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Theoretical Study on the Blueshifting Halogen Bond

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A new type of intermolecular bond, termed a blueshifting halogen bond, is found in the chlorotrifluoromethane-, bromotrifluoromethane-, chlorotrifluorosilicane-, and chlorodifluoroamine-related complexes. Counterpoise-corrected gradient optimization performed at a correlated ab initio level (MP2(full)/6-311++G(d,p)) shows a shortening of the C−Cl (C−Br, Si−Cl, or N−Cl) bond of the proton donor and a blueshifting of the corresponding C−Cl (C−Br, Si−Cl, or N−Cl) stretching frequency. In contrast to the conventional hydrogen bond and the blueshifting hydrogen bond, the topological and electronic properties and the origin of blueshifting halogen bond are also investigated.

Introduction

The number of individual crystal structures, in which weak interactions have been reported to be important, has grown rapidly in recent years.[1−3] By consideration that crystal packing results as the sum of many different contributions of directional and nondirectional intermolecular interactions, it is important that different types of interactions be considered jointly in structure analysis. Although research has traditionally focused on the more well known hydrogen-bonded interactions,[3−6] a growing body of experimental and theoretical evidences confirms that interactions such as −X···Y− (X = Cl, Br, or I; Y = N, O, S, or π) and even interactions such as −X···Y− (X = Cl, Br, or I; Y = Cl, Br, or I) also play distinctive roles in crystal engineering;[7−28] as we know, such interactions are the so-called halogen bonding.

Generally, the hydrogen bond was classified as the $n \rightarrow \sigma^*$ type of charge-transfer (CT) complexes in which the CT effect is thought to be the dominant factor to determine the supramolecular structure.[29] However, the consideration of only the charge-transfer interaction may not be sufficient in describing the ground-state stabilization in halogen-bonding complexes. Allen et al. analyzed the nature of intermolecular interactions between carbon-bonded halogens (C−X, X = F, Cl, Br, or I) and electronegative atoms (N, O, or S) in detail.[15] They concluded that the attractive nature of the interaction is mainly due to electrostatic effects, but polarization, charge-transfer, and dispersion contributions all play an important role and the directionality of halogen···oxygen and halogen···nitrogen contacts is primarily the result of the anisotropic distribution of electron density around the halogen nucleus. Usually, the formation of a hydrogen bond results in an elongation of an X−H bond, which is accompanied by a redshift of the X−H fundamental stretching frequency and increased intensity of the respective X−H band. Recently, a new type of intermolecular bonding, termed blueshifting hydrogen bond, is broadly investigated.[30] The blueshifting hydrogen bond is characterized by a contraction of the X−H bond and a blueshifting of the respective X−H stretching frequency, which is opposite to the conventional hydrogen bond. For the halogen bonding, to the best of our knowledge, there is no report on the blueshifting halogen bond up to now. Although the natures of hydrogen bond and halogen bond are different, it is still significant to research the blueshifting halogen bond and it is also important to compare the blueshifting hydrogen bond with the blueshifting halogen bond in order to find the nature of bond length variation during molecular interaction. So in this paper, we present the results of quantum chemical calculations on a series of halogen-bonded complexes. Note that the halogen atom acceptors used in this paper are simple but representative. As will be seen in the following discussion, the core of the blueshifting halogen bond lies in the halogen atom donors, so for other halogen atom acceptors or their derivatives, results are very similar.

Computational Details

The second-order Møller−Plesset theory (MP2) is applicable to the study of complexes and gives reliable estimates of geometry and interaction energy with moderate basis sets.[31] The 6-31G(d,p) basis set has been proven to produce consistent data on hydrogen bonding previously.[32] But to obtain more reliable calculated results, the basis set applied here is 6-311++G(d,p). The basis-set superposition error (BSSE) was eliminated by the standard counterpoise (CP) correction method of Boys and Bernard.[33] Again, some authors claimed that the normal recipe of counterpoise correction of carrying out a single-point correction using medium basis sets without further optimization could not find the correctly optimized structures and frequencies. They advocated that geometrical parameters, vibrational frequencies, and energies should be determined using explicit BSSE corrections.[34−37] So in the present study, ab initio structures of complexes were determined using counterpoise-corrected gradient optimization at the MP2(full)/6-311++G(d,p) level. No symmetries were constrained in optimizations. The counterpoise-corrected harmonic frequencies were also evaluated for all complexes; no scaling was applied.

