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A theoretical investigation on the nature of Cl···N and Br···N halogen bonds in F—Ar—X···NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH₂, CH₃ and CN)

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A B S T R A C T

A theoretical study was performed to examine intermolecular halogen bonds interactions in F—Ar—X···NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH₂, CH₃ and CN). Examination of the electrostatic potentials of the NCY monomers indicates that the addition of substituents has a large influence upon the most negative electrostatic potential on the surface of the interacting nitrogen and thus modulates these halogen-bonding interactions. The calculated CCSD(T)/aug-cc-pVTZ interaction energies for the complexes span from −0.88 to −3.20 kcal/mol. The nature of Cl···N and Br···N interactions has been identified in terms of the bond critical point analysis within the quantum theory of atoms in molecules (QTAIM). According to energy decomposition analysis, the stabilities of the F—Ar—X···NCY interactions are predicted to be attributable mainly to electrostatic and polarization effects, while dispersion forces play a smaller role in stabilizing these complexes.

1. Introduction

There is now a growing awareness of the importance of noncovalent interactions, due to their essential role in areas ranging from crystal engineering [1,2] to biological recognition processes [3,4]. The hydrogen bond (HB), the chief mode of interaction of which is through electrostatic and charge-transfer (delocalization) forces, has been the subject of many investigations and it is believed to be the best characterized type of noncovalent interactions [5–8]. The HB 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. However, there are also so-called unconventional HBs such as C—H···Y, X—H···C, X—H···π-electrons or even C—H···C [9]. One can also mention dihydrogen bonds, a special kind of HB where the negative charged H-atom is a proton acceptor [10]. Besides the HB, there are also other important noncovalent interactions. The term "halogen-bonding" is usually taken to mean the non-covalent RX···YZ interaction, where X is a halogen (typically chlorine, bromine, or iodine) that is part of the molecule RX and YZ is a Lewis base; Y is often an atom, such as oxygen, nitrogen, or sulfur, that has a lone pair [11,12]. Halogen bonds share many physical properties with the more commonly encountered HBs [13,14] and Houplain et al. have shown via infrared spectra that the former can compete and interfere with the latter [15,16]. It is increasingly recognized that halogen-bonding plays a critical role in a wide variety of biochemical phenomena such as protein–ligand complexation [2,17,18], and can be utilized effectively in drug design.

Since bonded halogens are commonly viewed as being negative in character, such "negative–negative" interactions were puzzling, until Brinck et al. [19], and subsequently others [20,21], showed that the halogen atoms X in some molecules RX have regions of positive electrostatic potential on their outer surfaces, on the extensions of the R—X bonds. This electron-deficient outer portion is called a "σ-hole", because it is centered on the R—X axis and is surrounded by negative electrostatic potential. Experimental results [22,23] and theoretical calculations [24–27] consistently show that the greater the polarizability and the lower the electronegativity of a halogen atom, the more positive is its σ-hole and the stronger is the halogen bond to which it gives rise. The strength of halogen bond formed by a halogen derivative with a given electron rich moiety (halogen bond acceptor) thus decreases in the order I > Br > Cl. As a result of a combination of extreme electronegativity and limited polarizability, the F atom is frequently deemed to not participate in halogen-bonding. The electron density distribution around F is nearly spherical rather than anisotropic and consequently, F is most likely to behave as halogen bond acceptors. However, it has recently been shown that fluorine atom has the capability of forming halogen bonds and can also affect recognition and self assembly processes, but only under specific circumstances [28,29].

As a noble atom is inserted into a molecule, the properties of this molecule suffer a big change. For example, the dipole moment of HF is evaluated to be 0.701 au at the MP4-[SDTQ] level [30],

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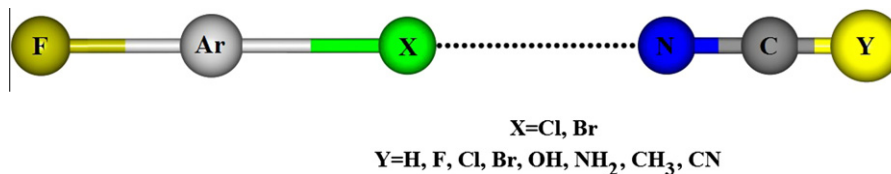E-mail address: esrafili@maragheh.ac.ir (M.D. Esrafili).

