53	1.16				1.50	0.50	1.05	0.38	3.75	2.63
4-F-phenyl-	3.24	1.78				2.75	1.70	1.60	0.87	4.59	3.42
4-NO_2-phenyl-	3.92	2.43				4.06	2.97	2.15	1.38	5.47	4.25
4-pyridyl-	3.55	2.09				3.16	2.10	1.87	1.15		
HC(O)-	2.76	1.49	2.90	1.72	2.60	2.28	1.44	1.60	1.02		
MeC(O)-	2.32	0.97	2.39	1.28	2.14	1.56	0.73	1.30	0.68		

[a] All values are given in kcal mol^{-1}. [b] BS1: MP2(full)/Aug-cc-PVDZ; BS2: MP2(full)/Aug-cc-PVTZ; BS3: MP2(full)/Lanl2DZ*. [c] CCSD(T): CCSD(T)/Aug-cc-PVDZ.

0.537 and 0.277 kcal mol^{-1}, respectively, which shows once again that the MP2/Lanl2DZ* results are, at least in a relative sense, acceptable.

As follows from the data in Table 2, the halogen-bond strengths (ΔE_{HalB}) vary over a broad range, roughly from 0.2 to 20 kcal mol^{-1}. This energy span is comparable to the strengths of neutral hydrogen bonds.[30] Note that some chlorine-bonded systems give negative ΔE_{HalB} values when the BSSE correction is included. Although the chlorine-containing molecules and the ammonia are weakly bound in these complexes, as revealed by long intermolecular distances (the values are larger than the sum of the VDW radii as presented above), the BSSE substantially overcorrects the interaction energy. This is not surprising since the counterpoise method is controversial[31] and the BSSE-corrected interaction energies have frequently been found to be inferior to the uncorrected ones.[32] As expected, the dihalogen systems, which have been extensively studied in the context of charge-transfer interactions, have the strongest halogen bonds.[4a,5,6] Our own calculations on these systems show that 1) the ΔE_{HalB} values are above 6 kcal mol^{-1}, 2) the heterodihalogen molecules with large dipole moments have large interaction energies, that is, they decrease in the order IF > BrF > ICl > IBr > BrCl (MP2/Lanl2DZ* result) and BrF > ClF > BrCl (MP2/Aug-cc-PVDZ result), and 3) for the homodihalogen systems, the interaction energies decrease in the order $I_2 > Br_2 > Cl_2$. These findings are in agreement with previous publications[6e] in which the results have been rationalized on the basis of the first-order approximation of the charge redistribution effect.

The complexes involving HOX and NH_2X have not been examined previously. In principle, multiple minima are possible in such systems (and also in other complexes), however in this work we consider only the minimum associated with the halogen bond, although in some cases, this may not be the global minimum on the potential energy surface. For the halogen-bonded complexes formed between HOX and ammonia, it has been revealed that the interaction energies are reasonably large, 5.43 kcal mol^{-1} for HOCl···NH_3 and 9.16 kcal mol^{-1} for HOBr···NH_3. These values, although smaller than those for dihalogen systems, are significantly larger than those for complexes involving carbon-bound halogen atoms (see Table 2). Similar results were observed for the intermolecular distances: the d(X···N) values for the HOCl···NH_3 and HOBr···NH_3 complexes were estimated to be 2.649 and 2.582 Å, similar to those of the complexes of dihalogen molecules and significantly less than those for carbon-bound halogen systems, which are all predicted to be greater than 3.0 Å. However, in the case of NH_2X···NH_3 complexes, although their intermolecular distances [d(X···N)] are somewhat short (< 3.0 Å), the uncorrected interaction energies are 2.29 kcal mol^{-1} for NH_2Cl···NH_3 and 4.80 kcal mol^{-1} for NH_2Br···NH_3, which are not as large as one might expect. These ΔE_{HalB} values are markedly lower than the corresponding values for the HOX···NH_3 complexes, and even lower than those of some carbon-bound halogen complexes (e.g., CF_3X).