The bonding characteristics of the different conformers were analyzed by using the "atoms in molecules" (AIM) theory of Bader,[38] which is based on a topological analysis of the electron

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TABLE 1: Optimized Geometries, Frequencies, Number of Imaginary Frequencies (N_{img}), Interaction Energies (ΔE), and Changes of Dipole Moments ($\Delta\mu$) of Halogen-Bonded Complexes Calculated at the MP2(full)/6-311++G(d,p) Level[a]

halogen-bonded complexes	halogen-donor monomer	complex with halogen acceptor		
		NH_3	OH_2	Br^-
		$F_3C-Cl...YH_n$		
∠C−Cl...Y		179.8	179.9	179.7
Cl...Y		3.2106	3.1123	3.3886
C−Cl	1.7456	1.7390	1.7386	1.7223
freq (C−Cl)	1133.8 (532.5)	1144.6 (475.1)	1143.1 (543.6)	1154.4 (563.1)
N_{img}	0	1	1	0
ΔE		2.14	1.76	7.27
$\Delta\mu$		0.57	0.45	10.19
		$F_3C-Br...YH_n$		
∠C−Br...Y		179.9	179.6	179.7
Br...Y		3.1282	3.0955	3.2489
C−Br	1.9197	1.9150	1.9130	1.9092
freq (C−Br)	1101.2 (557.5)	1117.2 (114.6)	1111.3 (559.6)	1119.5 (536.2)
N_{img}	0	1	1	0
ΔE		3.29	2.45	10.61
$\Delta\mu$		0.92	0.65	9.21
		$F_3Si-Cl...YH_n$		
∠Si−Cl...Y		177.1	177.9	179.3
Cl...Y		3.5274	3.3357	3.5814
Si−Cl	1.9956	1.9903	1.9901	1.9711
freq (Si−Cl)	603.0 (102.2)	606.2 (90.5)	606.8 (88.7)	614.1 (46.0)
N_{img}		0	1	0
ΔE		1.11	1.04	6.06
$\Delta\mu$		0.46	0.42	12.00
		$F_2N-Cl...YH_n$		
∠N−Cl...Y		177.9	178.3	177.0
Cl...Y		2.9039	2.9355	2.9737
N−Cl	1.7562	1.7517	1.7457	1.7774
freq (N−Cl)	733.5 (93.2)	737.3 (60.3)	746.9 (79.9)	662.0 (0.4)
N_{img}	0	0	0	0
ΔE		3.77	2.65	11.74
$\Delta\mu$		0.93	0.56	5.46

[a] Bond lengths are in Å, bond angles in degrees, dipole moment in Debye, interaction energies in kcal/mol, and frquencies in cm^{-1} with IR intensities (in km/mol) in parentheses.

charge density and its Laplacian. The AIM theory has proved itself a valuable tool to conceptually define what an atom is and above all what a bond is in a quantum calculation of a molecular structure. The analysis went further with those obtained by means of the natural bond obital (NBO) theory of Weihnhold and co-workers.[39] The NBO analysis will allow us to quantitatively evaluate the charge transfer (CT) involving the formation of halogen bond.

All ab initio calculations were carried out using the Gaussian 03 suite of programs running on a 2.6-GHz PC.[40] AIM analysis has been performed with the AIM2000 code with all default options.[41] The AIM analysis was performed using the MP2 wave functions as input. NBO analysis used the MP2-optimized structures, the Hartree−Fock (HF) densities, and the built-in subroutines of the Gaussian 03 program.

Results and Discussion

Geometrical Parameters, Interaction Energies, and Vibrational Frequencies. The geometrical parameters and interaction energies for the halogen atom donors and halogen-bonded complexes considered in the present study are given in Table 1. Since it is not the purpose of this paper to systematically explore the potential-energy surface of these complexes, we only concentrate on one halogen-bonded structure for each complex no matter whether it is a minimum or a transition state. All the structures studied in this paper can be seen from Figure 1. Table 1 shows that there is a contraction of the C−Cl, C−Br, Si−Cl, or N−Cl bond upon dimers formation except for the N−Cl bond of $F_2NCl\cdots Br^-$, for which a decrease of 0.0053−0.0245 Å is observed. The calculated interaction energies increase in the order $H_2O < H_3N < Br^-$. This order is reasonable because the gas-phase basicity of the halogen atoms acceptors is in the same order. It is also seen from Table 1 that the dipole moments in the dimers are all larger than the vector sum of the individual moments of the isolated monomers. All these properties behave very much like those of well-studied blueshifting hydrogen bonds.[42]

The corresponding harmonic vibational frequencies and IR intensities are also shown in Table 1. The frequency analysis reveals the blueshifting character of the C−Cl•••Y, C−Br•••Y, Si−Cl•••Y, or N−Cl•••Y interactions in the dimers. The only exception is again the N−Cl bond of $F_2NCl\cdots Br^-$. In agreement with the computed C−Cl, C−Br, Si−Cl, or N−Cl bond contraction, the C−Cl, C−Br, Si−Cl, or N−Cl strctching frequencies of the contacting C−Cl, C−Br, Si−Cl, or N−Cl groups are higher by 3.2−20.6 cm^{-1} in the dimers than the respective frequencies of the monomers. The individual blueshifts can be correlated directly to the magnitude of Si−Cl or N−Cl contraction. However, the individual blueshifts cannot be correlated directly to the magnitude of C−Cl or C−Br contraction because the C−Cl or C−Br stretching modes consist of a mixture of the C−Cl or C−Br and C−F internal coordinates. As expected, the IR intensities behave in the same way although it is in inverse proportion to bond contraction. It must be pointed out that C−Cl motion, as well as other vibrational motions, is anharmonic, and this may cast doubt on

