Origin of the X−Hal (Hal = Cl, Br) Bond-Length Change in the Halogen-Bonded Complexes

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The origin of the X−Hal bond-length change in the halogen bond of the X−Hal···Y type has been investigated at the MP2(full)/6-311++G(d,p) level of theory using a natural bond orbital analysis, atoms in molecules procedure, and electrostatic potential fitting methods. Our results have clearly shown that various theories explaining the nature of the hydrogen bond cannot be applied to explain the origin of the X−Hal bond-length change in the halogen bond. We provide a new explanation for this change. The elongation of the X−Hal bond length is caused by the electron-density transfer to the X−Hal σ^* antibonding orbital. For the blue-shifting halogen bond, the electron-density transfer to the X−Hal σ^* antibonding orbital is only of minor importance; it is the electrostatic attractive interaction that causes the X−Hal bond contraction.

Introduction

Noncovalent interactions between molecules play a very important role in supramolecular chemistry, molecular biology, and material science. Among the various types of intermolecular interactions, the hydrogen bond is, without doubt, the most important one.[1−4] The hydrogen bond is most frequently defined as an X−H···Y interaction, where X and Y are electronegative elements and Y possesses one or more lone electron pairs. Despite some initial controversy, it is now generally accepted that the C−H···π interaction is also a kind of hydrogen bonding, although the electronegativity of C is almost the same as that of H and the proton acceptor does not have lone-pair electrons.[3] This means that a hydrogen bond, in fact, should be defined as a bond between electron-deficient hydrogen and a region rich in electron density.[5] Besides the hydrogen bond, there are also other important noncovalent interactions. The interaction between the halogen atom and the electron donor was first reported by Guthrie in 1863,[6] but the key role of the halogen bond (X−Hal···Y−Z) in molecular recognition, crystal engineering, and biomolecular systems has only been revealed recently.[7−25] Considering, however, that the halogen atom (Hal) and the halogen-bond electron donor (Y) are negatively charged, the very existence of a halogen bond is surprising. The problem was explained by Auffinger et al.,[10] Politzer et al.,[11] and Clark et al.,[12] who showed the existence of an electropositive crown called the σ-hole (the region of positive charge) at the top of the halogen atom directed toward the electron donor (Y). Like hydrogen-bonded complexes, halogen-bonded complexes were originally classified as charge-transfer complexes in which the charge-transfer is considered to be the dominant factor in determining the complex structure. Now, we know that neither for the hydrogen bond nor for the halogen bond may the consideration of only the charge-transfer interaction be sufficient in describing their ground-state stabilization and the electrostatic effect; polarization, charge-transfer, and dispersion contributions all play an important role.[13] The nature of the halogen bond including symmetry-adapted perturbation theory (SAPT) analyses has recently been investigated in our laboratory.[14] Resnati et al. have defined the halogen bond as a bond in which the halogen atom is an acceptor of electron density, which is similar to the general definition of a hydrogen bond.[15] Extensive studies have shown that many properties of the halogen bond are analogous to those of the hydrogen bond;[7−10,15−25] hence, we can apply the existing explanations for the hydrogen-bond phenomena to the behavior of the halogen bond, and vice versa. This can help us gain new insight into the nature of the two types of molecular interactions.

Formation of the hydrogen bond is connected with the spectral shift, whether it be red or blue.[26,27] Accordingly, formation of the halogen bond is connected with the red- or blue-shift of the X−Hal stretching frequency.[16] In crystal engineering, polyhaloalkanes are frequently used as halogen-atom donors. This is because the higher the number of the electron-withdrawing atom, the stronger the halogen bond. As we know, the presence of the electron-withdrawing atom or group always results in a blue-shifting halogen bond.[16] Consequently, the blue-shifting phenomena should be very common in these halogen-bonded complexes. Furthermore, it has also been noticed that the magnitude of the contraction of the X−Hal bond in the blue-shifting halogen bond is generally high. For example, a large contraction (0.0245 Å) of the Si−Cl bond was observed in the halogen-bonded complex $F_3Si{-}Cl\cdots Br^-$.[16] Zou and co-workers also found that “the blue-shifting phenomenon for halogen-bonded complexes is more frequent than one might expect”.[17] However, to the best of our knowledge, there is still no experimental report of the blue-shifting halogen bond up to know.[22−25] There are mainly two reasons. (a) Iodoperfluoroalkanes are always used as halogen-atom donors in the halogen-bonding-based crystal engineering,[23−25] but the C−I bond length always becomes longer upon the halogen-bond formation because of the strong electron-accepting ability of the C−I σ^* antibonding orbital.[21] For example, in the $F_3C{-}I\cdots NH_3$ complex, over 75% of the electron-density transfer goes into the C−I σ^* antibonding orbital.[28] The significant increase of electron density in the C−I antibonding orbital results in the C−I bond elongation and the corresponding red-shift of the C−I