X=Cl, Br
Y=H, F, Cl, Br, OH, NH$_2$, CH$_3$, CN

Fig. 1. Structure of F—Ar—X· · ·NCY complexes.

whereas it is 2.57 au for HArF calculated using CCSD(T)/ aug-cc-pVTZ method [31]. However, it is natural to inquire if the noble gas (Ng) atom can be inserted between the F and the X atom (where X = Cl or Br). The resultant compounds would have the FNgX structure, which is a fluorine analog of the HNgX compounds observed in matrix-isolation studies [32–35]. In the present study, we use a spectrum of quantum chemical methods – CCSD(T), MP2, and DFT-to perform a systematic analysis of geometric structure and energetic stability of the FArX and FArX· · ·NCY complexes, where X = Cl, Br and Y = H, F, Cl, Br, OH, NH$_2$, CH$_3$ and CN (Fig. 1). In addition to the energetic aspects, the calculations address the lengths of the halogen bonds, including perturbations induced in the internal geometry of each monomer. The work also addresses electron density shifts induced by halogen bond formation, and how they are altered by the presence of electron-donating and electron-withdrawing groups.

2. Computational details

All molecular orbital calculations were performed using GA-MESS electronic structure package [36]. The geometries for all stationary points have been optimized using the M06-2X/aug-cc-pVTZ level of theory. The inclusion of diffuse functions in the aug-cc-pVTZ basis set is a clear requirement to adequately describe halogen-bonded systems [37]. According to Zhao and Truhlar [38–41], the M06 series of functionals implicitly account for "medium-range" electron correlation because of the way they are parametrized, and this is sufficient to describe the dispersion interactions within many complexes [41]. These authors define "medium-range" correlation to be that found in complexes separated by about 5 Å or less [42]. While initial tests of these functionals have been very promising [43], they have yet to be fully benchmarked for biologically relevant noncovalent interactions.

The interaction energies of all F—Ar—X· · ·NCY complexes have been computed as the differences between the total energies of the dimers and the energies of the isolated monomers and have been corrected for basis set superposition error (BSSE) using the counterpoise method [44]. Electrostatic surface potentials were calculated at MP2/aug-cc-pVTZ level using WFA program [45]. The quantum theory of atoms in molecules (QTAIM) [46] analysis was preformed with the help of AIM 2000 software [47] using the wave functions generated at the MP2/aug-cc-pVTZ level.

In order to analyze halogen bonds properties in terms of meaningful physical components, interaction energies were decomposed using [48]:

$$E_{int} = E_{elst} + E_{exch-rep} + E_{pol} + E_{disp} \qquad (1)$$

where E_{elst} is the first-order electrostatic term describing the classical columbic interaction of the occupied orbitals of one monomer with those of another monomer, $E_{exch-rep}$ is the repulsive first-order exchange component resulting from the Pauli exclusion principle, E_{pol} and E_{disp} correspond to polarization and dispersion terms. The polarization term contains all classical induction, exchange-induction, etc., from the second order up to infinity. All energy components were calculated using GAMESS package [36].

3. Results and discussion

3.1. Electrostatic potential and geometries

We will look first at the overall electrostatic potential on the surface of F—Ar—Cl and F—Ar—Br molecules. For this purpose, we compute electrostatic potential on the molecular "surface" which we define, following Bader et al. [49] as the 0.001 electrons/bohr^3 contour of the electronic density $\rho(r)$ [45]. This surface potential is labeled $V_{S(r)}$. The graphical illustration of the $V_{S(r)}$ for the F—Ar—Cl and F—Ar—Br monomers is shown in Fig. 2. The most striking feature is the small positive electrostatic potential cap at the end region of the Cl or Br atom along the Ar—X bond vector, which is surrounded by an electroneutral area and, next, a large electronegative domain. An electronegative atom/group prefers to approach the positive cap, thereby giving rise to a directional interaction. Consistent with the usual trend that σ-holes become more positive in going to the heavier elements in a Group, the Br $V_{S,max}$ (39.6 kcal/mol) is more positive than the corresponding Cl (25.1 kcal/mol). Such halogen positive region is referred as the "σ-holes", because it is centered on the Ar—X axis and is surrounded by negative electrostatic potential [11]. This is invoked as the explanation for "halogen-bonding," which is a noncovalent interaction between a covalently bound halogen on one molecule and a negative site on another. Thus, it is expected that the stabilities of the F—Ar—X· · ·NCY complexes depend upon both the magnitudes of the $V_{S,max}$ and $V_{S,min}$ that give rise to the σ-hole bonding.