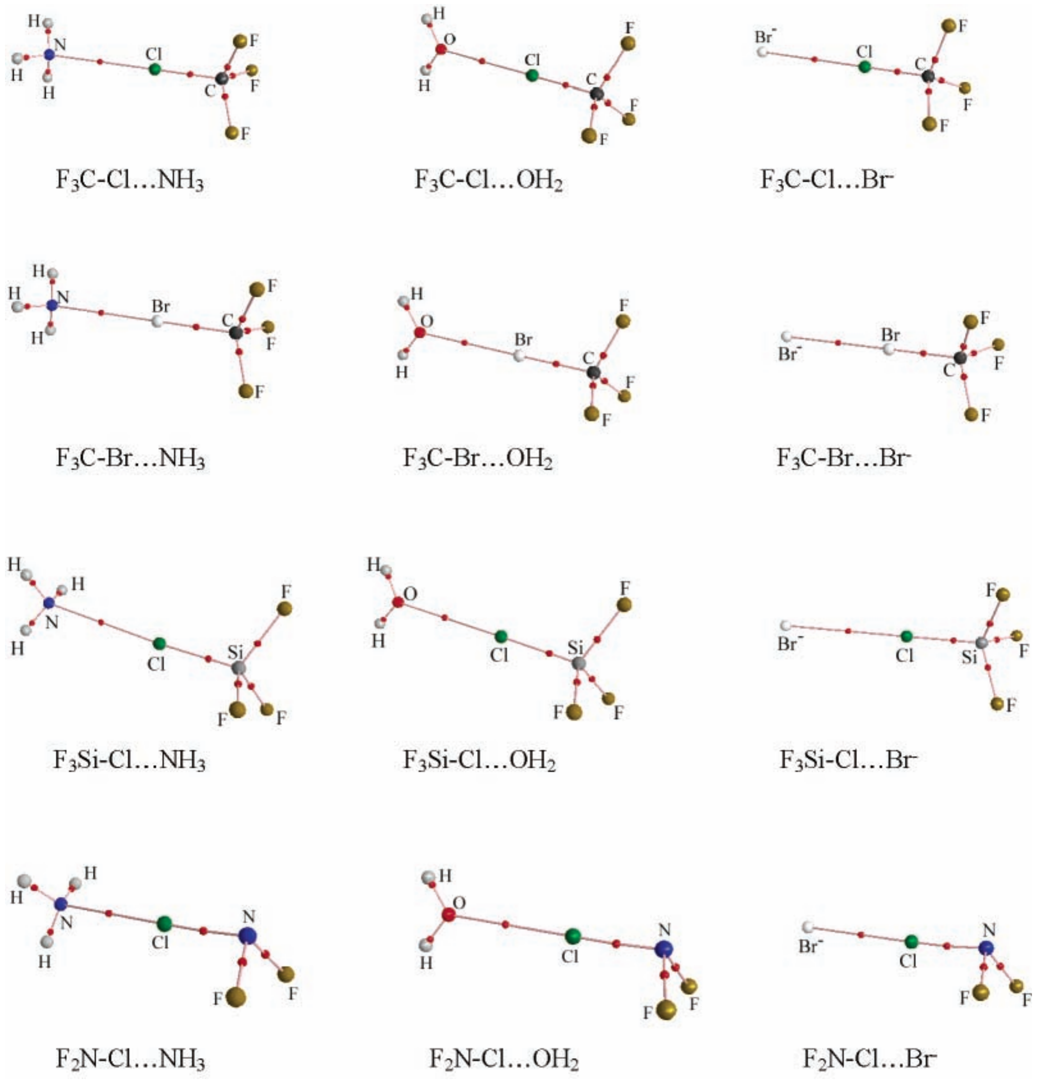

Figure 1. Molecular graphs for the twelve studied halogen-bonded complexes. Small red dots represent critical points.

the “harmonic” results, but information from the study of blueshifting hydrogen bond indicates the promising adequacy of the harmonic model.[43]

AIM Analysis. The rigorous AIM theory has been successfully applied in characterizing hydrogen bonds of different strengths in a wide variety of molecular complexes.[44,45] Popelier proposed a set of criteria for the existence of H bonding within the AIM formalism.[44,45] The most prominent evidence of hydrogen bonding is the existence of a bond path between the donor hydrogen nucleus and the acceptor, containing a interatomic surface (IAS) and a bond critical point (BCP) at which the electron density (ρ_b) ranges from 0.002 to 0.035 au and the Laplacian of the electron density ($\nabla^2\rho_b$) ranges from 0.024 to 0.139 au. The five other criteria deal with changes of atomic charge q(H), atomic polarization moment M(H), atomic volume v(H), atomic energy E(H), and atomic radius r(H) of the hydrogen atom upon formation of the hydrogen bond. In the present study, these eight AIM criteria of hydrogen bonds will be systematically applied to the blueshifting halogen bonds in order to gain deep insight into this special type of molecular interaction.