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stretching frequency. (b) The X−Hal bond length is also elongated in most cases upon the halogen-bond formation if the electron-donating ability of the halogen-atom acceptor is strong enough to force the electon density transfer into the X−Hal σ^* antibonding orbital.[22]

The origin of the X−H bond-length change of the hydrogen bond has now become clear although previous explanations were not general enough to apply in other cases.[26−27,29−35] For the halogen bond, the situation is different. The explanation for the red-shifting halogen bond is similar to the explanation of the red-shift in the hydrogen bond. The intermolecular or intramolecular charge transfer is directed to the X−Hal σ^* antibonding orbital, which causes the weakening of the bond and its elongation followed by a red-shift of the X−Hal stretch frequency. In this case, the charge-transfer plays a dominant role. The problem is in accounting for the blue-shifting halogen bond. Four different theories based on the hydrogen bond should be considered. The first one attributes the X−H bond contraction to the negative dipole moment derivative of the proton donor.[29,30] Schlegel et al., however, suggested that the Pauli repulsion between two fragments leads to compression of the X−H bond, and the orbital interactions cause X−H bond elongation.[31] The third explanation is based on Bent's rule. The authors have concluded that it is a subtle balance of hyperconjugation and rehybridization that determines the X−H bond-length change.[32] In a very recent paper, Jemmis and Joseph proposed a new explanation for the X−H bond-length change in the hydrogen bond. They argued that it is a net gain of electron density at the X−H bond region that causes an X−H bond contraction, and that the electrostatic interaction between the positive H and the negative Y forces is responsible for X−H bond elongation.[33] Are these explanations applicable to the blue-shifting phenomena or the X−Hal bond-length change in the halogen-bonded complexes? Wong et al. have explained the origin of the blue-shifting halogen bond in a series of fluorine-substituted halogen-bonded complexes employing the permanent dipole moment derivative of the halogen-atom donor,[16] but it is still not known whether the sign of the dipole moment derivative also determines the X−Hal bond-length change in the other halogen-bonded complexes without fluorine substitution. The other three theories have not been examined for the halogen-bonded complexes up to now. The aim of the present study is to investigate and identify the origin of the X−Hal bond-length change.

In general, the bond-length change of the hydrogen bond or the halogen bond correlates with the vibrational frequency shift. It means that the bond shortening is connected with blue-shift, whereas the bond lengthening is connected with red-shift. There are some exceptions arising from computational inaccuracy or the coupling with other vibrational modes.[16,34] In this study, we thus focus only on the X−Hal bond-length change of the halogen bond.

Computational Details

It has been shown that the X−H bond-length change in the hydrogen bond at equilibrium structure quite strongly depends on the computational method.[35] Electron correlation calculations with extended basis sets are thus required for the study of the bond-length change upon complex formation. In the present study, unless stated otherwise, structures and energies of the monomers and dimers were determined at the second-order Møller-Plesset theory (MP2) with the 6-311++G(d,p) basis set. The basis set superposition error (BSSE) was eliminated by using the standard counterpoise (CP) correction method of Boys and Bernardi.[36] The inner-shells were systematically included. The dimer structures were optimized by the CP-corrected gradient optimization, where the BSSE was eliminated in each gradient cycle. The use of CP-corrected geometry and energy calculations with the 6-311++G(d,p) basis set ensured the high quality of theoretical results, which were supposed to be close to real values.

The definition of atomic charge is always arbitrary. In order to avoid the flaw of their arbitrary definition, the atomic charges were evaluated at the MP2(full)/6-311++G(d,p) level of theory using four different methods: Mulliken populations, natural-bond orbital analyses (NBO),[37] electrostatic potential fitting method (ChelpG),[38] and the atoms in molecules (AIM)[39] procedure.

