

Competition between hydrogen bonds and halogen bonds in complexes of formamidine and hypohalous acids

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Abstract Quantum chemical calculations have been performed for the complexes of formamidine (FA) and hypohalous acid (HOX, X = F, Cl, Br, I) to study their structures, properties, and competition of hydrogen bonds with halogen bonds. Two types of complexes are formed mainly through a hydrogen bond and a halogen bond, respectively, and the cyclic structure is more stable. For the F, Cl, and Br complexes, the hydrogen-bonded one is more stable than the halogen-bonded one, while the halogen-bonded structure is favorable for the I complexes. The associated H-O and X-O bonds are elongated and exhibit a red shift, whereas the distant ones are contracted and display a blue shift. The strength of hydrogen and halogen bonds is affected by F and Li substituents and it was found that the latter tends to smooth differences in the strength of both types of interactions. The structures, properties, and interaction nature in these complexes have been understood with natural bond orbital (NBO) and atoms in molecules (AIM) theories.

Keywords Competition · Formamidine · Halogen bond · Hydrogen bond · Hypohalous acids

Introduction

Intermolecular interactions have been attracting much attention due to their extensive applications in fields of chemistry, biology, and physics [1, 2]. Hydrogen bond (HB) is one of the most important intermolecular interactions and its formation is mainly due to electrostatic interaction, together with induction and dispersion interactions [3, 4]. Halogen bond (XB) is

another important intermolecular interaction and recently more attention has been paid to XB because it exhibits similar applications to HB [5–10]. The origin of XB formation is dependent on the nature of halogen donor and acceptor [11–15]. The above applications of HB and XB are related to their directionality and strength. The directionality of XB is often attributed to anisotropic distribution of electrostatic potentials on the covalent halogen atomic surface [16]. Very recently, Stone studied some simple halogen-bonded complexes using symmetry-adapted perturbation theory (SAPT) and concluded that electrostatics are not single decisive factor for their geometries and the strong tendency to linearity of XB is a consequence of exchange-repulsion in some particular cases [17].

Besides the atoms having lone pair electrons such as O and N, the halogen acceptors in XBs include π systems, metal hydrides, radicals, and carbenes [18–22]. The strength of XB is also dependent on the nature of halogen atom. Fluorine seldom participates in XB, although it sometimes does when it combines with strong Lewis bases or strong electron-withdrawing groups adjoin with it [23]. The strength of XB increases as follows: F < Cl < Br < I, and iodine forms the strongest XB. In general, XB is comparable to HB in strength, thus they show competition when the hydrogen and halogen donors exist simultaneously [24]. A versatile strategy for the assembly of discrete supermolecules and heteromeric molecular architectures was suggested by means of structural competition between HBs and XBs [25].

Hypohalous acids play an important role both in atmospheric chemistry involved in catalytic cycles in the seasonal depletion of the ozone layer in the stratosphere [26–28] and in pathophysiological processes as oxidants with potent antibacterial properties [29] as well as in the immune defense of mammals [30]. Because of chemical instability of the hypohalous acids, it is a challenge to probe and quantify them [31, 32]. The coexistence of H and X atoms in hypohalous acids makes them act as the proton and halogen donors in HB

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and XB. Both types of interactions are of importance for the understanding of the above chemical and biological processes. More importantly, they provide a good model to study the competition of HB with XB [33–45]. In general, the hydrogen-bonded complexes are more stable for HOCl and HOBr, while the halogen-bonded isomers are more stable for HOI. In addition, the halogen acceptor and substituents have an effect on their stability. H₂CS forms a stronger halogen bond with HOBr than the hydrogen bond [41]. Some studies paid attention to dimers of hypohalous acids [46–48]. Theoretical calculations play a prominent part in unveiling the structures, properties, and nature of these complexes involved with hypohalous acids.

People are interested in amidines because they exhibit a unique and fascinating biological activity, including bactericidal and antiprotozoal effects, antihelminthic, fungicidal and herbicidal properties, and the insecticidal and acaricidal actions [49, 50]. These functions may be related with proton transfer occurring in complexes of amidines with itself [51], formic acid [52], formamide [53], glycnamide [54], water [55], and alcohols [56].

