



Prediction and characterization of halogen bonds involving formamidine and its derivatives



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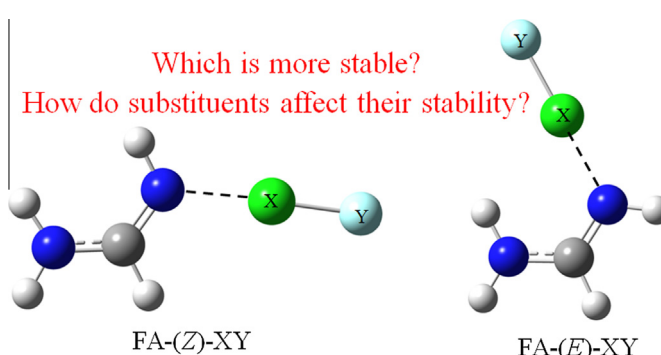
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HIGHLIGHTS

- Formamidine (FA) is a good electron donor in halogen bonding.
- The FA-(E) complex is more stable than the FA-(Z) counterpart.
- The strong halogen bond has a nature of partially covalent interaction.
- The strength of halogen bond can be regulated by substituents.

GRAPHICAL ABSTRACT



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ABSTRACT

Ab initio calculations have been carried out for the complexes of formamidine (FA) and some representative halogenated molecules XY (X = Cl, Br, and I; Y = F, CCH, CF₃, CN, and NC). The FA-(Z) complex combines with the halogenated molecule through a halogen bond, while the FA-(E) complex is stabilized jointly by both a halogen bond and a X...H interaction. The FA-(E) complex is more stable than the FA-(Z) counterpart, with the interaction energy of -3.4 to -23.4 kcal/mol, indicating that FA is a good electron donor in halogen bonding. The methyl substituent particularly one at the imino nitrogen atom of FA has an enhancing effect on the strength of halogen bond. The similar effect is found for the phenyl and pyridyl substituents, depending on the FA conformation and substitution position of pyridyl. The stability of stronger halogen bonding is mainly attributed to electrostatic and polarization energies, which is different from the weak one with an electrostatic nature.

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Introduction

Amidines, a dinitrogen analog of carboxylic acid and ester, display a rich chemistry because of their unique structures and diverse binding properties. It was acknowledged that amidines

are of great importance in biological and chemical processes, particularly they have a unique and fascinating biological activity, ranging from bactericidal and antiprotozoal effects, through antihelminthic, fungicidal and herbicidal properties to the insecticidal and acaricidal actions [1,2]. As a consequence, they have been extensively used as pharmacological agents such as pesticides [3–5]. On the other hand, they have proved to be intermediates in the synthesis of some metallocyclic complexes [6–8] and heterocyclic complexes [9–11]. Recently, Singh presented a review on the

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structure and reactivity of various amidines as well as their complexation behavior with different metal ions [12].

Because of the effect of resonance-stabilized cations, amidines are often taken as organosuperbases with strong basicity [13], depending on the extent and type of substitution at the amino and imino nitrogen atoms as well as at the functional carbon atom [13]. Consequently, they can serve as multidentate ligands [14–16]. For instance, *N*-phenyl-*N'*-cyano-formamidine can form some functional coordination polymers with AgX (X = NO₃⁻, SO₃CF₃⁻, and BF₄⁻) through a combination of both metal–ligand interaction and other weak non-covalent interactions [15] and Archibald et al. found that silver complexes of phenyl-functionalized *N,N'*-diphenylformamidinate have a better thermal stability with increasing coordination number [16].

Also it has been established that amidines can form strong hydrogen-bonded complexes with itself [17,18], formic acid [19–21], formamide [22,23], glycinamide [24], water [21,25], and alcohols [26]. In the study of these hydrogen-bonded complexes, much attention has been paid to proton transfer, particularly multiproton transfer, because it plays an important role in the proton relay occurring in enzymatic reactions, transport phenomena in biological membrane, and DNA mutations. The double-proton transfer occurs asynchronously in formamidine-formic acid complex, with a lower barrier height than that of the concerted reactions in both formamidine dimer and formic acid dimer [19]. Interestingly, water could promote the tautomerization of formamidine by drastically lowering its barrier [27].

Recently, more attention has been paid to another important intermolecular interaction – halogen bonding, due to its applications in the various fields such as biological systems [28–30], crystal engineering [31–33], and molecular recognition [34–36]. Halogen bonding [37–39] is a highly directional non-covalent interaction between a region of positive electrostatic potential on the outer side of a covalent halogen atom and a negative site, including lone pairs on F, O or N, π -electrons in unsaturated systems [40–42], metal hydrides [43–45], radicals [46–48], and carbenes [49,50]. Herein, molecules containing N such as NH₃ or HCN are often used to be the halogen acceptor in halogen bonding. However, the study of halogen bonds involving amidines is few [51].