Ab initio calculations were performed using the Gaussian 03 suite of programs.[40] The NBO analyses, Mulliken population analyses, ChelpG fitting, and AIM analyses were carried out with the built-in subroutines of the Gaussian 03 program.

The halogen-atom donors studied in this paper are mainly a series of fluorine-substituted or unsubstituted halocarbons and the halogen-atom acceptors are H_2O, NH_3, and Br^-. Besides the C−Hal···Y systems, we have also studied the Si−Hal···Y, N−Hal···Y, and O−Hal···Y systems. Fluorocarbons are poor halogen-bonding donors, and iodoperfluoroalkanes are always involved in the red-shifting halogen bond; thus, we considered only X−Hal···Y (X = Cl, Br) systems in the present study.

Results and Discussion

Monomers. The nature of the hydrogen bond is determined by the properties of the proton donor as well as of the proton acceptor. It means that replacing the proton acceptor (with the same proton donor) can result in both red-shifting and blue-shifting hydrogen bonds. In this section, we investigate only the halogen-atom donors. In particular, we attempt to answer the question of which halogen-atom donor forms the blue-shifting halogen bond and which forms the red-shifting bond.

Table 1 summarizes the atomic charges calculated by means of four different methods and the permanent dipole moment derivatives for different halogen-atom donors. The changes of the C−Hal bond lengths for these systems and the corresponding interaction energies upon their complexation with NH_3 are also shown. When investigating the change of the C−Hal bond upon complexation, we found that the majority of complexes exhibit bond contraction, which means that these complexes are characterized by a blue-shifting halogen bond. Table 1 further shows that only the F_3CCl and F_3CBr subsystems have a negative dipole moment derivative which was considered as a necessary prerequisite for the formation of the blue-shifting hydrogen bond.[29,30] Evidently, the halogen-atom donors with positive dipole moment derivatives can also form the blue-shifting halogen bond. The sign of the dipole moment derivative is thus not responsible for the X−Hal bond-length change in the halogen bond.

Table 1 shows that charges on the C, Cl, and Br atoms are very sensitive to the methods used. Evidently, the Mulliken charges are not suitable, because the Mulliken charge at the carbon of the F_3CCl system is negative while NBO, ChelpG, and AIM procedures provide highly positive charges. For the fluorine-substituted halocarbons, the ChelpG, NBO, and AIM charges are in very good agreement with each other. On the other hand, for the halocarbons without fluorine substitution, the NBO charges differ from the ChelpG and AIM ones. The agreement between ChelpG and AIM charges is quite good except for some charges which are close to zero. Considering

TABLE 1: Atomic Charges (in e−) Calculated Using Four Different Methods and the Permanent Dipole Moment Derivatives (in D/Å) for Different Halogen-Atom Donors (Changes of the C−Hal (Hal = Cl, Br) bond lengths and the corresponding interaction energies upon their complexing with NH_3 are also listed.)

	Mulliken		NBO		ChelpG		AIM				
monomer	q_C	$q_{Cl(Br)}$	q_C	$q_{Cl(Br)}$	q_C	$q_{Cl(Br)}$	q_C	$q_{Cl(Br)}$	du^0/dr_{C-Hal}	$\Delta r_{(C-Hal)}{}^a$	ΔE^a
H_3C-Cl	−0.588	0.064	−0.518	−0.057	−0.089	−0.178	0.094	−0.237	+2.45	−0.0011	0.52
FH_2C-Cl	−0.391	0.124	0.095	−0.040	0.196	−0.145	0.671	−0.196	+1.11	−0.0034	1.50
F_2HC-Cl	−0.259	0.174	0.581	−0.020	0.348	−0.097	1.291	−0.148	+ or −	−0.0058	2.19
F_3C-Cl	−0.021	0.225	0.986	0.010	0.448	−0.039	1.947	−0.085	−5.27	−0.0063	3.19
MeH_2C-Cl	−0.458	0.102	−0.339	−0.060	0.068	−0.208	0.114	−0.254	+3.03	−0.0029	0.38
Me_2HC-Cl	0.064	0.039	−0.188	−0.060	0.274	−0.234	0.124	−0.267	+3.29	−0.0046	0.27
Me_3C-Cl	0.652	−0.060	−0.053	−0.054	0.455	−0.256	0.128	−0.275	+3.36	−0.0055	0.26
H_3C-Br	−0.386	−0.083	−0.600	0.003	−0.050	−0.161	−0.050	−0.112	+1.77	+0.0009	2.17
FH_2C-Br	−0.200	−0.031	0.035	0.006	0.190	−0.122	0.537	−0.073	+1.00	−0.0045	2.98
F_2HC-Br	−0.076	0.018	0.536	0.018	0.300	−0.068	1.160	−0.024	+ or −	−0.0064	3.89
F_3C-Br	0.091	0.076	0.946	0.051	0.361	−0.002	1.809	0.050	−4.55	−0.0019	5.21
MeH_2C-Br	−0.191	−0.105	−0.409	−0.006	0.033	−0.179	−0.019 (0.105)[b]	−0.138	+2.49	−0.0016	1.88
Me_2HC-Br	0.113	−0.127	−0.246	−0.007	0.192	−0.195	0.001	−0.158	+2.88	−0.0039	1.68
Me_3C-Br	0.382	−0.120	−0.101	−0.001	0.353	−0.209	0.013	−0.171	+3.06	−0.0055	1.54