Because of the important role of amidines and hypohalous acids in both atmospheric and biological processes, there is an interest in studying the interactions between them. In the present paper, the complexes of formamidine (FA) with hypohalous acids HOX (X = F, Cl, Br, I) have been investigated to study the competition between HB and XB in these complexes. To the best of our knowledge, neither theoretical nor experimental data regarding the structural information for these complexes are available in the literature. The present work presents a detailed examination of the stabilities, electronic structure, and vibrational frequencies of these complexes.

Theoretical methods

The structures have been optimized at the MP2 computational level with the aug-cc-pVTZ basis set for all atoms except I atom, for it the aug-cc-pVTZ-PP basis set was adopted. Frequency calculations have been carried out at the same level to confirm that the structures obtained correspond to energetic minima. The interaction energy was calculated with supermolecular method by subtracting the energy sum of the isolated monomers from the energy of the complex. The interaction energy with such method is susceptible to basis-set superposition error (BSSE), which can be removed with the counterpoise method suggested by Boys and Bernardi [57]. All calculations were performed using the Gaussian 09 package of codes [58].

The natural bond orbital (NBO) method [59] implemented within the Gaussian 09 program has been used to analyze the interaction of occupied and empty orbitals as well as charge

transfer in these complexes. The AIM2000 package [60] was used to obtain bond properties in view of topology including electron density, Laplacian, and energy density. The electrostatic potentials at the 0.001 electrons Bohr⁻³ isodensity surfaces were calculated with the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) program [61].

Results and discussion

FA-(Z)-HOX systems

Figure 1 shows the structures of FA-(Z)-HOX and FA-(Z)-XOH (X = F, Cl, Br, I) complexes. In FA-(Z)-HOX, two types of HBs coexist. One is OH⋯N HB with the imino nitrogen atom as the proton acceptor and HOX as the proton donor, the other is CH⋯X HB, which the halogen as the proton acceptor and the C-H proton as the donor. In FA-(Z)-XOH, there is an OX⋯N XB with the imino nitrogen atom as the halogen acceptor and HOX as the halogen donor, together with a similar CH⋯X contact to that in FA-(Z)-HOX. It has been demonstrated that HB and XB are electrostatically-driven [11, 16, 62, 63], thus the formation of HB and XB in the FA complexes with HOX can be understood with the electrostatic potentials of FA and HOX, as shown in Fig. 2. The positive region of electrostatic potentials on the H and X atoms in HOX points to the negative region of electrostatic potentials on the N atom in FA. Simultaneously, the negative region of electrostatic potentials on the X atom in HOX is close to the negative region of electrostatic potentials on the H atom in FA. The OH⋯N HB and OX⋯N XB are dominant in the