Recent studies[1b,8] of carbon-bound halogen systems have indicated that some of them are capable of yielding reasonably strong halogen-bonded complexes with appropriate electron donors. We address, first, the effect of the hybridization state of the carbon atom bonded to the halogen atom on halogen bonding. It has been revealed that the intermolecular distances vary in the order $HC{\equiv}CX < H_2C{=}CHX \approx O{=}CHX \approx C_6H_5X < CH_3X$, while the binding energies vary in the reverse order. That is, sp-hybridized carbon-bound halogen atoms form the strongest halogen bond, followed by sp^2- and then sp^3-hybridized carbon-bound halogen atoms. This behavior very much resembles that of the corresponding hydrocarbons as hydrogen-bond donors.[33] In addition to the hybridization, substitution may significantly affect the halogen-bond strength. In a recent publication, Meille and co-workers[11] explored the effect of progressive fluorine substitution by examining the complexes formed between fluoromethyl iodides and ammonia. Indeed, they found that the halogen-bond energies increase with increasing fluorine substitution, which closely parallels the hydrogen bonding in the corresponding fluoromethanes as hydrogen-bond donors. By performing calculations with the Lanl2DZ* basis set we estimated the ΔE_{HalB} values to be 3.2 kcal mol^{-1} for the CH_3I···NH_3 complex and 7.7 kcal mol^{-1} for CF_3I···NH_3, which are very similar to previous results[11] (3.1 and 7.3 kcal mol^{-1}, respectively). On going from CH_3I to CF_3I, the binding energy is enhanced by 0.8–2.2 kcal mol^{-1} with progressive fluorine substitution, whereas these increments are estimated to be a little smaller for fluoromethyl bromides (0.7–1.3 kcal mol^{-1}) and for fluoromethyl chlorides (0.6–1.0 kcal mol^{-1}). Variations in the N···X distances, which are shortened by 0.04–0.12 Å with increasing fluorine substitution, were also observed.In the same way we examined the effect of methyl substitution and discerned the reverse trend to that observed with fluorine substitution, that is, as the number of methyl groups increases, the interaction energy decreases and the intermolecular distance increases. In particular, for the CH_3Cl···NH_3 complex, which is reasonably weak as indicated by its long intermolecular distance and small binding energy, the halogen-bond strengths appear to be negligibly small when the hydrogen atoms in CH_3Cl are replaced by methyl groups. The interaction energies even become negative if the BSSE correction is taken into account, so higher-level calculations seem necessary to determine the accurate binding energies of these systems.

The complexes of several *para*-substituted halobenzenes have also been investigated. We noted that remote substitution effects also work on the halogen bond. While electron-withdrawing fluoro and nitro substituents enhance the halogen-bond strength, with the latter having a larger effect, the electron-donating amino substituent slightly reduces the interaction energy. For example, the ΔE_{HalB} values of the complexes of iodobenzene, 4-F-, 4-NO_2-, and 4-NH_2-iodobenzene with ammonia are 4.07, 4.59, 5.47, and 3.75 kcal mol^{-1}, respectively; the corresponding values for the bromobenzene series are 2.98, 3.24, 3.92, and 2.53 kcal mol^{-1} and 1.36, 1.60, 2.15, and 1.05 kcal mol^{-1} for the chlorobenzene series.

Similarly, we examined the case of 4-X-pyridine (X = Cl and Br) for which somewhat larger interaction energies have been observed than for the corresponding halobenzene (by ca. 0.5 kcal mol^{-1} regardless of X), which has been ascribed to the electron-withdrawing effect of the nitrogen atom in the aromatic ring. In addition, the halogen bond lengths increase in the order 4-NO_2-C_6H_4X < C_6H_4NX < 4-F-C_6H_4X < C_6H_5X < 4-NH_2-C_6H_4X, which is the reverse of the trend in the interaction energy.

As a result of the good consistency between the interaction energies and the intermolecular distances, as presented above, we explored the quantitative relationship between them. Plots of the interaction energies (ΔE_{HalB}) versus the intermolecular distances [d(N···X)] are displayed in Figure 1 in which the three lines represent the quadratic polynomial regression analysis. These nonlinear relationships suggest that the halogen bonds are much stronger when they are very short. Similar findings were found in previous studies of hydrogen-bonded systems.[32,34,35] For example, Espinosa et al.[34] systematically examined 83 X−H···O hydrogen bonds by X-ray charge density and ab initio methods and revealed that the relationship between the hydrogen-bonding energies and the H···O distances appeared to be nonlinear.

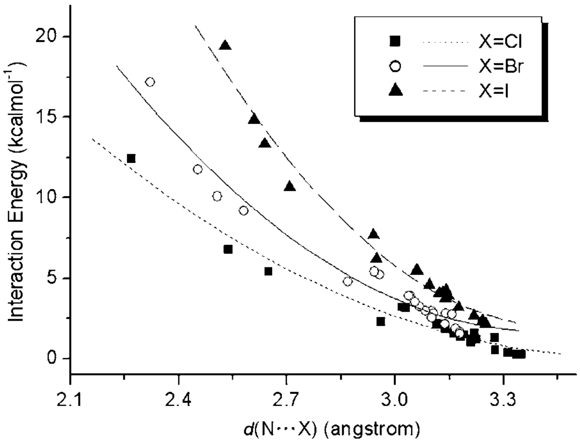

Figure 1. Dependence of the interaction energy on the intermolecular distance d(X···N) for halogen-bonded RX···NH_3 complexes.