[a] From ref 17. [b] Obtained by another integration algorithm.

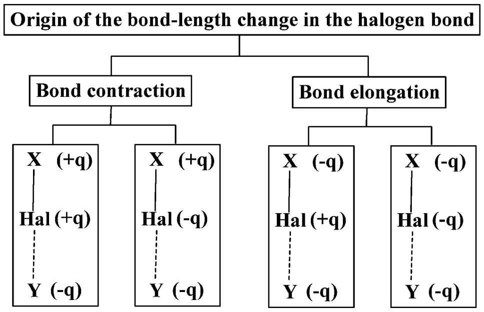

Figure 1. Electrostatic model for the origin of the X−Hal bond-length change in the halogen bond. This model is valid only when there is no or little electron-density transfer to the X−Hal σ* antibonding orbital. The X−Hal bond is elongated if the dominant part of the electron-density transfer is directed toward the X−Hal σ* antibonding orbital.

the H_3CCl and H_3CBr systems, we expect that the carbon charge on the former system should be more positive than that on the latter system. This is due to higher electronegativity of Cl in comparison with Br, which is true for AIM charges, unlike for the ChelpG ones. In the text that follows, we will therefore focus only on the AIM charges.

When investigating the AIM carbon charges, we ascertained that they were all positive with the exception of the H_3CBr system. Table 1 further shows that these charges correlate with the changes of the C−Hal bond length; a positive carbon charge indicates a bond contraction, whereas a negative carbon charge results in elongation. This effect can easily be accounted for by the basic electrostatic principle. As shown in Figure 1, the situation is straightforward when the charge on halogen is negative and that on carbon is positive (which is the most frequent case, see Table 1). The electrostatic repulsion between the halogen atom and the electron-donor atom Y and the simultaneous electrostatic attraction between the carbon atom and the atom Y clearly result in contraction of the C−Hal bond. When the charge on halogen is positive (which happens only in the case of the F_3CBr system, see Table 1), the C−Hal bond is also contracted. In this subsystem, the positive charge on the carbon atom is much higher than the positive charge on the bromine atom, and the simple electrostatic model again explains why the X−Hal bond is contracted. It should be added here that the electron-density transfer to the X−Hal σ* antibonding orbital always weakens the X−Hal bond and elongates it. For the halogen bond shown in Table 1, there is no or little electron-density transfer to the X−Hal σ* antibonding orbital. Analyzing the halogen charges, we found that an increase of negative charge is systematically connected with a decrease in the respective stabilization energy.

Dimers. The formation of a halogen-bonded complex is accompanied by a charge transfer from the halogen-atom acceptor to the halogen-atom donor. Naturally, under the negative electric field, the electron density will be shifted from the halogen atom to X and to the more remote part of the halogen-atom donor. As shown in Table 2, the charges on C all become more negative and the charges on Cl and Br more positive upon complexation. However, the charges on C all still remain positive in the blue-shifting halogen bond and negative in the red-shifting halogen bond. The only exception is the $F_2NCl\cdots Br^-$ complex, and hence the simple electrostatic model fails. Despite the positive charges on both carbon and halogen atoms, the C−Hal bond is elongated. The explanation is based on the very large charge transfer from Br^- to F_2NCl. Table 2 shows that this charge transfer is by far the largest among all complexes studied. The NBO analysis shows that the largest part (70%) of the electron-density transfer goes into the N−Cl σ* antibonding orbital. The significant increase of electron density in the N−Cl antibonding orbital results in substantial N−Cl bond elongation. For other halogen-bonded complexes investigated here, the electron density in the X−Hal σ* antibonding orbital increased only slightly or even decreased. Providing that the charge transfer from the electron donor to the X−Hal σ* antibonding orbital is negligible, the interaction energy correlates well with atomic charges at the Cl or Br atom.