Tables 1 gives the computed nitrogen $V_{S,min}$ values for a series of individual NCY derivatives. As has been pointed out [21], the positive outer portions of some halogen surfaces can interact with negative parts of other molecules, and thus give rise to halogen-bonding. It is evident from Table 1 that the magnitude of a negative nitrogen potential depends upon the electron-withdrawing/donating power of the Y. Also apparent is that the presence of electron-withdrawing groups on the NCY results in lower nitrogen $V_{S,min}$ values, while the electron-donating OH and NH$_2$ substituent leads to higher $V_{S,min}$ values.

Table 1 also presents the evaluated geometrical parameters for various F—Ar—X· · ·NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH$_2$, CH$_3$, and CN). Quantitatively, all the complexes indicate the presence of Cl· · ·N or Br· · ·N interaction due to the short intermolecular distances. From Table 1, it is apparent that the estimated Cl· · ·N distances are in a range of 2.78–3.03 Å which is much smaller than the sum of Van der Waals radii for chlorine and nitrogen (about 3.3 Å). The binding distance is calculated to be 2.87 Å in the F—Ar—Cl· · ·NCH complex. However, the presence of the electron-donating groups makes an increase of binding distance. More especially, the substitution of electron-donating groups (OH and NH$_2$) in the NCY moiety makes a 0.04 and 0.09 Å decrease of the binding distance, respectively, whereas the electron-withdrawing groups (F and CN) result in a 0.01 and 0.16 Å increase of the binding distance. The calculated binding distance in methyl substituted complex is 2.81 Å, which is 0.06 Å shorter than that of F—Ar—Cl· · ·NCH. An interesting aspect of the results presented in Table 1 is the fact that the binding distance of the systems tends to decrease as the size of the substituted halogen increases, which corresponds to a decreasing value of the halogen atom electronegativity.
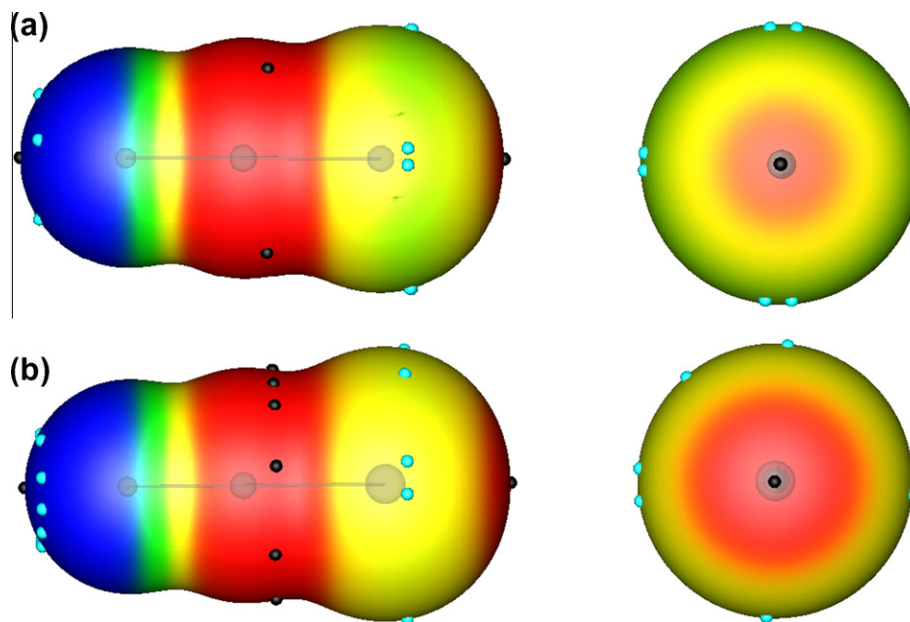
Fig. 2. Calculated MP2/aug-cc-pVTZ electrostatic potential of (a) F—Ar—Cl and (b) F—Ar—Br. Color ranges for $V_{S(r)}$, in kcal mol^{-1}: for F—Ar—Cl (red >14.7, yellow 14.7 to −1.5, green −1.5 to −17.8, blue <−17.8) and for F—Ar—Br (red >19.1, yellow 19.1 to −1.3, green −1.3 to −21.7, blue <−21.7). Black circles surface maxima, blue surface minima. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. QTAIM analysis