Topology. Figure 1 clearly demonstrates the existence of a BCP for each blueshifting halogen bond, roughly lying in the middle. The expected bond paths associated with the blueshifting halogen bond BCPs can also be visualized in Figure 1. Furthermore, the characteristic flat blueshifting halogen bond IAS appears in Figure 2. We only demonstrate three F_3CCl-related contour maps of the electronic charge density because others behave in the same way. Certainly, the atomic basin of the halogen atom is strikingly larger than that of corresponding hydrogen atom in a blueshifting hydrogen bond.

The Electron Density of the BCP. The electron density (ρ_b) of the BCP is listed in Table 2 for the Cl(Br)···N(O, or Br$^-$) bond. The value for the Cl(Br)···N(O, or Br$^-$) bond does fall within the proposed range of 0.002−0.035 au for the hydrogen bond. Again it has been shown that ρ_b is related to the bond order and thus to the bond strength. As a result, the value for ρ_b is much lower for the Cl(Br)···O bond compared to the Cl(Br)···N(Br$^-$) bond.

The Laplacian of the Electron Density of the BCP. The two negative eigenvalues of the Hessian matrix of electron density (λ_1 and λ_2) measure the degree of contraction of ρ_b perpendicular to the bond toward the critical point, whereas the positive eigenvalue (λ_3) measures the degree of contraction parallel to the bond and from the BCP toward each of the neighboring nuclei. The Laplacian $\nabla^2\rho_b$ is simply the sum of the eigenvalues λ_1, λ_2, and λ_3. It has been observed that for closed-shell interactions (ionic bonds, hydrogen bonds, and van der Waals interactions), $\nabla^2\rho_b$ is positive. According to Table 2, the blueshifting halogen bonds are also typical closed-shell interactions, the positive values for $\nabla^2\rho_b$ lying in the proposed range of 0.024−0.139 au (allowing for small differences in basis set).

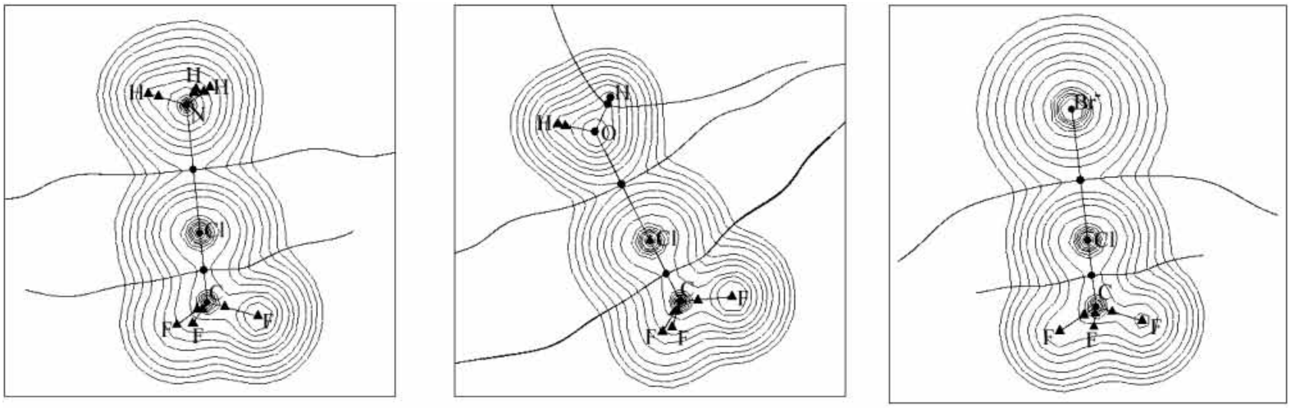

Figure 2. Superpositions of the contour lines of the electron density and the molecular graphs and IASs for the F_3CCl-related dimers at the MP2(full)/6-311++G(d,p) level. BCPs and the nuclei are both denoted by circles when they lie in the plane and by triangles when they do not lie in the plane. The IASs of the nuclei that do not lie in the plane are omitted for clarity.

TABLE 2: Density (ρ), Density Laplacian ($\nabla^2\rho$), Eigenvalues of the Hessian Matrix (λ_1, λ_2, λ_3), and Ellipticity (ϵ) at BCPs between Halogen-Bond Acceptors and Halogen-Bond Donors at the MP2(full)/6-311++G(d,p) Level of Theory (au)