Alabugin et al. have ascribed the X−H bond-length change in the hydrogen bond to a subtle balance between hyperconjugation and rehybridization.[32] When the hyperconjugative interaction is dominant, the X−H bond will lengthen. The X−H bond will shorten if the bond-shortening effect, due to an increase in the s-character and polarization of the X−H bond, overcomes the bond-lengthening effect of the hyperconjugative interaction. Our explanation of the X−Hal bond-length change in the halogen bond is similar. The bond elongation is also attributed to the hyperconjugation. The situation is different for the bond contraction. We have attributed the X−Hal bond contraction to electrostatic attraction (see above) and not to rehybridization. Tables 2 and 3 show that the s-character in the X hybrid orbital in the X−Hal bond increases upon complex formation, and the increase correlates well with the X−Hal bond contraction if the electron-density transfer to the X−Hal σ* antibonding orbital is small. Table 3 presents the second-order

TABLE 2: NBO Charges (in e$^-$) and Their Changes on the C, Cl, and Br Atoms, the Change of the C−Hal Bond Length (in Å), Interaction Energies (in kcal/mol), the Change of the Electron Density, and the Hybridization for the Halogen-Bonded Complexes[a]

dimer	q_C	Δq_C	$q_{Cl(Br)}$	$\Delta q_{Cl(Br)}$	$\Delta \boldsymbol{r}_{(C-Hal)}$	ΔE	ΔED(σ_{C-Hal})	ΔED(σ^*_{C-Hal})	CT	Δs-char(X)
F_3C-**Cl**···**N**H_3	1.127	−0.016	0.024	0.017	**−0.0066**	−2.14	−0.0003	−0.0022	0.0034	+0.82%
F_3C-**Cl**···**O**H_2	1.129	−0.014	0.021	0.014	**−0.0070**	−1.76	−0.0001	−0.0037	0.0013	+0.71%
F_3C-**Cl**···**Br**$^-$	1.099	−0.044	0.087	0.080	**−0.0233**	−7.27	+0.0012	−0.0041	0.0154	+2.68%
F_3C-**Br**···**N**H_3	1.068	−0.024	0.092	0.041	**−0.0047**	−0.92	−0.0007	+0.0003	0.0087	+1.12%
F_3C-**Br**···**O**H_2	1.073	−0.019	0.087	0.036	**−0.0067**	−0.65	−0.0002	−0.0040	0.0026	+0.89%
F_3C-**Br**···**Br**$^-$	1.028	−0.064	0.155	0.104	**−0.0105**	−9.21	+0.0009	+0.0141	0.0443	+3.38%
F_3Si-**Cl**···**N**H_3	2.384	−0.015	−0.364	0.023	**−0.0053**	−1.11	−0.0011	−0.0009	0.0001	+0.60%
F_3Si-**Cl**···**O**H_2	2.385	−0.014	−0.364	0.023	**−0.0055**	−1.04	−0.0014	−0.0014	0.0015	+0.58%
F_3Si-**Cl**···**Br**$^-$	2.343	−0.056	−0.303	0.084	**−0.0245**	−6.06	−0.0005	−0.0025	0.0051	+2.51%
F_2N-**Cl**···**N**H_3	0.306	−0.027	0.202	0.039	**−0.0045**	−3.77	−0.0010	+0.0088	0.0149	+1.52%
F_2N-**Cl**···**O**H_2	0.313	−0.020	0.199	0.036	**−0.0105**	−2.65	−0.0004	−0.0009	0.0036	+1.27%
F_2N-**Cl**···**Br**$^-$	0.267	−0.066	0.232	0.069	+0.0212	−11.74	−0.0010	+0.0611	0.0881	+3.05%
H_3C-**Cl**···**N**H_3[b]	0.091	−0.003	−0.216	0.021	**−0.0012**	0.23	−0.0001	+0.0005	0.0002	+0.35%
H_3C-**Br**···**N**H_3[b]	−0.058	−0.008	−0.081	0.031	+0.0013	−0.64	−0.0008	+0.0034	0.0032	+0.62%