A great deal of information about the nature of halogen bonds interactions in the F—Ar—X···NCY complexes can be obtained from topological analysis of its electron density. Based on the QTAIM theory, the electron density (ρ), its Laplacian ($\nabla^2\rho$) and electronic energy density (H_{BCP}) at a bond critical point (BCP) give us information about the strength and characteristic of the bond [46]. The electronic energy density is obtained from the equation $H_{BCP} = G_{BCP} + V_{BCP}$, where G_{BCP} and V_{BCP} are the local kinetic and potential energy densities, respectively. The energy density term G_{BCP} is calculated based on equation $(1/4)\nabla^2\rho_{BCP} = 2\ G_{BCP} + V_{BCP}$.

As pointed above, the origin of halogen-bonding is connected with formation of the so-called σ-hole, a region of positive electrostatic potential on the outermost region of the halogen atom surface, centered on the extension of the R—X bond [11]. The presence of the σ-hole in some halogen derivatives forming halogen bonds allows one to suspect that this interaction is rather electrostatic in nature [50,51]. However, it has been reported that interaction between the R—X and Lewis base cannot be simply reduced to electrostatic interaction and that other contributions to the interaction energy are also decisive. Table 1 shows the ρ_{BCP}, $\nabla^2\rho_{BCP}$, and the total energy density H_{BCP} values for all of the complexes examined in this work. Our results indicate that, despite falling in a region of charge depletion with $\nabla^2\rho_{BCP} > 0$, most of the Cl···N and Br···N BCPs are characterized by a small value of the electron density ρ_{BCP} and $H_{BCP} > 0$, indicating that the kinetic energy overcomes the potential energy density at the BCPs and the Cl···N and Br···N bonds are mainly electrostatic in nature. The estimated values of ρ_{BCP} in X···N BCPs are in the range 0.009–0.025 au, whereas the values of $\nabla^2\rho_{BCP}$ are between 0.043 and 0.087 au. For the F—Ar—Cl···NCH complex, the calculated ρ_{BCP} and $\nabla^2\rho_{BCP}$ values are 0.014 and 0.061 au, respectively. These values increase to 0.015, 0.065 and 0.017, 0.068 au for the OH, and NH$_2$ electron-donating groups, respectively, which is in accordance with the evidence for small stabilization of the Cl···NCH. For the halogen substituted compounds, QTAIM analysis indicates the capacity of the F—Ar—X···NCY complexes to concentrate electrons at the

Table 1
Calculated surface electrostatic potential $V_{S(r)}$ (in kcal/mol), binding distances (in Å) and QTAIM parameters (in 10^{-3} au) of the F—Ar—X···NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH$_2$, CH$_3$, and CN).

Molecule	$V_{S(r)}$	F—Ar—Cl				F—Ar—Br			
		$r_{Cl\cdots N}$	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	$r_{Br\cdots N}$	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
NCH	−31.56	2.87	13.7	61.0	2.8	2.87	16.0	63.9	2.2
NCF	−28.85	2.86	12.9	58.1	2.8	2.90	14.6	59.6	2.2
NCCl	−32.16	2.87	13.5	60.6	2.8	2.86	16.3	64.7	2.2
NCBr	−33.75	2.86	13.7	61.3	2.8	2.84	16.8	66.4	2.2
NCOH	−38.05	2.83	14.7	65.0	2.8	2.77	19.5	74.4	1.9
NCNH$_2$	−42.18	2.78	16.8	67.9	2.4	2.66	25.0	87.0	−1.0
NCCH$_3$	−40.53	2.81	15.5	67.5	2.8	2.74	21.2	79.3	0.7
NCCN	−21.77	3.03	9.4	43.4	2.4	2.98	12.3	51.3	2.2

X···N BCPs enhance considerably with the size of halogen atom. This conclusion is completely the same as that drawn from X···N bond distances.