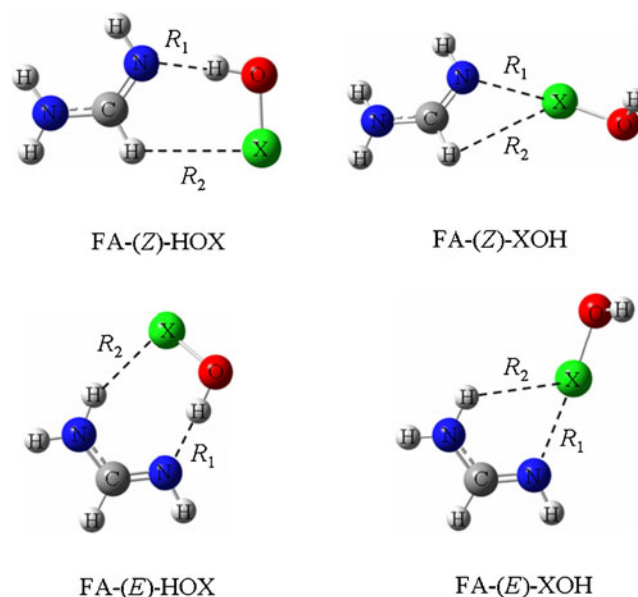


Fig. 1 The structures of FA-(Z)-HOX and FA-(E)-HOX (X = F, Cl, Br, I) systems

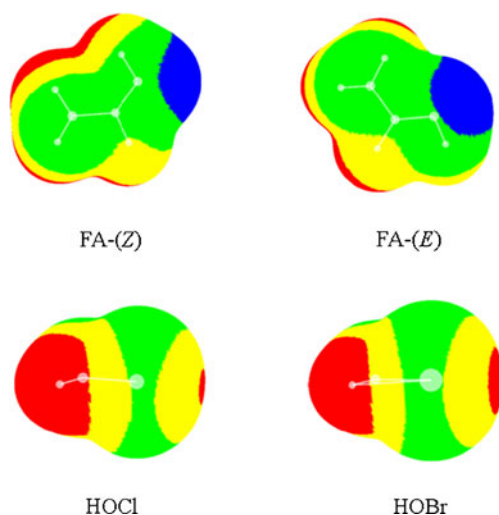


Fig. 2 The electrostatic potentials of FA and HOX calculated at the MP2/aug-cc-pVTZ level. Color ranges, in kcal mol⁻¹, are: *red*, greater than 18.8; *yellow*, between 18.8 and 0; *green*, between 0 and -25.1; *blue*, less than -25.1

corresponding isomers, while the CH \cdots X contact is a secondary one. The respective binding distances are summarized in Table 1. The H \cdots N distance is 1.71–1.73 Å, X \cdots N distance is 2.44–2.55 Å, and the H \cdots X distance is 2.55–3.26 Å. The values of H \cdots N and X \cdots N distances are smaller than the sum of the van der Waals radii of the respective atoms (2.6 Å for H and N atoms, 3.3 Å for Cl and N atoms, 3.5 Å for Br and N atoms, 3.6 Å for I and N atoms). This supports the presence of the OH \cdots N HB in FA-(Z)-HOX and the OX \cdots N XB in FA-(Z)-XOH. The H \cdots X distance almost amounts to or larger than the sum of the van der Waals radii of the respective atoms (2.5 Å for H and F atoms, 2.9 Å for H and Cl atoms, 3.1 Å for

Table 1 Interaction energy (ΔE , kcal mol⁻¹), binding distances (R , Å), change of bond lengths (Δr , Å), and frequency shifts of bond stretch vibrations ($\Delta \nu$, cm⁻¹)

	ΔE	R_1	R_2	$\Delta r_{\text{H-O}}$	$\Delta r_{\text{X-O}}$	$\Delta \nu_{\text{H-O}}$	$\Delta \nu_{\text{X-O}}$
FA-(Z)-HOF	-12.6	1.727	2.557	0.030	0.007	-592	4
FA-(Z)-HOCl	-12.8	1.710	2.978	0.033	-0.009	-655	12
FA-(Z)-HOBr	-12.5	1.715	3.008	0.033	-0.012	-652	18
FA-(Z)-HOI	-11.9	1.728	3.135	0.032	-0.018	-635	23
FA-(Z)-ClOH	-5.5	2.542	3.058	-0.001	0.028	16	-72
FA-(Z)-BrOH	-8.9	2.441	3.139	-0.002	0.046	19	-75
FA-(Z)-IOH	-12.8	2.488	3.253	-0.003	0.045	31	-62
FA-(E)-HOF	-14.0	1.696	2.082	0.038	0.008	-732	4
FA-(E)-HOCl	-14.1	1.674	2.482	0.042	-0.012	-808	15
FA-(E)-HOBr	-13.5	1.679	2.552	0.041	-0.016	-801	23
FA-(E)-HOI	-12.8	1.693	2.732	0.039	-0.022	-767	30
FA-(E)-ClOH	-6.3	2.511	2.644	-0.001	0.033	13	-88
FA-(E)-BrOH	-10.0	2.397	2.674	-0.001	0.055	16	-104
FA-(E)-IOH	-14.1	2.453	2.807	-0.002	0.051	30	-66

H and Br atoms, 3.3 Å for H and I atoms). This shows that the H \cdots X interaction is very weak in both types of isomers. These interactions are confirmed by the presence of intermolecular bond critical points (BCPs) (red small points in Fig. 3). In FA-(Z)-HOX, the combination of the main interaction with the secondary one results in formation of a ring structure. This can be confirmed with the presence of a ring critical point (RCP) in the structure (a yellow small point in Fig. 3).