[a] Δs-char(X) is the change of the s-character (%) in the X (X = C, Si, or N) hybrid orbital in the X−Hal bond; ΔED is the change of electron density in the X−Hal σ antibonding orbital; CT is the total charge transfer from the halogen-atom acceptor to the halogen-atom donor. [b] According to the discussion in the Monomer section, we have used AIM charges of the C, Cl, and Br atoms.

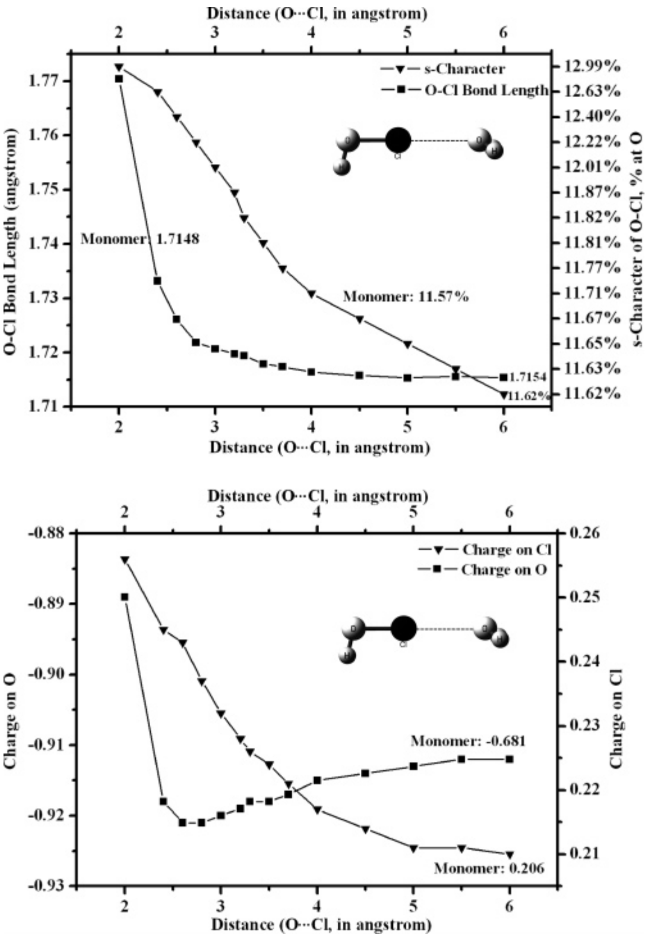

Figure 2. Variation of O−Cl bond length, hybridization at O (HOCl), charge on O (HOCl) or charge on Cl with the distance between O (H_2O) and Cl.

stabilization energies, which are proportional to the hyperconjugative interaction. It seems that the balance between hyperconjugation and rehybridization can explain the X−Hal bond-length change in the halogen bond. However, when we examined the hyperconjugation and rehybridization of two interacting molecules HOCl and H_2O at long distances (Figure 2), we found that the O−Cl bond is elongated despite an increase of the s-character in the oxygen hybrid orbital. Note that there is no hyperconjugative interaction at long distances. Hence the increase in the s-character does not always mean bond contraction. For the $F_2NCl\cdots Br^-$, $F_3CCl\cdots Br^-$, $F_3CBr\cdots Br^-$, and $F_3SiCl\cdots Br^-$ complexes (cf. Table 3), the situation was different. The X−Hal bond was contracted with the increase of the s-character in the X hybrid orbital at long distances. What is the origin of the increase in the s-character? It arises from Figure 2 that the net electron density on Cl decreases and the charge on O increases when H_2O approaches HOCl. The increase of the net electron density increases the s-character in the O hybrid orbital. It must be pointed out that, at very short distances (Figure 2), the O−Cl bond begins to break and the s-character in the O hybrid orbital also increases, because the hybrid orbital of O shifts from sp^3 to sp^2. The change of the electron density on X and Hal is the same for the complexes presented in Table 3. Therefore, we can see that the increase of the s-character in the X hybrid orbital is a result of the increase of the electron density on X and not the origin of the X−Hal bond-length change in the halogen bond.