As pointed out earlier, the electron energy density H_{BCP} is a more appropriate index to gain a deeper understanding of noncovalent interactions [52,53]. Recently, Lu et al. [52] indicated a good relationship between the charge densities and their Laplacians evaluated at the halogen bond critical points and the strength of halogen-bonding interaction. Their QTAIM analysis also suggested that strong halogen bonds are more covalent in nature, while weak ones are mostly electrostatic interactions. According to Rozas et al. [53], the character of X—Y interaction could be classified as a function of the total electron energy density H_{BCP} with Laplacian of the electron density at X—Y BCP ($\nabla^2\rho_{BCP}$). It means that for strong X—Y interactions ($\nabla^2\rho_{BCP} < 0$ and $H_{BCP} < 0$) the covalent character is established, for medium strength X—Y ($\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$) their partially covalent character is defined, and weak X—Y ($\nabla^2\rho_{BCP} > 0$ and $H_{BCP} > 0$) are mainly electrostatic. Therefore, most of the X···N interactions for the complexes studied here are electrostatic in nature. On the other hand, negative value of H_{BCP} is predicted for the F—Ar—Br···NCNH$_2$ complex, suggesting that the interaction in this halogen bond has some degree of covalent character. The evaluated H_{BCP} values at the X···N BCPs of the
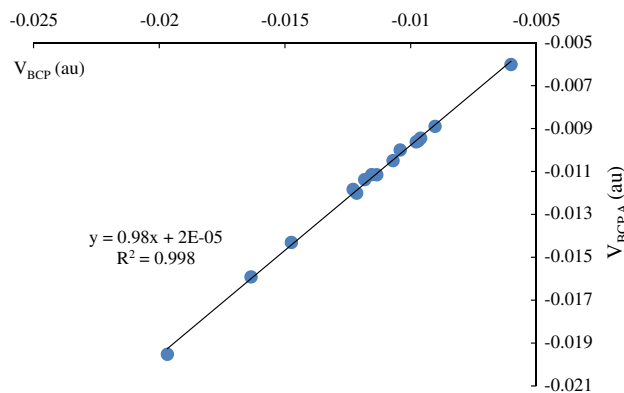
Fig. 3. Correlation of Abramov's local electronic potential energy density $V_{BCP,A}$ with the calculated electronic potential energy density V_{BCP} of F—Ar—X···NCY complexes.

systems tends to decrease as the size of the substituted halogen increases, which corresponds to a decreasing value of the halogen atom electronegativity. In terms of Espinosal's proposal [54], the local electronic potential energy density (V_{BCP}) can represent the capacity of the complexes in concentrating electrons at the X···N BCP and gives an approach to describing the X···N strength. Abramov [55] has proposed the evaluation of the local electronic potential energy density from the experimental electron density distribution. The Abramov's local electronic potential energy density $V_{BCP,A}$ can be evaluated according to the following expression:

$$V_{BCP,A} = -\left(\frac{3}{5}(3\pi^2)^{2/3}\rho^{5/3} + \frac{1}{12}\nabla^2\rho\right) \qquad (2)$$

Fig. 3 compares the calculated values of $V_{BCP,A}$ from Eq. (2) with the V_{BCP} data from the topological analysis for the 16 X···N bonds. As evident from Fig. 3, the distribution of the points exhibits a very good linear relationship between V_{BCP} and $V_{BCP,A}$. The graphical representation indicates that Eq. (2) can equivalently evaluate the capacity of the F—Ar—X···NCY complexes in concentrating electrons at the X···N BCPs and therefore the X···N strength.

3.3. Interaction energies and EDA

The interaction energy provides a measure of the strength of the interaction between F—Ar—X and NCY molecules. Table 2 gives the interaction energies of the F—Ar—X···NCY complexes calculated by means of the all electron MP2, M06-2X, and CCSD(T) methods using aug-cc-pVTZ basis set. Estimation of the BSSE for all of the structures presented here was performed by the full counterpoise method [44].

Considering the results listed in Table 2, it can be seen that all the methods indicate the presence of a relatively weak halogen-bonding interaction due to the interaction energies between −1.16 and −6.71 kcal/mol. Here it can be seen that, the substitution of various groups onto the NCY moiety has a significant effect upon halogen bond strengths. Computed interaction energies range from −1.16 (F—Ar—Cl···NCCN) to −6.71 kcal/mol (F—Ar—Br···NCNH$_2$). There are several other important aspects of these data that can immediately be seen in these tables. One of the most pronounced patterns is the relationship between interaction energies and nitrogen $V_{S,min}$ values: higher $V_{S,min}$ (more negative σ-holes) result in complexes that are more strongly bound. Fig. 4 shows a plot of interaction energy versus nitrogen $V_{S,min}$ for the title complexes. The correlation is remarkably good, with a correlation coefficient of 0.952 (for F—Ar—Cl) and 0.994 for (F—Ar—Br). This demonstrates the importance of the positive

