

Insights into the strength and nature of carbene⋯halogen bond interactions: a theoretical perspective

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Abstract Halogen-bonding, a noncovalent interaction between a halogen atom X in one molecule and a negative site in another, plays critical roles in fields as diverse as molecular biology, drug design and material engineering. In this work, we have examined the strength and origin of halogen bonds between carbene CH₂ and XCCY molecules, where X=Cl, Br, I, and Y=H, F, COF, COOH, CF₃, NO₂, CN, NH₂, CH₃, OH. These calculations have been carried out using M06-2X, MP2 and CCSD(T) methods, through analyses of surface electrostatic potentials $V_S(r)$ and intermolecular interaction energies. Not surprisingly, the strength of the halogen bonds in the CH₂⋯XCCY complexes depend on the polarizability of the halogen X and the electron-withdrawing power of the Y group. It is revealed that for a given carbene⋯X interaction, the electrostatic term is slightly larger (*i.e.*, more negative) than the dispersion term. Comparing the data for the chlorine, bromine and iodine substituted CH₂⋯XCCY systems, it can be seen that both the polarization and dispersion components of the interaction energy increase with increasing halogen size. One can see that increasing the size and positive nature of a halogen's σ -hole markedly enhances the electrostatic contribution of the halogen-bonding interaction.

Keywords DFT · Electrostatic potentials · Halogen bond · Hydrogen bond · σ -hole

Introduction

Halogen-bonding interactions play a critical role in supra-molecular chemistry, molecular biology, and material

science [1–8]. A halogen bond is defined as a short-range R–X⋯Y interaction, where the halogen X acts as a Lewis acid and Y is any negative site, including Lewis bases, π regions of aromatics or molecules containing double bonds, and anions. Halogen bonds share numerous physical properties with the most commonly encountered hydrogen bonds (HBs). In fact, it has been reported that halogen-bonding may be competitive to HBs [9–12], and similarly as HB, it may play the crucial role in structure stabilization of crystals [13, 14] and biomolecular systems [15, 16] and also may be used in new drug design and material engineering [17, 18]. This noncovalent interaction can be strong enough to control the aggregation of organic molecules [19]. Halogen bond interaction energies are fairly broad, with values varying from about 1.2 kcal mol⁻¹ (Cl⋯Cl) to about 43.0 kcal mol⁻¹ (I₃⁻⋯I₂) [20].

The phenomenon of halogen-bonding has been discussed in numerous theoretical works [20–25] and remains a subject of intense research. According to Politzer's viewpoint [26], when a half-filled *p* orbital participates in forming a covalent bond, its electron normally tends to be somewhat localized in internuclear region, thereby diminishing the electronic density in the outer lobe of that orbital. Through this positive region, which has been labeled a “ σ -hole” [26], the halogen atom can interact attractively with a negative site. This positive region is usually, but not always, surrounded by a belt of negative electrostatic potential, which accounts for the possibility of interacting laterally with a positive site. The strength of a halogen bond depends on the polarizability of the halogen, the electron-withdrawing power of the R group to which X is bonded, and the nucleophilicity of the Lewis base [27–30]. The size of the σ -hole increases with halogen size from chlorine to iodine, an observation that was found in several studies [25–30]. As a result of a combination of extreme electro-negativity and limited polarizability, fluorine atom is

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frequently deemed to not participate in halogen-bonding. 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 [31, 32]. Then, in FCN molecule, the electron-withdrawing CN group is sufficient to create a positive electrostatic potential on the fluorine atom [31]. Numerous studies demonstrated that, for a given negative site, the strengths of halogen bonds correlate with the magnitudes of the σ -hole potentials [9, 16, 29]. This may emphasize the largely electrostatic nature of these interactions. However, the consideration of only the electrostatic interaction may not be sufficient in describing the ground-state stabilization of halogen-bonding complexes. On the other hand, the polarization and dispersion contributions play also an important role [2, 3, 12, 16, 24, 29, 33–35]. Recently, Riley et al. [36] indicated that halogens with larger, more positive σ -holes tend to exhibit weaker dispersion interactions, which are attributable to the lower local polarizabilities of the larger σ -holes.