Charge transfer and electrostatic interactions: It has been well documented that charge transfer plays a crucial role in halogen bonding in dihalogen systems.[6] However for relatively weak halogen-bonded complexes between fluoroalkyl halides and ammonia or other electron donors, the most important contribution to the intermolecular interactions has been demonstrated to be electrostatic.[11]We consider first the situation of RBr···NH_3 as a representative complex. Table 3 summarizes the amount of charge that is transferred (Q_{CT}) from ammonia to the bromine-containing molecules, as determined by Mulliken and natural population analyses, and by the molecular electrostatic potential-fitted method (Chelpg). As can be seen from the table, the Q_{CT} values are method-dependent. The values obtained by the Mulliken approach are less reliable: the monomer NH_3, which acts as the electron donor and should lose electrons upon complex formation, is predicted to be negatively charged (i.e., it receives electrons from RBr) in some complexes, for example, PhBr···NH_3. Szefczyk et al.[36] recently studied several Lewis acid–base complexes to determine the optimal method for evaluating the magnitude of intermolecular charge transfer. It was concluded that the amount of charge transfer determined by the Chelpg approach closely matched the available experimental values, and therefore it was thought to be the most reasonable method. However, in our systematic investigations of halogen-bonded complexes, the charge transfer in the BrCl···NH_3 complex was calculated to be 253 me by the Chelpg method, which is larger than that in the BrF···NH_3 (245 me) and Br2···NH_3 (244 me) complexes, in disagreement with previous conclusions.[6] Moreover, the amount of charge transfer in the weak HBr···NH_3 complex was determined to be 131 me, which is considerably larger than that for complexes of comparable or larger bond strength. Evidently, this value is seriously overestimated. In contrast, the NPA method yields no abnormal results, although the amount of transferred charge obtained by using this approach is systematically underestimated.[36] As the amount of charge transfer determined by the NPA method is deemed to be more reliable, at least in a relative sense, these values will be used in the following discussion.

Besides the method-dependence, it has also been shown that the amount of charge transfer is dependent on the computation level. In fact, for the RBr···NH_3 complexes, the Q_{CT} values obtained by using the NPA method at the MP2(full)/Lanl2dz* level of theory and those at the MP2(full)/Aug-cc-PVDZ level of theory differ significantly from each other (Table 3). The exact amount of charge transfer is trivial, however, since we are concerned more with the relative magnitudes than with the absolute Q_{CT} values. Moreover, the Q_{CT} values calculated at these two different levels are shown to highly correlate with the correlation coefficient being as high as 0.998.

Our MP2(full)/Aug-cc-PVDZ calculations indicate that the Q_{CT}(NPA) values for the BrF···NH_3, BrCl···NH_3, and Br_2···NH_3 complexes are 149, 108, and 92 me, and 63 and 20 me for the HOBr···NH_3 and NH_2Br···NH_3 complexes, respectively. This order of decreasing Q_{CT} values is fully consistent with the variation in the interaction energies of these five complexes (series I). A further examination of the relationship between the interaction energies and the amount of charge transfer shows that there is an excellent linear correlation (Figure 2, the solid line) for this series of complexes. These findings, in conjunction with previous studies of the complexes of dihalogen systems, demonstrate that charge transfer plays a dominant role in the halogen bonding in these complexes.

For the complexes involving HBr and the carbon-bound bromine molecules (series II), the calculations indicate that the amount of charge transfer is very small or even negligible (in the range of 2–14 me), although there is a rough

Table 3. The amount of charge transfer (Q_{CT}) from ammonia to the bromine-containing molecules as determined by different methods and the electrostatic potentials at different sites.[a]

Complex	Q_{CT} [e] (Mulliken)	Q_{CT} (NPA) [e]		Q_{CT}[e] (Chelpg)	ESP[c] [kcal mol^{-1}]				ESP[d] [kcal mol^{-1}]				
		BS1[b]	BS2[b]		R = 1.95 Å	R = 1.85 Å	R = 1.54 Å	ρ = 0.001 au	ρ = 0.002 au[e]	ρ = 0.002 au[f]	ρ = 0.003 au	ρ = 0.005 au	ρ = 0.008 au
F–Br···NH_3	0.07036	0.14923	0.12376	0.24461	53.10	61.67	105.81	56.72	74.90	79.20	88.47	111.16	139.71
Cl–Br···NH_3	0.02854	0.10786	0.08242	0.25285	40.67	48.06	87.54	37.89	51.55	53.08	62.57	81.24	104.58
Br–Br···NH_3	0.02055	0.09159	0.07373	0.24356	35.68	42.60	80.27	32.00	44.20	42.24	54.11	71.01	93.34
HO–Br···NH_3	0.02969	0.06280	0.05527	0.15411	34.99	42.05	80.48	32.62	45.85	50.47	56.66	75.15	98.44
NH_2–Br···NH_3	0.01627	0.02036	0.01958	0.09356	20.19	25.96	59.50	15.61	24.99	27.66	30.69	47.65	66.65
H–Br···NH_3	0.00318	0.00482	0.00581	0.13105	20.18	23.79	57.01	15.91	24.37	24.41	31.52	44.07	61.12
CH_3–Br···NH_3	0.01108	0.00630	0.00544	0.08299	8.94	13.66	43.02	4.37	11.11	10.35	17.29	28.56	44.56
CH_2F–Br···NH_3	0.01082	0.00739	0.00677	0.10580	17.14	22.35	53.38	12.25	19.82	19.39	26.65	42.91	61.01
CHF_2–Br···NH_3	0.01042	0.00975	0.00972	0.13010	25.10	30.83	63.72	20.13	28.94	29.16	36.70	50.26	67.98
CF_3–Br···NH_3	0.01214	0.01389	0.01541	0.15186	33.98	40.34	75.47	29.44	39.98	41.09	48.57	63.27	82.78
$MeCH_2$–Br···NH_3	0.00934	0.00579	0.00478	0.09506	5.75	10.21	38.66	1.17	7.15	6.78	12.75	23.57	38.66
Me_2CH–Br···NH_3	0.00640	0.00577	0.00452	0.09931	3.20	7.44	35.14	−1.28	4.13	4.06	9.31	19.44	33.71
Me_3C–Br···NH_3	0.00248	0.00615	0.00454	0.10041	1.20	5.27	32.39	−3.12	1.72	2.06	6.80	16.50	30.28
$H_2C{=}CH$–Br···NH_3	−0.00322	0.00725	0.00677	0.09244	14.53	19.61	50.21	9.94	17.66	17.04	24.19	36.37	52.61
$HC{\equiv}C$–Br···NH_3	−0.01749	0.01441	0.01502	0.12417	32.36	47.01	94.07	29.46	40.24	40.02	49.45	64.53	84.24
Ph–Br···NH_3	−0.01444	0.00849	0.00770	0.11017	14.02	19.06	49.53	9.63	17.12	16.48	23.97	36.28	52.74
4-NH_2-Ph–Br···NH_3	−0.01656	0.00737	0.00722	0.10242	9.28	14.11	43.82	5.01	11.99	11.25	18.49	30.28	46.17
4-F-Ph–Br···NH_3	−0.01514	0.00891	0.00863	0.11110	17.28	22.47	53.40	12.90	20.74	20.42	27.49	40.00	56.64
4-NO_2-Ph–Br···NH_3	−0.01819	0.01117	0.01015	0.12032	25.49	31.04	63.22	21.07	29.50	29.44	37.15	50.00	67.41
4-pyridine–Br···NH_3	−0.00872	0.00992	0.00920	0.11962	20.93	26.31	57.91	16.50	24.53	22.60	31.87	44.87	61.20
HC(O)–Br···NH_3	0.00271	0.00668	0.00630	0.10849	21.21	26.57	57.92	15.73	23.46	24.17	30.22	42.17	58.72
$CH_3C(O)$–Br···NH_3	0.01972	0.00196	0.00505	0.04438	14.11	18.96	48.69	8.69	15.18	14.58	21.35	32.57	47.93