interaction	ρ_b	$\nabla^2\rho_b$	λ_1	λ_2	λ_3	ϵ
			$Cl(Br)\cdots N$			
$F_3C-\mathbf{Cl}\cdots\mathbf{N}H_3$	0.0088	0.0309	−0.0059	−0.0059	0.0428	0.0000
$F_3C-\mathbf{Br}\cdots\mathbf{N}H_3$	0.0122	0.0378	−0.0081	−0.0081	0.0541	0.0001
$F_3Si-\mathbf{Cl}\cdots\mathbf{N}H_3$	0.0051	0.0182	−0.0032	−0.0032	0.0247	0.0010
$F_2N-\mathbf{Cl}\cdots\mathbf{N}H_3$	0.0156	0.0526	−0.0115	−0.0114	0.0755	0.0083
			$Cl(Br)\cdots O$			
$F_3C-\mathbf{Cl}\cdots\mathbf{O}H_2$	0.0075	0.0328	−0.0057	−0.0048	0.0433	0.1780
$F_3C-\mathbf{Br}\cdots\mathbf{O}H_2$	0.0093	0.0368	−0.0068	−0.0057	0.0493	0.1803
$F_3Si-\mathbf{Cl}\cdots\mathbf{O}H_2$	0.0050	0.0221	−0.0037	−0.0031	0.0289	0.1731
$F_2N-\mathbf{Cl}\cdots\mathbf{O}H_2$	0.0106	0.0452	−0.0082	−0.0070	0.0604	0.1681
			$Cl(Br)\cdots Br^-$			
$F_3C-\mathbf{Cl}\cdots\mathbf{Br}^-$	0.0101	0.0337	−0.0055	−0.0055	0.0448	0.0000
$F_3C-\mathbf{Cl}\cdots\mathbf{Br}^-$	0.0156	0.0440	−0.0089	−0.0089	0.0617	0.0000
$F_3Si-\mathbf{Cl}\cdots\mathbf{Br}^-$	0.0073	0.0250	−0.0039	−0.0039	0.0327	0.0000
$F_2N-\mathbf{Cl}\cdots\mathbf{Br}^-$	0.0227	0.0626	−0.0151	−0.0150	0.0927	0.0065

The ellipticity ϵ is defined as $\lambda_1/(\lambda_2 - 1)$ and measures the extent to which charge is preferentially accumulated. The ellipticity provides a measure for not only the π character of a bond but also its structural stability. Substantial bond ellipticities reflect structural instability; that is, the bond can easily be ruptured. In Table 2 we see that $\epsilon(Cl(Br)\cdots O)$ is much larger than $\epsilon(Cl(Br)\cdots N(Br^-))$, confirming that the former bond is weaker, which is consistent with the case of interaction energy.

Mutual Penetration of Halogen and Acceptor Atoms. The nonbonded radius of an atom is defined as the distance of its nucleus to a given electron density contour (0.001 au) in the monomer. The bonded radius is then simply the distance from the nucleus to the BCP in question (in the dimer). The penetration is defined as the nonbonded radius minus the bonded radius. According to Table 3, the acceptor atom is penetrated more than the halogen atom, which is contrary to the case of the $C-H\cdots O$ hydrogen bond and is consistent with the case of dihydrogen bond.[44,45] There are two exceptions where the penetrations are almost equal. Again the correlation between the penetration data and interaction energy data is fairly good.

Increased Net Charge of the Halogen Atom. Upon dimerization, the charges of the donor halogen atoms all increase, as illustrated by Table 3. It must be pointed out that the charges of halogen atoms in $F_3CCl\cdots NH_3$-, $F_3CCl\cdots OH_2$-, and F_3SiCl-related complexes are negative, contrary to the others.

The smaller loss of charge of halogen atom does not correspond with the energetically weaker complex. For example, the charge of the Cl atom increases from 0.1303 in the monomer F_2NCl to 0.1577 in the dimer $F_2NCl\cdots Br^-$, which corresponds to a little loss of 0.0274*e*, but the interaction energy of $F_2NCl\cdots Br^-$ is the greatest one in the complexes studied in this paper.

Energetic Destabilization of the Halogen Atom. This criterion means the energy of a halogen atom should rise upon complex formation. It can be seen from Table 3 that the energies of halogen atoms indeed rise in $F_3CCl\cdots Br^-$-, $F_2NCl\cdots Br^-$-, and F_3SiCl-related complexes, but for other complexes, the energies of halogen atoms decrease. The strength of the blueshifting halogen bonds is also not reflected in these values. So the energetic destabilization of the donor halogen atom is not a dramatic and dominant effect for the stabilization of complexes.

Decrease of Dipolar Polarization of the Halogen Atom. From Table 3 it is obvious that the magnitude of the dipolar polarization, $M(\Omega)$, of the halogen atomic distribution is decreasing upon complex formation. However, three exceptions are noted, three F_3SiCl-related complexes, where magnitudes of the first moments are increasing upon complex formation.

Decrease of the Halogen Atom's Volume. A final property of interest is the halogen atom's volume in Table 3. This quantity is decreasing for all the halogen atoms. In general, the degree of halogen atom shrinking is in proportion to the strength of the blueshifting halogen bond.

From the above discussion, we can see that though the first three criteria for the hydrogen bond are all echoed in the blueshifting halogen bond, the five other criteria are different between the hydrogen bond and the blueshifting halogen bond. This indicates the different nature of the two types of intermolecular interactions.