The interaction energy is a convincing measurement for the stability of complexes. For the HOCl and HOBr complexes, FA-(Z)-HOX is more stable than FA-(Z)-XOH, while a reverse result is found for the HOI complexes. Interestingly, the interaction energies are almost equal for FA-(Z)-HOF, FA-(Z)-HOCl, and FA-(Z)-HOBr complexes, although three halogen atoms have different electronegativity. The greater electronegativity of F in HOF should make the proton form a stronger HB than HOCl and HOBr. However, the H \cdots N distance in FA-(Z)-HOF is larger than in the respective HOCl and HOBr systems. This abnormal result has been demonstrated in the hydrogen-bonded complexes of hypohalous acids with nitrogenated bases [39]. This may be attributed to the nature of O-X bond in HOX. The O-F bond is a covalent, polarized bond, while other O-X bond is of electron donor-acceptor-type with the halogen donating electron density to the valence shell of oxygen [64]. For FA-(Z)-HOX (X = Cl, Br, I), with the increase of the halogen atom mass the interaction energy becomes less negative, the H \cdots N distance is bigger, and the H \cdots X distance is also increased. This agrees with the change of the heavier halogen atom electronegativity and its atom radius. For FA-(Z)-XOH, with the increase of the halogen atom mass the interaction energy becomes more negative, and this result is consistent with the most positive electrostatic potential on the halogen atomic surface in HOX [39]. This indicates that the electrostatic interaction is very important in the formation of halogen bond. An interesting result is found for the smallest Br \cdots N distance, although the

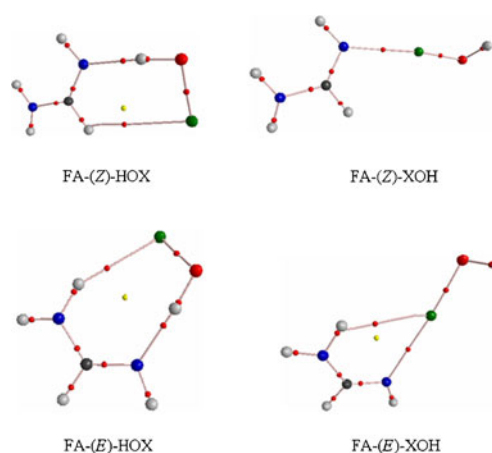


Fig. 3 Molecular graphs of FA-(Z)-HOX and FA-(E)-HOX (X = F, Cl, Br, I) systems. Small red balls indicate the bond critical points and yellow ones show the ring critical point

interaction strength is not largest and the Br atomic radius is not smallest. The H⋯X distance in FA-(Z)-XOH is greater than that in FA-(Z)-HOX, indicating a much weaker contact in the former.

Upon complexation, the H-O bond is elongated in FA-(Z)-HOX and shortened in FA-(Z)-XOH, whereas the X-O bond is lengthened in FA-(Z)-XOH and contracted in FA-(Z)-HOX except in FA-(Z)-HOF. The value of the bond elongation is bigger than that of the bond contraction. Accompanied with the bond elongation and contraction, the respective bond stretch vibrations exhibit a red shift and blue shift except for the F-O bond in FA-(Z)-HOF. The red shift is more prominent for the H-O bond than for the X-O bond owing to the lighter mass of H atom.

In nearly all of the cases there are simultaneous interactions that contribute to the computed total interaction energies. Thus the orbital interaction between the orbital donor and the acceptor is used to understand the formation of the complexes, although it is not observed physically [65]. The analyzed orbital interactions are $LP_N \rightarrow BD^*_{O-H}$ and $LP_X \rightarrow BD^*_{C-H}$ in FA-(Z)-HOX, while they are $LP_N \rightarrow BD^*_{O-X}$ and $LP_X \rightarrow BD^*_{C-H}$ in FA-(Z)-XOH. These orbital interactions are estimated with the second-order perturbation energy, and the corresponding results are given in Table 2. The $LP_X \rightarrow BD^*_{C-H}$ orbital interaction is far smaller than $LP_N \rightarrow BD^*_{O-H}$ and $LP_N \rightarrow BD^*_{O-X}$ ones, showing the secondary interaction can be negligible. The $LP_X \rightarrow BD^*_{C-H}$ orbital interaction in FA-(Z)-HOX is larger than that in FA-(Z)-XOH, and this is in