[a] All values refer to the results obtained at the MP2/Aug-cc-PVDZ level of theory unless otherwise specified. [b] BS1: MP2(full)/Aug-cc-PVDZ; BS2: MP2(full)/Lanl2DZ*. [c] The electrostatic potentials along the R–Br axis corresponding to different distances from the bromine atom. [d] The electrostatic potentials along the R–Br axis corresponding to different electron densities. [e] BS1. [f] BS2.

linear correlation between the interaction energies and the amount of charge transfer, as presented in Figure 2 (the dotted line). However, it is evident that this correlation deviates from that for the complexes of series I. These results, together with the literature data for some of the complexes in series II, provide evidence that the halogen bonding in these complexes mainly results from an electrostatic contribution rather than from charge transfer.

Molecular electrostatic potentials not only allow a qualitative understanding of the electrostatic charge distribution within a molecule, but they have also been proven to be very effective for quantitatively predicting various noncovalent interactions, such as hydrogen bonding[37] and cation–π interactions.[38] To gain a deeper insight into the electrostatic contribution to the binding energy, and especially to seek an optimal measure of the electrostatic contribution in bromine-containing molecules, the electrostatic potentials at some given sites have been calculated for the monomer RBr. In view of the relatively good linearity of the R–Br···N arrangement in the halogen-bonded complexes, we considered first the point along the R–X bond vector at which the distance from the bromine atom is equal to the VDW radius of bromine (1.95 Å, Pauling's definition).[39] For those complexes that are not perfectly linear, the corresponding point along the Br···N axis was considered for each complex. It appears that the calculated ESP values at these two different points are almost equivalent (the relative difference is no more than 5%) except for in the MeCOBr···NH_3 complex which has a somewhat large difference due to a significant deviation of R–Br···N from linearity (vide supra). As the position along the R–X bond vector is easier to locate and independent of the geometry of the complex, the electrostatic potential at a given point along this axis is thought to be a good parameter for describing the electrostatic contribution of the bromine atom in the bromine-containing species.

For comparison, the Bondi radius of bromine[39] and that established by Nyburg and Faerman,[40] 1.85 and 1.54 Å, respectively, were also used in the calculations of the electrostatic potentials. The latter is considerably smaller than the Bondi and Pauling radii as the so-called "polar flattening effect"[10] of the halogen atoms has been taken into account. Moreover, we also computed the electrostatic potentials at the points along the R–Br axis at which the electronic densities correspond to 0.001, 0.002, 0.003, 0.005, and 0.008 au, respectively. The *ESP* values calculated by the MP2/Aug-cc-PVDZ method at the above-mentioned sites are also listed in Table 3. We can see from these data that the electron density at the site along the R–Br axis at which the distance from the bromine atom in RBr is equal

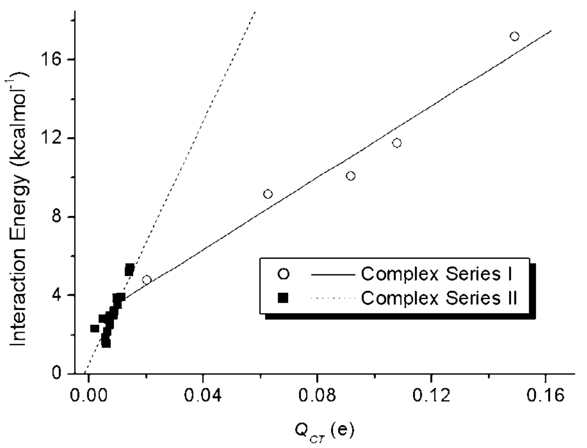

Figure 2. The interaction energy as a function of the amount of charge transfer.