In the present paper, we performed a systematic study of halogen bonding between formamidine (FA) and some halogenated compounds. The representative halogenated molecules include XF, XCCH, XCF₃, XCN, and XNC (X = Cl, Br, and I), which are often taken as the halogen donors in halogen bonds. Formamidine has two configurations of FA-(*Z*) and FA-(*E*) (Fig. 1), so we compared their ability to form halogen bonds with these halogenated compounds. The FA derivatives have been attracted much attention [52,53] and methyl group plays an interesting role in halogen bonds [54], we thus focused on the effect of substituents including methyl, phenyl, and pyridyl groups in FA on the strength of halogen bonding. This study of combining amidines with halogen bonding is significant in view of their applications in biological systems and crystal engineering.

Theoretical methods

The geometries of all complexes were optimized at the MP2/aug-cc-pVTZ level of theory by means of the Gaussian 09 software [55]. For iodine, the aug-cc-pVTZ-PP basis set was adopted to account for relativistic effects. Frequencies were computed to ensure that the structures are equilibrium structures. The interaction energies were corrected for basis set superposition error (BSSE) by using the counterpoise technique of Boys and Bernardi [56]. Topological properties at bond critical points (BCPs) were

obtained by AIM methodology as implemented in the AIM2000 program [57]. Natural bond orbital (NBO) analysis was performed using the NBO program [58] available in the Gaussian 09 software. Energy decomposition analysis was carried out using a localized molecular orbital (LMO) method [59] implemented in GAMESS program [60]. The electrostatic potentials (MEPs) 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

Geometries and interaction energies

Based on the value of negative MEP on the imino nitrogen atom of FA (Fig. 1), it is concluded that the imino nitrogen atom of FA-(*Z*) is a better proton acceptor in hydrogen bonding than that of FA-(*E*). However, the *E* conformation is often found to participate in hydrogen bonds [17–26]. This is due to the fact that the *E* isomer of FA can form a double hydrogen bond with both the imino nitrogen atom as the electron donor and the amino hydrogen atom as the proton donor simultaneously. As a result, both types of hydrogen bonds are cooperatively responsible for the stability of the hydrogen-bonded complexes of FA-(*E*). Here we focus only on the possibility of the imino nitrogen atom of both FA-(*Z*) and FA-(*E*) to form halogen bonding with halogenated molecules XF, XCCH, XCF₃, XCN, and XNC (X = Cl, Br, and I) (Fig. 2). Their geometrical data and interaction energies are summarized in Tables 1 and 2 for the *Z* and *E* complexes of FA, respectively.

It is found from Fig. 2 that a linear halogen bond is formed between FA and the halogen donor molecule in both types of structures. Furthermore, the existence of the halogen bond in each structure can be characterized by the presence of N···X BCP in Fig. 3. One can see that the complex with *E* conformation displays a little larger angle N···X–Y than that in the *Z* counterpart. Interestingly, the C–N···X angle follows a similar change in both types of structures: the X atom inclines to the H(2) in the *Z* complex and the H(3) in the *E* one. Moreover, this inclination becomes a little prominent with the increase of the halogen electronegativity in most complexes, which can be explained with the anisotropic distribution of electrostatic potentials on the halogen atomic surface [39]. In the *E* structure, there is also a H···X interaction between

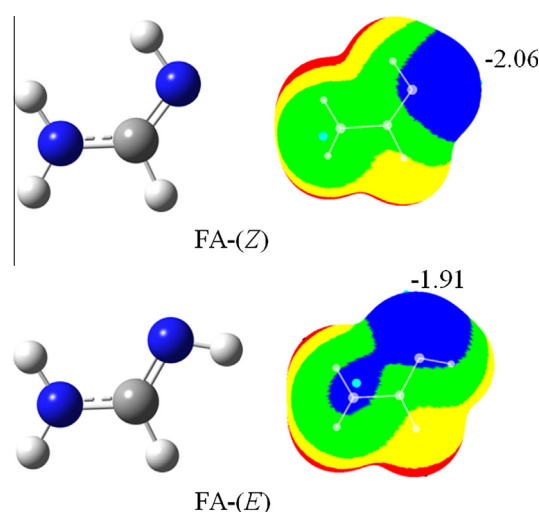


Fig. 1. Structures of both isomers of FA and their MEP map at the MP2/aug-cc-pVTZ level. Color ranges, in eV, are: red, greater than 0.82; yellow, between 0.82 and 0; green, between 0 and -0.82; blue, less than -0.82. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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