To the best of our knowledge, and in contrast with the large number of experimental and theoretical investigations aimed to deepen the understanding of the halogen-bonding interactions, the carbene \cdots halogen bond interactions have received less attention especially from the theoretical point of view. Recently, we have performed a series of studies to comprehensively characterize the strength and nature of different halogen-bonding interactions in either the gas phase or lattice [23, 29, 37–39]. We have analyzed the strengths and nature of the halogen \cdots halogen, halogen \cdots oxygen and halogen \cdots nitrogen interactions using the topology of the charge density distribution and energy decomposition analysis. Herein we report our density functional theory study of CH₂ \cdots XCCY complexes, where X=Cl, Br and I; Y=H, F, COF, COOH, CF₃, NO₂, CN, NH₂, CH₃, OH (Fig. 1). Although carbene has two classes: singlet and triplet, we only consider the singlet one due to the presence of a free electron pair in singlet state. The energy decomposition scheme is applied to gain more detailed insight into the nature of the interactions. In addition, the charge density analysis has also been applied. One of the aims of this study is to answer the following questions: What is the nature of carbene \cdots halogen interactions in these complexes? What is the substitution effect on the stabilization of these complexes? Is there any relationship between the size of a halogen's σ -hole and a given energy component?

Computational details

Geometry optimizations of CH₂ \cdots XCCY complexes were performed with the GAMESS program suite [39] using

M06-2X density functional. No symmetry was used in the optimization of the structures. All optimized structures were characterized as potential energy minima at the same theoretical levels by verifying that all vibrational frequencies are real. According to Zhao and Truhlar [40–43], the M06 series of functionals implicitly account for “medium-range” electron correlation because of the way they are parameterized, 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 [44]. While initial tests of these functionals have been very promising [45], they have yet to be fully benchmarked for biologically relevant noncovalent interactions. For complexes containing chlorine and bromine the aug-cc-pVTZ basis [46] was used for optimization, while for systems containing iodine a mixed basis set approach was used; here the iodine atom is described using the pseudopotential based aug-cc-pVTZ-PP basis [47] and the aug-cc-pVTZ is used for other atoms.

The interaction energies of the all optimized CH₂ \cdots XCCY complexes were calculated using M06-2X, MP2 and CCSD(T) methods. They 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 [48]. Electrostatic surface potentials were calculated using WFA code [49].

In order to analyze carbene \cdots halogen bonds properties in terms of meaningful physical components, interaction energies were decomposed using [50]:

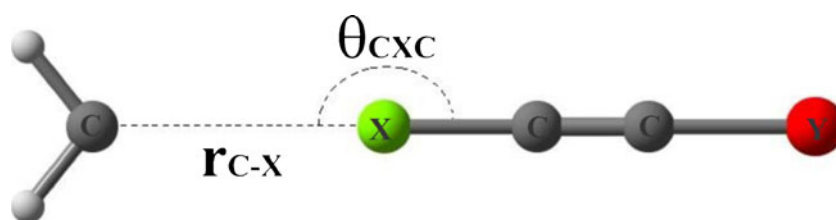
$$E_{int} = E_{elst} + E_{exch-rep} + E_{pol} + E_{disp}, \quad (1)$$

where E_{elst} is the first-order electrostatic term describing the classical Coulomb 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 [39].

Results and discussion

In this article we describe the possibility of halogen bond formation between the carbene and XCCY moieties, where X=Cl, Br, I and Y=H, F, COF, COOH, CF₃, NO₂, CN, NH₂, CH₃, OH (Fig. 1). Electrostatic potentials and geometries of the stable CH₂ \cdots XCCH dimers performed at M062X/aug-ccpVTZ or M062X/aug-ccpVTZ-PP will be presented. Then, a comparison of halogen bonds characteristics in different CH₂ \cdots XCCH is presented based on the

Fig. 1 Structure of $\text{CH}_2 \cdots \text{XCCY}$ complexes ($X = \text{Cl, Br, and I}$; $Y = \text{H, F, COF, COOH, CF}_3, \text{NO}_2, \text{CN, OH, NH}_2, \text{CH}_3$)



evaluated interaction energies and energy decomposition analysis results. Here we evaluate the role of different energy terms, and we seek to find the main factors that stabilize the $\text{CH}_2 \cdots \text{XCCH}$ complexes in gas phase. Unless otherwise noted, the following results are referred for the M06-2X results.