to Pauling's VDW radius for bromine lies between 0.002 and 0.003 au, and is between 0.003 and 0.005 au at a distance equal to Bondi's radius and between 0.005 and 0.008 au at a distance equal to Nyburg and Faerman's radius. However, despite their different definitions and the fact that they correspond to different electronic densities, the electrostatic potentials at these sites are shown to closely correlate with one another (the correlation coefficients are all greater than 0.98). This means that these electrostatic potentials, which have been derived by using different criteria, whether distance-based or density-based, are almost equally effective when used to describe the relative electrostatic contribution to the halogen bonds. In particular, the so-called "polar flattening effect", although helpful to our understanding of the experimentally observed halogen-bonded geometries,[10,41] is completely unimportant for describing the electron-accepting propensities of the halogen-containing molecules.

For the complexes of series II, correlation analyses were carried out on the interaction energies and the derived electrostatic potentials. Good linear relations were obtained and the density-based electrostatic potentials yield slightly better results than those obtained by the distance-based methods. In fact, the electrostatic potentials on the isodensity contour maps, especially on the 0.001 au electron-density contour, which is commonly viewed as the molecular surface,[42] have been proven to be very suitable for describing the molecular electrostatic distribution and the underlying derived parameters have been successfully used to characterize the hydrogen-bond-donating or -accepting abilities of a compound.[43–45] However, for some of the bromine-containing molecules considered, the electrostatic potentials that correspond to an electron density of 0.001 au along the R$-$Br axis are negative and their interactions with ammonia are predicted to be repulsive, whereas the electrostatic potentials corresponding to an electron density of 0.002 au are all positive and so their use in the evaluation of the electrostatic contribution of the halogen-containing species to the halogen bonding seems more appropriate. Moreover, in some previous publications,[46,47] the 0.002 au electron-density contour has indeed been designated as the molecular surface. For these reasons, the electrostatic potentials that correspond to the 0.002 au electron density along the R$-$X axis are considered to be the optimal descriptor of the electrostatic contribution to the binding energy and will, accordingly, be used in the following discussion.

Figure 3 presents a plot of the interaction energy versus the calculated $ESP_{0.002}$ value. Although there is a pretty good linear correlation for the complexes of series I (the solid line), again, the relation is different to that for the complexes of series II (the dotted line). It can be readily appreciated from Figure 3 that the interaction energies for the complexes of series I will be underestimated by the relationship established for the complexes of series II, which demonstrates, from another aspect, that charge transfer may play a crucial role in the halogen bonding in the complexes that involve dihalogen, HOX, and NH_2X molecules as electron acceptors. Note here that although the $NH_2Br\cdots NH_3$ complex exactly conforms to the correlations for the complexes of series I, it does not deviate seriously from those established for the complexes of series II (see Figure 2 and Figure 3). This suggests that charge transfer and electrostatic interactions may play an approximately equal role in determining the halogen-bond strength in this complex.

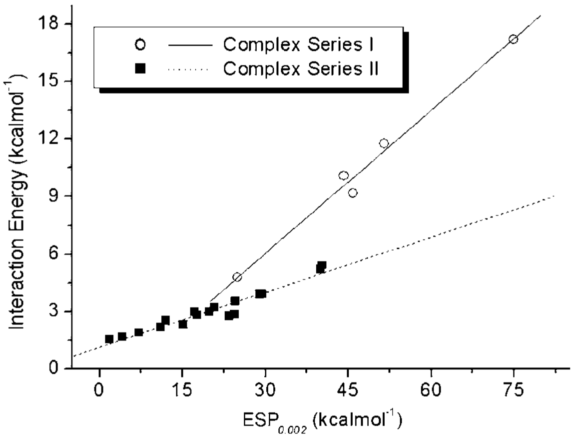

Figure 3. The interaction energy as a function of the electrostatic potential corresponding to an electron density of 0.002 au along the R$-$X axis.

In view of the importance of both charge transfer and electrostatic contributions, a two-parameter model that relates the interaction energy with the amount of charge transfer and the electrostatic potential has been established [Eq. (1)]. The multiple correlation coefficient is as high as 0.998. Figure 4 (the solid line) presents the relationship between the calculated ΔE_{HalB} values and those predicted by Equation (1).

$$\Delta E_{\mathrm{HalB}} = 64.1032 Q_{\mathrm{CT}} + 0.0857 \mathrm{ESP}_{0.002} + 0.8507 \\ N = 22,\ R = 0.998,\ Sd = 0.2813 \tag{1}$$

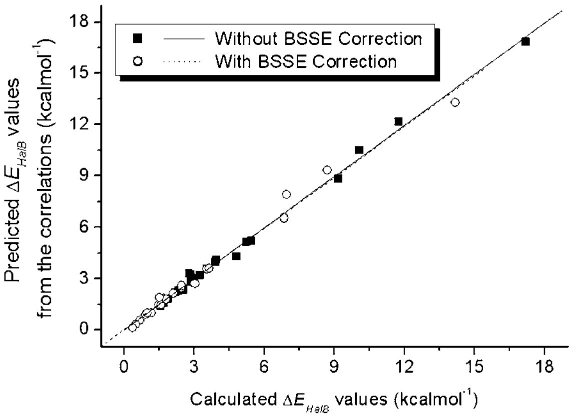

Figure 4. Plots of the interaction energies calculated by the MP2/Aug-cc-PVDZ method with and without BSSE correction versus those predicted by Equation (1) and Equation (2).