NBO Analysis. For a better understanding of the blueshifting halogen bond, NBO analysis has been carried out at the HF/6-311++G(d,p) level of theory using MP2(full)/6-311++G(d,p) geometry. The occupancy (δ) of frontier molecular orbitals involving the CT between subsystems, the second-order perturbation energy lowering (ΔE^2) due to the interaction of donor and acceptor orbitals, and the difference ($\Delta\epsilon$) of energies between acceptor and donor NBOs, provided by NBO analysis, are collected in Table 4.

Let us first repeat that the formation of a hydrogen-bonded complex, either a conventional hydrogen bond or a blueshifting hydrogen bond, involves CT from the proton acceptor to the proton donor. This results in the increase of electron density in the $X-H$ antibonding orbitals of the proton donor. Since the charge-transfer accompanies the formation of hydrogen bonds and plays a major role in it, ΔE^2 can be taken as an index to

TABLE 3: Cl and Br Atomic Basin Integrated Properties and Cl, Br, and A (O, N, or Br^-) Bond Radii in the Halogen Bonded Structures[a]

halogen atom	$q_{Cl(Br)}$	$\Delta q_{Cl(Br)}$	$M_{Cl(Br)}$	$\Delta M_{Cl(Br)}$	$\upsilon_{Cl(Br)}$	$\Delta\upsilon_{Cl(Br)}$	$-E_{Cl(Br)}$	$\Delta E_{Cl(Br)}$	$r_{Cl(Br)}$	$\Delta r_{Cl(Br)}$	r_A	Δr_A	$L_{Cl(Br)}$
$F_3C-\mathbf{Cl\cdots NH_3}$	**−0.0492**	−0.0352	0.148	0.051	206.2	1.3	459.9900	**0.1986**	3.00	0.61	3.07	0.88	0.2358
$F_3C-\mathbf{Cl\cdots OH_2}$	**−0.0483**	−0.0361	0.136	0.063	205.0	2.5	459.7931	**0.0017**	3.03	0.58	2.85	0.62	0.0267
$F_3C-\mathbf{Cl\cdots Br^-}$	0.0109	−0.0953	0.142	0.057	202.6	4.9	459.7389	−0.0525	2.94	0.67	3.46	1.13	0.0849
$F_3C-\mathbf{Br\cdots NH_3}$	0.0968	−0.0437	0.307	0.079	248.3	2.1	2571.9327	**0.1133**	2.99	0.83	2.92	1.03	−0.0420
$F_3C-\mathbf{Br\cdots OH_2}$	0.0981	−0.0450	0.296	0.090	249.2	1.2	2571.9731	**0.1537**	3.08	**0.74**	2.77	**0.70**	0.0499
$F_3C-\mathbf{Br\cdots Br^-}$	0.1552	−0.1021	0.273	0.113	246.1	4.3	2571.8587	**0.0393**	2.89	0.93	3.25	1.34	−0.7357
$F_3Si-\mathbf{Cl\cdots NH_3}$	**−0.6996**	−0.0079	1.045	**−0.083**	232.2	2.3	460.0608	−0.1011	3.29	0.41	3.38	0.57	0.0051
$F_3Si-\mathbf{Cl\cdots OH_2}$	**−0.6959**	−0.0116	1.050	**−0.088**	230.9	3.6	460.0579	−0.1040	3.26	**0.44**	3.04	**0.43**	0.0051
$F_3Si-\mathbf{Cl\cdots Br^-}$	**−0.6848**	−0.0227	1.176	**−0.214**	230.4	4.1	459.8694	−0.2925	3.14	0.56	3.63	0.96	−0.0039
$F_2N-\mathbf{Cl\cdots NH_3}$	0.1624	−0.0321	0.402	0.071	200.0	8.5	459.7035	**0.0261**	2.72	0.89	2.77	1.18	0.0172
$F_2N-\mathbf{Cl\cdots OH_2}$	0.1730	−0.0427	0.400	0.073	203.6	4.9	459.7252	**0.0478**	2.85	0.76	2.70	0.77	0.0616
$F_2N-\mathbf{Cl\cdots Br^-}$	0.1577	−0.0274	0.353	0.120	199.3	9.2	459.4605	−0.2169	2.59	1.02	3.03	1.56	−0.0544

[a] For each atomic property X, ΔX represents the difference of the property between the halogen-bond-free molecule and the halogen-bound molecule. L is the value of the Laplacian, integrated over the halogen atomic basin. All units are atomic units. The value in bold font is of great interest.