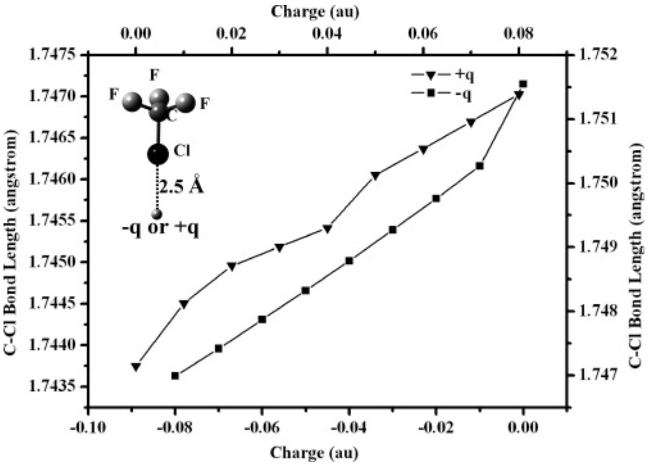

Figure 3. Variation of the C−Cl bond length with the point charge. The distance between Cl and the negative charge is kept constant (2.5 Å).

For the hydrogen-bonded complexes, Schlegel et al. suggested that the Pauli repulsion between two fragments leads to the compression of the X−H bond.[31] Using the interaction of a proton donor with a point charge as a model, they determined that the electrostatic interaction of a negative point charge cannot

TABLE 3: Change of X−Hal Bond Length (in Å), Hybridization, Second-Order Stabilization Energy E^2 (in kcal/mol) or NBO Charge upon Complex Formation with the Distance between Halogen Atom and Y (in Å)

$\mathrm{F_2N}$-**Cl···Br**$^-$

distance (**Cl···Br**$^-$)	$\Delta r_{\mathrm{(C-Cl)}}$	Δs-char(N)	$E^2_{\mathrm{(LP(Br)\rightarrow BD^*(N-Cl))}}$	q_{N}	q_{Cl}
3.0000	+0.0177	+3.05%	17.13	0.268	0.234
3.5000	−0.0175	+2.98%	3.95	0.281	0.253
4.0000	−0.0234	+2.53%	1.00	0.290	0.246
4.5000	−0.0227	+2.13%	0.25	0.298	0.235
5.0000	−0.0206	+1.81%	0.06	0.303	0.224
5.5000	−0.0184	+1.57%	NO	0.307	0.215
6.5000	−0.0145	+1.18%	NO	0.314	0.202

$\mathrm{F_3C}$-**Cl···Br**$^-$

distance (**Cl···Br**$^-$)	$\Delta r_{\mathrm{(C-Cl)}}$	Δ%s-char(C)	$E^2_{\mathrm{(LP(Br)\rightarrow BD^*(C-Cl))}}$	q_{C}	q_{Cl}
2.0888	+0.2870	+5.33%	347.83	0.916	−0.078
2.2888	+0.1188	+4.63%	113.20	1.036	−0.025
2.3888	+0.0709	+4.45%	74.21	1.060	0.003
2.4888	+0.0398	+4.27%	50.43	1.072	0.029
2.5888	+0.0190	+4.08%	35.29	1.080	0.049
2.8888	−0.0114	+3.50%	13.59	1.090	0.081
3.0888	−0.0192	+3.14%	7.58	1.094	0.088
3.2888	−0.0229	+2.83%	4.33	1.097	0.088
3.4888	−0.0244	+2.55%	2.51	1.100	0.086
3.6888	−0.0245	+2.33%	1.45	1.103	0.082

$\mathrm{F_3C}$-**Br···Br**$^-$

distance (**Br···Br**$^-$)	$\Delta r_{\mathrm{(C-Br)}}$	Δ%s-char(C)	$E^2_{\mathrm{(LP(Br)\rightarrow BD^*(C-Br))}}$	q_{C}	q_{Br}
2.3762	+0.1473	+5.56%	150.06	0.932	0.049
2.5762	+0.0732	+4.94%	73.19	0.981	0.091
2.7762	+0.0297	+4.42%	38.02	1.005	0.124
2.9762	+0.0053	+3.95%	20.93	1.017	0.144
3.0762	−0.0023	+3.73%	15.77	1.022	0.150
3.1762	−0.0080	+3.53%	11.96	1.025	0.153
3.2762	−0.0120	+3.34%	9.13	1.028	0.155
3.3762	−0.0152	+3.17%	6.99	1.031	0.156
3.5762	−0.0189	+2.86%	4.15	1.036	0.155