This excellent two-parameter correlation indicates that almost all the variations in the binding energy can be explained by the charge transfer and the electrostatic terms, and it also provides a good quantitative model with which to evaluate the electron-accepting propensities of the covalently bonded halogen atoms. Furthermore, we considered the effect of including the BSSE correction, and obtained a correlation equation [Eq. (2)] as high in quality as Equation (1) (see Figure 4, the dotted line).

$$\Delta E_{\mathrm{HalB}}{+}\mathrm{BSSE} = 51.6111Q_{\mathrm{CT}}{+}0.0790\mathrm{ESP}_{0.002}{-}0.3232 \quad (2)$$
$$N = 22,\ R = 0.994,\ Sd = 0.3686$$

This equation predicts the electrostatic contribution to be slightly more important than does Equation (1); it does not, however, actually affect the evaluation of the electron-accepting ability of RBr. We also considered the method-dependence, that is, the results obtained at the MP2/Lanl2DZ* level of theory. The resulting excellent correlations, Equation (3) and Equation (4), were not drastically different to those obtained at the MP2/Aug-cc-PVDZ level of theory, which further supports the rationality of the results obtained by this relatively low-level method.

$$\Delta E_{\mathrm{HalB}} = 72.4340Q_{\mathrm{CT}}{+}0.1051\mathrm{ESP}_{0.002}{-}0.1272 \quad (3)$$
$$N = 22,\ R = 0.998,\ Sd = 0.2477$$

$$\Delta E_{\mathrm{HalB}}{+}\mathrm{BSSE} = 53.8153Q_{\mathrm{CT}}{+}0.0997\mathrm{ESP}_{0.002}{-}0.8350 \quad (4)$$
$$N = 22,\ R = 0.998,\ Sd = 0.2190$$

Similarly, the halogen-bonded complexes of chlorine- and iodine-containing molecules with ammonia have been examined. Table 4 gives the calculated Q_{CT} and $\mathrm{ESP}_{0.002}$ values for these complexes. These data clearly indicate that both the amount of charge transfer and the electrostatic potential at the position along the R–X axis with an electron density of 0.002 au increase in the order RI > RBr > RCl. Note that the $\mathrm{ESP}_{0.002}$ values for the $(CH_3)_nCH_{3-n}Cl$ ($n = 1$–3) complexes are quite small or negative, which suggests that the electrostatic interactions in these three complexes, whilst not repulsive as the electrostatic potentials suggest, are basically negligible. This, together with very small amounts of charge transfer, indicates that their halogen-bond strengths are fairly weak, which is in accordance with the calculated interaction energies. Quantitatively, excellent relationships between the interaction energy and both the amount of charge transfer and the electrostatic potential have also been ob-

Table 4. The calculated Q_{CT} and $ESP_{0.002}$ values for the RCl···NH_3 and RI···NH_3 complexes.

	RCl···NH_3 (Aug-cc-PVDZ)		RI···NH_3 (Lanl2DZ*)	
R =	Q_{CT} (NPA) [e]	$\mathrm{ESP}_{0.002}$ [kcal mol$^{-1]}$]	Q_{CT} (NPA) [e]	$\mathrm{ESP}_{0.002}$ [kcal mol$^{-1]}$]
F-	0.13762	60.88	0.10340	91.49
Cl-	0.05722	39.15	0.09258	72.35
Br-			0.08527	60.91
I-			0.06999	48.10
HO-	0.03303	33.55		
H_2N-	0.00861	15.67		
H-	0.00151	14.62	0.01310	37.90
H_3C-	0.00156	3.84	0.01194	24.54
FH_2C-	0.00155	13.81	0.01399	33.00
F_2HC-	0.00358	23.33	0.01869	42.65
F_3C-	0.00529	33.59	0.02850	56.41
MeH_2C-	0.00153	0.60	0.01036	20.04
Me_2HC-	0.00164	−1.99	0.00971	16.32
Me_3C-	0.00190	−3.96	0.00969	13.68
$CH_2{=}CH$-	0.00237	10.74	0.01335	31.00
$HC{\equiv}C$-	0.00559	31.72	0.02647	54.13
phenyl-	0.00298	10.33	0.01482	30.33
4-NH_2-phenyl-	0.00260	5.13	0.01389	24.73
4-F-phenyl-	0.00326	13.64	0.01635	34.39
4-NO_2-phenyl-	0.00418	22.77	0.01902	43.84
4-pyridyl-	0.00376	17.83		
HC(O)-	0.00179	18.90		
MeC(O)-	0.00007	11.38		

tained [Eq. (5) and Eq. (6)]. A comparison of Equation (1) with Equation (5) (the Aug-cc-PVDZ level), in combination with the comparison of Equation (3) with Equation (6) (the Lanl2DZ* level), reveals that the relative contribution of the charge transfer component to the halogen bonding becomes more important on going from RCl to RBr to RI.