TABLE 4: Natural Bond Orbital Analysis at the HF/6-311++G(d,p)//MP2(full)/6-311++G(d,p) Level (ΔE^2 in kcal/mol, $\Delta\epsilon$ in Hartree)[a]

complexes	donor NBOs	δ	acceptor NBOs	δ	ΔE^2	$\Delta\epsilon$
$F_3CCl\cdots NH_3$	N lone pair	1.993 (1.997)	C−Cl antibond	0.069 (0.071)	1.44	0.83
$F_3CCl\cdots OH_2$	O lone pair	1.996 (1.997)	C−Cl antibond	0.067 (0.071)	0.69	1.24
$F_3CCl\cdots Br^-$	Br lone pair (π)	2.000 (2.000)	C−Cl antibond	0.067 (0.071)	3.29	0.61
$F_3CBr\cdots NH_3$	N lone pair	1.987 (1.997)	C−Br antibond	0.075 (0.075)	3.43	0.76
$F_3CBr\cdots OH_2$	O lone pair	1.995 (1.997)	C−Br antibond	0.071 (0.075)	1.50	1.16
$F_3CBr\cdots Br^-$	Br lone pair	2.000 (2.000)	C−Br antibond	**0.089 (0.075)**	0.53	1.10
	Br lone pair (π)	1.956 (2.000)	C−Br antibond	**0.089 (0.075)**	9.83	0.55
$F_3SiCl\cdots NH_3$	N lone pair	1.996 (1.997)	Si−Cl antibond	0.056 (0.057)	0.50	0.89
$F_3SiCl\cdots OH_2$	O lone pair	1.997 (1.997)	Si−Cl antibond	0.056 (0.057)	0.28	1.30
$F_3SiCl\cdots Br^-$	Br lone pair (π)	1.994 (2.000)	Si−Cl antibond	0.055 (0.057)	1.58	0.66
$F_2NCl\cdots NH_3$	N lone pair	1.981 (1.997)	N−Cl antibond	**0.048 (0.039)**	5.16	0.75
$F_2NCl\cdots OH_2$	O lone pair	1.994 (1.997)	N−Cl antibond	0.038 (0.039)	1.71	1.15
$F_2NCl\cdots Br^-$	Br lone pair	2.000 (2.000)	N−Cl antibond	**0.100 (0.039)**	0.89	1.07
	Br lone pair (π)	1.912 (2.000)	N−Cl antibond	**0.100 (0.039)**	18.60	0.51

[a] Data in the parentheses are the occupancy of corresponding NBO of isolated molecule. π-type lone pairs have been noted; other bonds are σ-type lone pairs or σ antibonds.

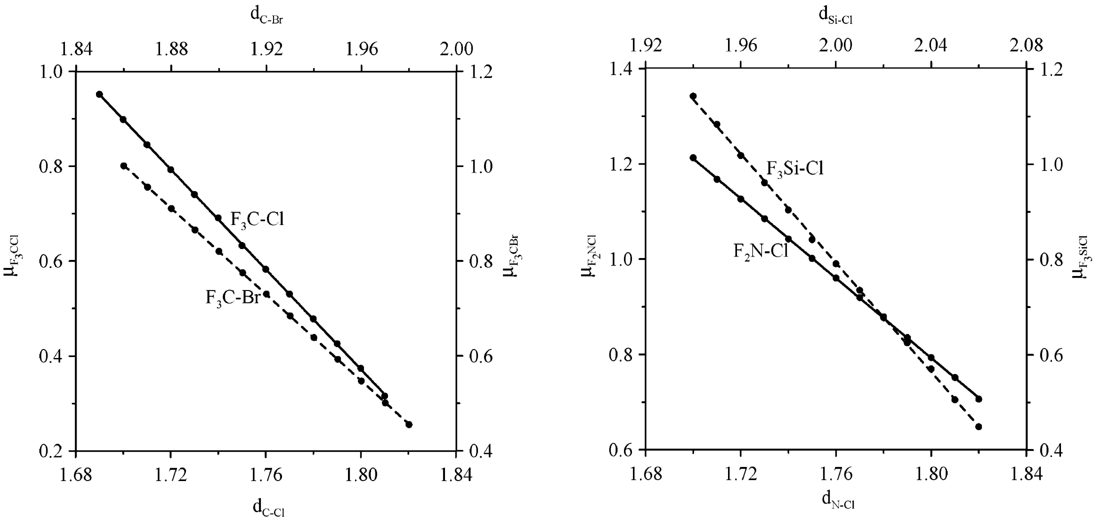

Figure 3. Change of MP2(full)/6-311++G(d,p) dipole moment (in Debye) of F_3CCl, F_3CBr, F_2NCl, or F_3SiCl upon variation of the corresponding C−Cl, C−Br, N−Cl, or Si−Cl bond length (in Å).

judge the strength of hydrogen bonds. For the blueshifting halogen bond, the case is substantially different. Though the CT from the lone pairs of the electron donor in the halogen atom acceptor is mainly directed to the X−Cl(Br) antibonding orbitals of the halogen atom donor, the increase of electron density occurs only in the C−Br antibond orbital of $F_3CBr\cdots Br^-$, the N−Cl antibond orbital of $F_2NCl\cdots NH_3$, and the N−Cl antibond orbital of $F_2NCl\cdots Br^-$. This indicates that a significant electronic structural reorganization of the halogen atom donor happens when two moieties approach and interact. The donor−acceptor interaction stabilization energy ΔE^2 in Table 4 for $F_3CCl\cdots Br^-$ is less than the relevant one for $F_3CBr\cdots NH_3$, which is opposite to the order of their intermolecular interaction energies, suggesting that the role of CT is not the most important one, but for complexes $F_3CBr\cdots Br^-$ and $F_2NCl\cdots Br^-$, the values of ΔE^2 are a little larger and the corresponding changes of electron densities for C−Br and N−Cl antibonds are also outstanding, which indicates larger contribution of CT.