$\mathrm{F_3Si}$-**Cl···Br**$^-$

distance (**Cl···Br**$^-$)	$\Delta r_{\mathrm{(Si-Cl)}}$	Δ%s-char(Si)	$E^2_{\mathrm{(LP(Br)\rightarrow BD^*(Si-Cl))}}$	q_{Si}	q_{Cl}
2.0483	+0.5444	+9.26%	562.93	1.735	−0.227
2.3483	+0.0726	+5.79%	60.64	2.241	−0.325
2.5483	+0.0143	+4.65%	28.12	2.293	−0.311
2.6483	+0.0009	+4.30%	20.32	2.306	−0.306
2.7483	−0.0084	+4.01%	14.96	2.315	−0.302
2.8483	−0.0142	+3.75%	11.18	2.322	−0.300
3.0483	−0.0210	+3.26%	6.40	2.330	−0.296
3.2483	−0.0241	+2.94%	3.76	2.335	−0.297
3.3483	−0.0248	+2.80%	2.89	2.338	−0.299
3.5483	−0.0254	+2.56%	1.72	2.342	−0.302

induce a blue-shift and a repulsive interaction of a positive charge is necessary for the blue-shift of the X−H bond. For the halogen bond, we also employed the point charge model to study the role of the electrostatic interaction. A negative point charge was put on the C−Cl axis of F_3CCl, and the distance between Cl and the negative point charge q was kept constant at 2.5 Å, with the geometries of F_3CCl subsequently fully optimized. As shown in Figure 3, an external negative charge contracts the C−Cl bond. Moreover, the C−Cl bond shortens in proportion to the negative point charge. On the other hand, if we place a positive charge near F_3CCl, the C−Cl bond elongates (Figure 3). It can thus be concluded that the electrostatic (attractive) interaction can be responsible for the blue-shifting halogen bond.

In a recent paper, Jemmis and Joseph provided a uniform explanation for the red-, blue-, or no shift in hydrogen bonds.[33] They claimed that the net gain of electron density at the X−H region encourages an X−H bond contraction, and the electrostatic attractive interaction between the positive H and the negative Y causes an X−H elongation. Allow us first to mention that in the case of a red-shifting hydrogen bond, the net gain of electron density at the X−H region mostly leads to X−H bond elongation. This is due to the fact that the electron-density transfer is directed mainly toward the X−H σ* antibonding orbital, which leads to a weakening of the X−H bond.[37] In addition, we believe that the attraction between H and Y is not strong enough to force X−H bond elongation. The results for the $F_3SiCl\cdots Br^-$ complex (cf. Table 3) clearly support this assumption. The charges on Cl are systematically negative at various distances. They are even more negative at shorter distances, where the Si−Cl bonds are elongated. In order to exclude the computational error caused by the arbitrary nature of charge definition, we also calculated the charges on Si and Cl atoms using the AIM method. The results were almost the same. Evidently, the attraction between Cl and Br^- is not strong enough to force Si−Cl bond elongation. The strong hyperconjugation is thus the only reason for Si−Cl bond lengthening. According to our simple electrostatic model (cf. Figure 1), it is the electrostatic repulsion between Cl and Br^- and the electrostatic attraction between Si and Br$^-$ that cause Si−Cl bond contraction at longer distances.

Conclusion

In this paper, we have provided a new explanation for the origin of the X−Hal bond-length change in the halogen bond. The X−Hal bond-length change upon complex formation is mainly determined by the hyperconjugative and electrostatic interactions. When the hyperconjugative interaction is dominant, the X−Hal bond is elongated. When the hyperconjugative interaction is weak, the electrostatic interaction is responsible for the X−Hal bond-length change of the halogen bond, and the resulting contraction or elongation of the X−Hal bond is determined by the charge on the central atom X. It was also ascertained that the nature and strength of the halogen bond can be predicted on the basis of electrostatic interactions between the atomic charges of the halogen-atom donor and electron donor.

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