$$\mathrm{RCl}\cdots\mathrm{NH_3}: \Delta E_{\mathrm{HalB}} = 55.2261 Q_{\mathrm{CT}} + 0.0789\,\mathrm{ESP}_{0.002} + 0.3163 \quad N = 21,\ R = 0.997,\ Sd = 0.2389 \tag{5}$$

$$\mathrm{RI}\cdots\mathrm{NH_3}: \Delta E_{\mathrm{HalB}} = 100.8081 Q_{\mathrm{CT}} + 0.0873\,\mathrm{ESP}_{0.002} - 0.1936 \quad N = 18,\ R = 0.996,\ Sd = 0.4770 \tag{6}$$

Halogen bonding in charged halogen-containing systems: It has been revealed in previous studies[19,31a] of hydrogen bonds that when one of the two partners in a complex bears an electric charge, the hydrogen bond is considerably stronger than the corresponding neutral complex. This so-called charge-assisted hydrogen bond can even have an interaction energy of as much as 40 kcal mol^{-1} (e.g., the $[\mathrm{F{-}H\cdots F}]^-$ system[48]). To elucidate the influence of charge on halogen bonding, especially on the electron-accepting abilities of the halogen atom when the system is positively charged, several complexes involving chlorine- and bromine-containing cations have been designed, although some of them may rarely be observed in real systems. The six halogenated carbocations and eight halogenated alkylammonium cations that have been studied in this work are presented in Table 5, together with the calculated interaction energies (with and without BSSE correction), the internuclear X···N distances, the amount of charge transfer, and the electrostatic potentials (0.002 au). As one would expect, the charged complexes have reasonably short intermolecular X···N distances (< 3.0 Å) and large interaction energies, which demonstrates that charge has a significant effect on the halogen bonding. This behavior very much resembles that of hydrogen bonds.[31a] The halogen bonds of the $\mathrm{CH_2^+{-}X\cdots NH_3}$ complexes have the greatest charge; their strengths (uncorrected interaction energies) are predicted to be 15.40 kcal mol^{-1} for X = Cl and 18.26 kcal mol^{-1} for X = Br, which are comparable to those of dihalogen systems. The halogen-bond strengths become somewhat weaker as methyl groups replace the hydrogen atoms bonded to the carbocations owing to the hyperconjugation effects of the methyl group on the carbocations. For instance, the ΔE_{HalB} values for the $\mathrm{CH_3CH^+{-}Cl}$ and $\mathrm{(CH_3)_2C^+{-}Cl}$ complexes are calculated to be 13.12 and 9.46 kcal mol^{-1}, that is, lower than that of the $\mathrm{CH_2^+{-}Cl\cdots NH_3}$ complex by 2.3 and 5.9 kcal mol^{-1}, respectively. Similarly, we examined some halogen-containing ammonium systems. The results indicate that the interaction energies of the halogen-bonded complex of the chloromethylammonium system and its bromo analogue are 8.46 and 11.73 kcal mol^{-1}, respectively. As the distance between the halogen atom and the positively charged nitrogen atom in the ammonium cation increases, the strengths of the halogen bonds weaken significantly; for example, the ΔE_{HalB} values for the complexes of $\mathrm{NH_3^+{-}CH_2Cl}$ and $\mathrm{NH_3^+{-}CH_2CH_2Cl}$ are 8.46 and 5.86 kcal mol^{-1}, respectively, and the intermolecular Cl···N distances are 2.86 and 2.94 Å, respectively. In addition, some aromatic systems have also been investigated. Our calculations predict that the interaction energies of the complexes of the 4-$\mathrm{NH_3^+}$-chlorobenzene and 4-Cl-pydridinium cations are 5.34 and 7.61 kcal mol^{-1}; these interaction energies are 4.3 and 5.7 kcal mol^{-1}, respectively, higher than the ΔE_{HalB} values of the corresponding neutral complexes.

In the same way, we computed the amount of charge transfer in these charged complexes and the electrostatic potentials of the halogen-containing monomers. Although the additional positive charge alters greatly the electrostatic potentials of the halogen-containing molecules, it does not change the nonspherical distribution of the electrostatic potential on the surface of the halogen atom. The most positive electrostatic potentials are still concentrated at the head of the C–X axis, which is consistent with the good linearity of the C–X···N arrangement in these charged complexes. As for the charge transfer, it has been noted that the Q_{CT} values, despite being larger than those for the corresponding neutral complexes, are remarkably lower than those of the neutral complexes of comparable strengths (cf. the data in Table 4 and Table 5). This allows us to conclude that for the charged halogen-bonded complexes,

Table 5. The charged systems studied, together with their calculated interaction energies (with and without BSSE correction), internuclear distances, amount of the charge transfer, and the electrostatic potentials at an electron density of 0.002 au along the R–X axis.