Table 2 Second-order perturbation energies (E , kcal mol⁻¹), charge transfer (CT , e), differences between NBO electron density (ED) in the complexes and the isolated HOX in H-O and O-X sigma bonding ($\Delta\sigma$) and sigma antibonding ($\Delta\sigma^*$) orbitals in the complexes

	E^1	E^2	CT	$\Delta\sigma_{H-O}$	$\Delta\sigma_{X-O}$	$\Delta\sigma^*_{H-O}$	$\Delta\sigma^*_{X-O}$
FA-(Z)-HOF	36.7	0.2	0.049	-0.000	-0.000	0.052	-0.001
FA-(Z)-HOCl	39.5	0.4	0.052	-0.001	-0.005	0.054	0.001
FA-(Z)-HOBr	38.2	0.7	0.049	-0.001	-0.004	0.052	0.001
FA-(Z)-HOI	35.8	1.1	0.044	-0.000	-0.003	0.049	0.002
FA-(Z)-ClOH	12.3	0.1	0.031	0.000	-0.001	0.000	0.035
FA-(Z)-BrOH	30.2	0.1	0.070	0.000	-0.003	0.000	0.074
FA-(Z)-IOH	41.7	0.4	0.089	-0.000	-0.003	0.000	0.094
FA-(E)-HOF	44.6	3.5	0.057	-0.000	-0.001	0.065	-0.001
FA-(E)-HOCl	48.7	4.7	0.056	-0.001	-0.004	0.068	0.001
FA-(E)-HOBr	46.8	6.6	0.049	-0.001	-0.004	0.066	0.002
FA-(E)-HOI	42.5	6.8	0.042	-0.001	-0.003	0.060	0.003
FA-(E)-ClOH	15.1	1.2	0.038	0.000	-0.002	-0.000	0.044
FA-(E)-BrOH	37.2	2.1	0.085	0.000	-0.003	0.000	0.093
FA-(E)-IOH	48.8	2.9	0.101	-0.000	-0.003	0.000	0.114

Note: E^1 is due to the $LP_N \rightarrow BD^*_{O-H}$ orbital interaction in FA-HOX and $LP_N \rightarrow BD^*_{O-X}$ in FA-XOH, E^2 is due to the $LP_X \rightarrow BD^*_{C-H}$ orbital interaction in FA-(Z)-HOX but $LP_X \rightarrow BD^*_{N-H}$ in FA-(E)-HOX

agreement with the H⋯X distance in both types of complexes. The perturbation energies due to the $LP_N \rightarrow BD^*_{O-H}$ and $LP_N \rightarrow BD^*_{O-X}$ orbital interactions have a consistent change with the interaction energy in both types of complexes, indicating the orbital interaction has a contribution to the formation of the complexes. For the Cl and Br complexes, the orbital interaction is stronger in FA-(Z)-HOX than that in FA-(Z)-XOH, however it is stronger in FA-(Z)-IOH. This means that the competition between HB and XB can be regulated through the change of halogen donor.

Accompanied with the above orbital interactions, charge transfer occurs from the electron donor to the acceptor. With the increase of the halogen atomic number, the charge transfer decreases in FA-(Z)-HOX (X = Cl, Br, I) but increases in FA-(Z)-XOH. A good relationship is found for the charge transfer and the interaction energy for the Cl, Br, and I complexes. These orbital interactions lead to the change of electron densities in the H-O and O-X sigma bonding and sigma antibonding orbitals. One can see from Table 2 that the electron densities in the sigma bonding orbitals have a small decrease, while they show a great increase for the σ^*_{H-O} in FA-(Z)-HOX and for the σ^*_{X-O} in FA-(Z)-XOH. This increase is responsible for the elongation and red shift of H-O and X-O bonds.