Table 2
Interaction energies and binding decomposition analysis of F—Ar—X···NCY complexes.[a,b]

Complex	E_{int}^{M06-2X}	E_{int}^{MP2}	$E_{int}^{CCSD(T)}$	E_{elst}	$E_{exch-rep}$	E_{pol}	E_{disp}
F—Ar—Cl···NCH	−2.35	−1.85	−1.82	−4.70	5.84	−2.18	−0.81
F—Ar—Cl···NCF	−2.02	−1.73	−1.65	−4.13	5.26	−1.84	−1.02
F—Ar—Cl···NCCl	−2.26	−1.97	−1.90	−4.51	5.72	−2.10	−1.08
F—Ar—Cl···NCBr	−2.34	−2.05	−2.02	−4.62	5.86	−2.18	−1.11
F—Ar—Cl···NCOH	−2.96	−2.20	−2.14	−5.53	6.63	−2.72	−0.58
F—Ar—Cl···NCNH$_2$	−3.62	−2.50	−2.43	−6.43	8.70	−3.77	−1.00
F—Ar—Cl···NCCH$_3$	−3.26	−2.35	−2.31	−6.04	7.21	−3.08	−0.44
F—Ar—Cl···NCCN	−1.16	−1.59	−1.48	−2.32	3.12	−0.88	−1.51
F—Ar—Br···NCH	−4.19	−2.51	−2.44	−7.68	10.50	−3.63	−1.70
F—Ar—Br···NCF	−3.63	−2.33	−2.26	−6.60	9.15	−2.97	−1.91
F—Ar—Br···NCCl	−4.08	−2.61	−2.51	−7.50	10.59	−3.71	−1.99
F—Ar—Br···NCBr	−4.24	−2.70	−2.62	−7.82	11.12	−3.95	−2.05
F—Ar—Br···NCOH	−5.30	−2.91	−2.84	−13.48	16.97	−5.38	−1.02
F—Ar—Br···NCNH$_2$	−6.71	−3.21	−3.20	−13.48	20.09	−8.58	−1.24
F—Ar—Br···NCCH$_3$	−5.86	−3.10	−3.03	−11.29	16.39	−6.32	−1.88
F—Ar—Br···NCCN	−2.18	−1.97	−1.89	−4.21	6.75	−1.87	−2.64

[a] All interaction energies and energy components are in kcal/mol.
[b] Calculated EDA component at MP2/aug-cc-pVTZ level of theory.

σ-hole, as reflected by the computed chlorine and bromine $V_{S,max}$, in determining the energetics of the X···N halogen bonds. Furthermore, these correlations indicate the role that electrostatics plays in these interactions, whether or not there are secondary ones.

Table 2 shows that, in general, the M06-2X method provides larger stabilization energy relative to the CCSD(T) benchmark values. The interaction energies calculated at the CCSD(T) level are smaller by about 0.1 kcal/mol than those at the MP2 levels. Even so, the change in interaction energy in the different systems is similar for the different levels of theory. While dominated by electrostatic interactions, dispersion interactions also play an important role in the binding of these complexes. The performance of M06-2X versus MP2 for halogen-bonded complexes shows that it is not sufficient to include only the "medium-range" electron correlation which M06-2X are said to capture. Inspection of Table 2 reveals that the CCSD(T) interaction energies increase in the order NH$_2$ > CH$_3$ > OH > H > Cl > Br > F > CN, which is the parallel trend shown in the binding distances. That is, upon complexation, electron-donating groups form the strongest X···N bond. The interaction strength for the F—Ar—Br is stronger than for the corresponding chlorine complexes. This result has also been found for other types of halogen bonds [56,57]. Focusing on CCSD(T) results, which are available for each type of system considered, it can be seen that NCBr molecule is bound about 3% more strongly than NCCl, which binds about 11% more strongly than NCF.