RX	d(X···N) [Å]	ΔE_{HalB} [kcal mol^{-1}]	ΔE_{HalB} + BSSE [kcal mol^{-1}]	Q_{CT} [e]	$\mathrm{ESP}_{0.002}$ [kcal mol^{-1}]
$\mathrm{CH_2^+}$-Cl	2.7528	15.40	14.22	0.01859	154.52
$\mathrm{CH_2^+}$-Br	2.7493	18.26	16.10	0.03350	158.60
$\mathrm{CH_3CH^+}$-Cl	2.7907	13.12	11.99	0.01638	139.97
$\mathrm{CH_3CH^+}$-Br	2.7728	15.99	13.91	0.03131	144.59
$\mathrm{(CH_3)_2C^+}$-Cl	2.8172	9.46	8.36	0.01565	108.72
$\mathrm{(CH_3)_2C^+}$-Br	2.7187	13.08	10.91	0.03947	116.08
$\mathrm{NH_3^+}$-$\mathrm{CH_2Cl}$	2.8559	8.46	7.48	0.01331	106.61
$\mathrm{NH_3^+}$-$\mathrm{CH_2Br}$	2.7705	11.73	9.75	0.0324	113.69
$\mathrm{NH_3^+}$-$\mathrm{CH_2CH_2Cl}$	2.9436	5.86	5.00	0.00924	82.55
$\mathrm{NH_3^+}$-$\mathrm{CH_2CH_2Br}$	2.8496	8.69	6.89	0.02380	89.97
4-Cl-pyridinium	2.8901	7.61	6.57	0.01182	98.04
4-Br-pyridinium	2.8157	10.43	8.47	0.02822	104.95
4-$\mathrm{NH_3^+}$-chlorobenzene	2.9702	5.34	4.37	0.00810	75.21
4-$\mathrm{NH_3^+}$-bromobenzene	2.8965	7.69	5.91	0.01989	82.05

the major contribution comes from electrostatic interactions.

Like the neutral complexes, good two-parameter models have also been developed to relate the binding energies of the charged complexes to the amount of charge transfer and the electrostatic potentials [Eq. (7) and Eq. (8)].

$$\begin{aligned} X = Cl: \Delta E_{HalB} &= 1.3621 Q_{CT} + 0.1281 ESP_{0.002} - 4.7110 \\ N &= 7,\ R = 0.996,\ Sd = 0.3976 \end{aligned} \quad (7)$$

$$\begin{aligned} X = Br: \Delta E_{HalB} &= 47.2827 Q_{CT} + 0.1304 ESP_{0.002} - 4.2311 \\ N &= 7,\ R = 0.997,\ Sd = 0.3631 \end{aligned} \quad (8)$$

Whereas the coefficients of the $ESP_{0.002}$ term in these two equations are larger than those in the equations established above (Equations (5) and (1), respectively) for the neutral complexes, those of the Q_{CT} term are smaller. Hence the overwhelming contribution of the electrostatic interaction to the halogen bonding in the charged complexes is further confirmed.

Finally, it is worth pointing out here that the energy decomposition analysis of interaction energies using the popular Morokuma method[49] and other approaches, such as the block-localized wave-function method,[50] may similarly provide an insight into the nature of halogen bonding. However, we believe that the correlation models established in this work will help to improve our understanding of the electron-accepting abilities of halogen atoms in different chemical environments.

Conclusions

A series of halogen-bonded complexes formed between covalently-bonded halogen atoms and a representative electron donor, ammonia, have been examined at different levels of theory to gain a deeper insight into halogen bonding. The theoretical calculations described herein have demonstrated that for halogen-bonded systems involving dihalogen molecules as well as HOX, the charge-transfer-type contribution is predominant in halogen bonding, whereas for complexes RX, where R = H, H_3C, FH_2C, F_2HC, F_3C, $CH_2{=}CH$, HC≡C, HC(O), MeC(O), phenyl, 4-NH_2-phenyl, 4-F-phenyl, 4-NO_2-phenyl, and 4-pyridyl, the interaction energy mainly stems from electrostatic interactions. The results for the NH_2X complex indicate that charge transfer and electrostatic interactions play an approximately equal role in determining the halogen-bond strength.

For carbon-bound halogen systems, the influence of the hybridization state of the carbon atom bonded to the halogen and substitution upon the electron-accepting ability of the halogen atom has been explored. It has been disclosed that 1) sp-hybridized carbon-bound halogen atoms form the strongest halogen bond, followed by sp^2- and then sp^3-hybridized carbon-bound halogen atoms, which very much resembles the behavior of the corresponding hydrocarbons as hydrogen-bond donors; 2) whereas the halogen-bond strength is significantly enhanced by progressive fluorine substitution, the substitution of a hydrogen atom by a methyl group in the $CH_3X\cdots NH_3$ complex weakens the halogen bonding in the $CH_3X\cdots NH_3$ complex; 3) the remote substituent effect also works although it is less significant. Finally, some positively charged systems have been investigated to explore the effect of charge on halogen bonding. As expected, the charged complexes have significantly larger interaction energies than the corresponding neutral complexes, which indicates the electrostatic nature of the halogen bond in carbon-bound halogen systems.

Acknowledgements

The authors are grateful to the Natural Science Foundation of China (Project No. 20173050) and the Ph.D. Fund of Ningbo (Project No. 2004A610010) for financial support.

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Received: September 8, 2004