The theory of atoms in molecules (AIM) is another means for judging the formation of complexes, estimating their strength, and unveiling the nature of interactions. For these goals, in Table 3 we analyzed these complexes with the topological parameters including the electron density (ρ), Laplacian ($\nabla^2\rho$), and energy density (H). For the H⋯N HB and X⋯N XB, the ρ values range from 0.03 au to 0.05 au, while the $\nabla^2\rho$ ones are in range of 0.08–0.13 au. The latter conforms to the range (0.02–0.15 au) suggested for HBs by Koch and Popelier [66], while the former in most complexes is out of the range (0.002–0.04 au) [66]. The ρ value has a consistent change with the interaction energy in both types of complexes and it can be used to estimate the interaction strength [67]. The greater ρ values mean stronger interactions in these complexes, which are confirmed by bigger interaction energies. The strong interactions in these complexes are also evidenced by the negative H value because the latter corresponds to partly covalent interactions [68]. An exception is found in FA-(Z)-ClOH, in which the electron density is small and the energy density is positive. For the H⋯X BCP in FA-(Z)-HOX, the electron density is much smaller than those for the H⋯N HB and X⋯N XB and the energy density is positive, corresponding to the weak interaction. The electron density at the H⋯X BCP in FA-(Z)-HOX (X = Cl, Br, I) has an increase for the heavier halogen complex, confirming the change of H⋯X HB strength. According to the formulas of $E_{HB} = 1/2V$ [69], where V is potential energy density, the interaction energies of H⋯N and H⋯Cl HBs are calculated to be -15.8 and -0.99 kcal mol⁻¹, respectively, in FA-(Z)-

Table 3 Electron densities (ρ_C), Laplacians ($\nabla^2\rho_C$), and electron energy densities (H_C) at the intermolecular bond critical points (BCPs) in the complexes

	$\rho_{N\cdots H(X)}$	$\nabla^2\rho_{N\cdots H(X)}$	$H_{N\cdots H(X)}$	$\rho_{X\cdots H}$	$\nabla^2\rho_{X\cdots H}$	$H_{X\cdots H}$
FA-(Z)-HOF	0.0484	0.0836	-0.0134	0.0062	0.0287	0.0013
FA-(Z)-HOCl	0.0503	0.0851	-0.0145	0.0057	0.0218	0.0011
FA-(Z)-HOBr	0.0497	0.0859	-0.0141	0.0068	0.0233	0.0010
FA-(Z)-HOI	0.0481	0.0873	-0.0129	0.0072	0.0212	0.0008
FA-(Z)-ClOH	0.0296	0.1130	0.0009	–	–	–
FA-(Z)-BrOH	0.0430	0.1277	-0.0043	–	–	–
FA-(Z)-IOH	0.0468	0.1232	-0.0077	–	–	–
FA-(E)-HOF	0.0529	0.0794	-0.0162	0.0145	0.0693	0.0028
FA-(E)-HOCl	0.0556	0.0812	-0.0179	0.0135	0.0454	0.0013
FA-(E)-HOBr	0.0548	0.0825	-0.0173	0.0146	0.0426	0.0006
FA-(E)-HOI	0.0527	0.0848	-0.0158	0.0135	0.0343	0.0004
FA-(E)-ClOH	0.0322	0.1186	0.0002	0.0097	0.0377	0.0018
FA-(E)-BrOH	0.0478	0.1322	-0.0065	0.0118	0.0412	0.0015
FA-(E)-IOH	0.0509	0.1282	-0.0099	0.0121	0.0362	0.0011

HOCl. This further shows that the contribution from the $H\cdots X$ HB is very small in FA-(Z)-HOX.

FA-(E)-HOX systems

Figure 1 also shows the structures of FA-(E)-HOX and FA-(E)-XOH (X = F, Cl, Br, I) complexes. The similar $H\cdots N$ HB and $X\cdots N$ XB are found for FA-(E)-HOX and FA-(E)-XOH, respectively. The difference is the $NH\cdots X$ HB formed between the proton of amino and the halogen atom. The existence of both types of interactions in FA-(E)-HOX and FA-(E)-XOH as well as the formation of cyclic complexes with them are evidenced with the BCPs and RCP respectively in Fig. 3. Clearly, the FA-(E)-HOX system is more stable than the FA-(Z)-HOX counterpart. The difference of the interaction energy between FA-(E)-HOX and FA-(Z)-HOX systems becomes smaller for the hydrogen-bonded complex but larger for the halogen-bonded complex with the increase of the halogen atom mass. The $H\cdots N$ and $X\cdots N$ distances in FA-(E)-HOX system are shorter than those in the FA-(Z)-HOX counterpart. The $H\cdots X$ distance in FA-(E)-HOX system shows a rise tendency with the increase of the halogen atom mass, and it is smaller in FA-(E)-HOX than in FA-(E)-XOH, showing a stronger $H\cdots X$ HB in the former. The H-O and X-O bond lengths as well as the respective frequency shifts in FA-(E)-HOX system show similar changes to those in FA-(Z)-HOX system.