Origin of the Blueshifting Halogen Bond. Today, there is hardly any doubt that the blueshifting hydrogen bond exists. However, explanations for the origin of the bond shortening are quite different.[30] Some authors, such as Scheiner and co-workers,[30a] contend that there are no fundamental differences in the bonding characteristics of blueshifting and conventional redshifting hydrogen-bonded complexes. In contrast, Hobza and co-workers proposed a CT mechanism between the proton donor and acceptor as the main reason for the blueshift after performing high-quality ab initio calculations for many blueshifting complexes.[30b] For fluoroform involved in some CH···O bonds, they suggest that it is the fluoroform molecule's negative sign of the dipole moment derivative with respect to the stretching coordinate, $d\mu^0/dr_{CH}$, which is responsible for the blueshift.[30c] In a recent paper,[30d] Hermansson extends this to all the blueshifting hydrogen bonds. He pointed out that a negative permanent dipole moment derivative, $d\mu^0/dr_{XH}$, for an isolated hydrogen bond donor molecule is a necessary but not sufficient condition for the formation of a blueshifting hydrogen bond and the blueshifting molecules and their relatives can also give rise to a redshifting hydrogen bond when the electric field from the acceptor is sufficiently strong at the intermolecular equilibrium distance. Krimm et al. also demonstrated that when the field and dipole derivative are antiparallel the bond shortens and blueshift results with the possibility of intensity decrease.[30e] For the present complexes, we also investigated the electrostatic characteristics of four halogen atom donor molecules. We found that contraction of the C−Cl, C−Br, Si−Cl, or N−Cl bond leads to an increase in their respective dipole moment (see Figure 3). The MP2(full)/6-311++G(d,p) value for $d\mu^0/dr_{CCl}$ at the isolated monomer equilibrium geometry is −5.27 D/Å; the other values are −4.55 D/Å for $d\mu^0/dr_{CBr}$, −5.72 D/Å for $d\mu^0/dr_{SiCl}$, and −4.18 D/Å for $d\mu^0/dr_{NCl}$. All these characteristics behave much like those of blueshifting hydrogen bonds. We have mentioned in the above discussion that there is one exception, that is, the elongation of the N−Cl bond upon complex $F_2NCl\cdots Br^-$ formation accompancied by a decrease of its vibrational stretching frequency (redshift) despite a negative permanent dipole moment derivative of F_2NCl. For complex $F_2NCl\cdots Br^-$, we noticed that the electric field from Br^- is the strongest one among three halogen atom acceptors whereas the absolute value of dipole moment derivative $d\mu^0/dr_{NCl}$ is the smallest one among four halogen atom donors. Such behavior is very much like the variation of C−H bond upon complex $F_3CH\cdots Cl^-$ formation.[30c] Similarly, we can derive that a molecule with "the capability of forming a blueshifting halogen bond" can also display a redshifting halogen bond when the electric field from the acceptor is "strong" enough to dominate over the overlap effects at the equilibrium intermolecular distance.

Conclusions

In summary, we have systematically described the results of quantum chemical calculations (MP2(full)/6-311++G(d,p) level) on the intermolecular interaction involving a series of representative blueshifting halogen-bonded complexes. From this study, the following conclusions can be obtained:

(i) Eleven halogen-bonded complexes exhibit blueshifting halogen bond characters. An decrease of 0.0053−0.0245 Å of the C−Cl, C−Br, Si−Cl, or N−Cl bond length upon dimer formation is observed, and the corresponding C−Cl, C−Br, Si−Cl, or N−Cl strctching frequencies are higher by 3.2−20.6 cm^{-1} in the dimers than the respective frequencies of the monomers.

(ii) By application of eight hydrogen-bonding criteria within the AIM formalism to the blueshifting halogen bond, the analysis discloses the different physical nature of the blueshifting halogen bond and hydrogen bond on the basis of the electron density.

(iii) Electron-density shifts accompanying the formation of the blueshifting halogen bond also show strong differences between blueshifting halogen bonds and hydrogen bonds or blueshifting hydrogen bonds. In many cases, there is an decreased density in the region between the C(Si, N) and Cl(Br) atoms.

(iv) Though the blueshifting halogen bond and blueshifting hydrogen bond are different in physical nature, the origin of involved bond shortening and frequency blueshifting is the same. The negative permanent dipole moment derivative of donor molecule is responsible for the blueshift. Note that a molecule with "the capability of forming a blueshifting halogen bond or a blueshifting hydrogen bond" displays a redshifting halogen bond or hydrogen bond when the electric field from the acceptor is "strong" enough at the equilibrium intermolecular distance.

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