Table 2 lists the EDA results for the different F—Ar—X···NCY complexes analyzed here. It can be seen from Table 2 that the stabilities of the F—Ar—X···NCY interactions are predicted to be attributable
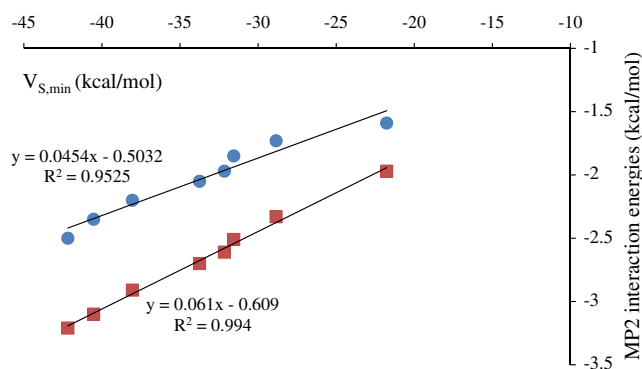

Fig. 4. Plot of MP2 interaction energies of F—Ar—X···NCY versus nitrogen $V_{S,min}$.

mainly to electrostatic and polarization effects, while dispersion forces, which have been widely believed to be responsible for these types of interactions, play a smaller role in stabilizing these complexes. Based on the EDA results, it is also found that electrostatic effects account for about 61% and 59% of the overall attraction in the F—Ar—Cl···NCH and F—Ar—Br···NCH complexes, respectively. By comparison, the polarization component of this interaction represents about 28% of the total attractive forces, while dispersion contributes 11% and 13% to the stability of these complexes, respectively. Therefore it can be said that the F—Ar—Cl···NCH and F—Ar—Br···NCH interaction is remarkably dependent on both electrostatic and polarization forces, with electrostatic playing the largest role in their stability. Consequently, the character of the X···N bond is almost equally due to covalency and ionicity.

It should be noted, unlike H-bonding interactions [58–60], the exchange energy term outweighs the electrostatic term for each complex studied here (Table 2). Based on our EDA results, the electrostatic contribution to the overall attraction energies of X = Cl(Br) and Y = F, Cl, Br, OH, NH$_2$, CH$_3$, and CN are 59%(57%), 59%(57%), 58%(57%), 63%(68%), 57%(58%), 63%(58%), and 49%(48%) respectively. What is more, the electrostatic contribution is largest for the electron-donating groups (OH, NH$_2$) and smallest for electron-withdrawing groups (F and CN). It is interesting to note that, although these types of interactions are largely dependent on electrostatic forces, the polarization interaction between the F—Ar—X and NCY moiety seems to play a significant role in determining the geometric structures of these complexes. As the size of the halogen substituent increases the electrostatic interaction would be expected to decrease. Comparing the data for the fluorine, chlorine, and bromine substituted F—Ar—X···NCY systems, it can be seen that both the dispersion and induction components of the interaction energy increase with increasing halogen size. Interestingly, there is a larger increase in the polarization energy, going from fluorine to bromine, than in the dispersion interaction.

4. Concluding remarks

Within this work, the halogen bond interactions between the F—Ar—X and NCY molecule have been investigated, where X = Cl, Br and Y = H, F, Cl, Br, OH, NH$_2$, CH$_3$ and CN. It has been demonstrated that there exists an attractive interaction when a covalently bonded bromine atom approaches the magnesium hydride. The results obtained from M06-2X, MP2 and CCSD(T) methods reveal the weak non-covalent Cl···N or Br···N interactions in all complexes. The M06-2X/aug-cc-pVTZ interaction energies of Cl···N and Br···N halogen bonds, depending on the substituted atom(s), range from −0.88 kcal/mol (F—Ar—Cl···NCCN) to −6.71 kcal/mol (F—Ar—Br···NCNH2). Our results indicate that, despite falling in a region of charge depletion with $\nabla^2\rho_{BCP} > 0$, most of the Cl···N and Br···N BCPs are characterized by a small value of the electron density ρ_{BCP} and $H_{BCP} > 0$, indicating that the kinetic energy overcomes the potential energy density at the BCPs and the Cl···N and Br···N bonds are mainly electrostatic in nature. We found a good correlation between interaction energies and nitrogen $V_{S,min}$ values: higher $V_{S,min}$ (more negative σ-holes) result in complexes that are more strongly bound. Although these types of interactions are largely dependent on electrostatic forces, the polarization interaction the F—Ar—X and NCY moiety seems to play a significant role in determining the geometric structures of these complexes.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.07.038.

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