Similar orbital interactions are analyzed for the $H\cdots N$ HB and $X\cdots N$ XB in FA-(E)-HOX system, except the $LP_X\rightarrow BD^*_{N-H}$ orbital interaction for the $NH\cdots X$ HB. The second-order perturbation energies due to the $LP_N\rightarrow BD^*_{O-H}$ and $LP_N\rightarrow BD^*_{O-X}$ orbital interactions have a similar change as shown in the above discussion, although they are much larger in FA-(E)-HOX system. The $LP_X\rightarrow BD^*_{N-H}$ orbital interaction of the secondary interaction in FA-(E)-HOX system is stronger

than the $LP_X\rightarrow BD^*_{C-H}$ orbital interaction of the secondary interaction in FA-(Z)-HOX system and it is stronger in FA-(E)-HOX than in FA-(E)-XOH. In both types of complexes, however, it is stronger for the heavier halogen atom. This is inconsistent with the halogen electronegativity and means the electrostatic interaction plays a minor role in the $NH\cdots X$ HB. Again, the electron density is increased in the σ^*_{H-O} and σ^*_{X-O} orbitals upon complexation.

The bigger electron densities at the $H\cdots N$ and $X\cdots N$ BCPs indicate the stronger HB and XB interactions in FA-(E)-HOX system. The partly covalent nature of $H\cdots N$ HB and $X\cdots N$ XB is confirmed with the negative H value in the complexes except in FA-(E)-ClOH. The $NH\cdots X$ HB corresponds to the smaller electron density and the positive H value at the $H\cdots X$ BCP.

Effect of Li and F substituents

The above results show that HB is stronger than XB in the Br complexes. It has been demonstrated that the strength of HB and XB can be regulated by substituents [41]. Thus the H atom of C-H bond in FA is replaced with F and Li substituents. The

Table 4 Interaction energy (ΔE , kcal mol⁻¹), binding distances (R , Å), change of bond lengths (Δr , Å), and frequency shifts of bond stretch vibrations ($\Delta\nu$, cm⁻¹)

	ΔE	R_1	R_2	Δr_{H-O}	Δr_{X-O}	$\Delta\nu_{H-O}$	$\Delta\nu_{X-O}$
F-FA-(E)-HOBr	-11.9	1.725	2.540	0.032	-0.014	-623	19
Li-FA-(E)-HOBr	-16.3	1.580	2.614	0.068	-0.019	-1280	30
F-FA-(E)-BrOH	-8.4	2.496	2.668	-0.001	0.035	13	-62
Li-FA-(E)-BrOH	-15.0	2.238	2.615	-0.002	0.122	18	-186

results of the corresponding Br complexes are presented in Table 4. The electron-withdrawing F group weakens the HB and XB interactions, while the electron-donating Li group strengthens them. The former brings out a similar weakening effect on the HB and XB, while the latter causes a greater enhancement on the XB. The difference in the interaction energy of HB and XB decreases from 3.5 kcal mol⁻¹ for the unsubstituted complex to 1.3 kcal mol⁻¹ for the Li-substituted one. The geometric and spectroscopic parameters undergone a corresponding change accompanied by the change in the strength of HB and XB. An abnormal result is that the H...Br distance becomes shorter due to the Li substitution. Surprisingly, a similar substitution makes the O-Br bond have a prominent elongation (0.122 Å). A very big red shift (-1280 cm⁻¹) is found for the H-O stretch vibration in Li-FA-(*E*)-HOBr. Although the Li substitution does not make XB stronger than HB, it decreases their difference in strength.

Conclusions

The complexes of formamidine and hypohalous acid (HOX, X = F, Cl, Br, I) have been investigated at the MP2/aug-cc-pVTZ level. Formamidine is not only a good proton acceptor but a good halogen acceptor as well. The hydrogen-bonded complexes are more stable for X = F, Cl, Br, while the halogen-bonded complexes are favorable for X = I. Their stability can be regulated by substitution effect. Both molecules have biological activity, thus the study on the interaction between them is interesting. This work is helpful for understanding the mechanism behind their biological activity.

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