Surface electrostatic potentials and geometries

Figure 2 shows electrostatic potentials maps for the CH_2 and XCCH molecules ($X = \text{Cl, Br and I}$). In each case, we computed electrostatic potential on the molecular “surface” which we define, according to Bader et al. [51], as the 0.001 electrons/bohr³ contour of the electronic density $\rho(\mathbf{r})$. This surface potential is labeled $V_S(\mathbf{r})$. From Fig. 2a, it is evident that the most negative regions of the CH_2 molecule are associated with the carbon atom; the $V_{S,\text{min}}$ is $-35.5 \text{ kcal mol}^{-1}$. Hence, this $V_{S,\text{min}}$ represents attractive channel for the approach of an electrophile to the carbene molecule. On the other hand, regions of positive electrostatic potential with $V_{S,\text{max}}$ are found above and below the carbon atom; these are what we label positive π -holes [26]. These are regions of low electronic density that are perpendicular to portions of a molecular framework instead of being along the extensions of bonds (as are σ -holes [26]). Their magnitudes are fairly strong, $43.9 \text{ kcal mol}^{-1}$, comparable to, and in some cases considerably exceed, those of σ -holes [25–27]. The most striking feature of Fig. 2b is the small positive electrostatic potential cap at the end region of the halogens along the C–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 [26], the iodine $V_{S,\text{max}}$ ($35.8 \text{ kcal mol}^{-1}$) is more positive than the corresponding bromine ($27.5 \text{ kcal mol}^{-1}$) or chlorine ($21.9 \text{ kcal mol}^{-1}$). Such halogen positive region is referred to as the “ σ -holes”, because it is centered on the C–X axis and is surrounded by negative electrostatic potential [25].

Table 1 lists 30 complexes formed between the XCCY molecules, acting as σ -hole donors through the halogen atom X, and carbene, acting as the acceptor through its carbon $V_{S,\text{min}}$. One interesting feature of the data presented in this table is the fact that for a given Y substitution, the magnitude of $V_{S,\text{max}}$ associated with the halogen atoms of the systems tends to increase as the size of the halogen increases. It is evident from Table 1 that the magnitude of the halogen’s σ -hole depends upon the electron-withdrawing/donating power of the Y. Also apparent is that the presence of electron-withdrawing groups on the XCCY results in higher halogen $V_{S,\text{max}}$ values while the electron-donating OH, CH_3 and NH_2 substituents lead to lower $V_{S,\text{max}}$ values.

Table 1 lists the intermolecular distances for the $\text{CH}_2 \cdots \text{XCCY}$ complexes. Here a clear trend can be seen where the systems containing the largest halogen, *i.e.*, iodine, are more strongly bound, with a binding distance in the range of 2.80–3.00 Å, which are less than the sums of van der Waals (vdW) radii of iodine (1.98 Å) and hydrogen

Fig. 2 Surface electrostatic maps of (a) CH_2 and (b) XCCH molecules. Color ranges in kcal mol⁻¹ for CH_2 : red > 24.10, yellow 4.24 to 24.10, green -15.61 to 4.24, blue < -15.61 ; for ClCCH : red > 23.50, yellow 11.96 to 23.50, green 0.43 to 11.96, blue < 0.43; for BrCCH : red > 23.31, yellow 11.60 to 23.31, green -0.12 to 11.60, blue < -0.12 ; for ICCH : red > 23.44, yellow 11.16 to 23.44, green -1.12 to 11.16, blue < -1.12 . Black circles surface maxima, blue surface minima

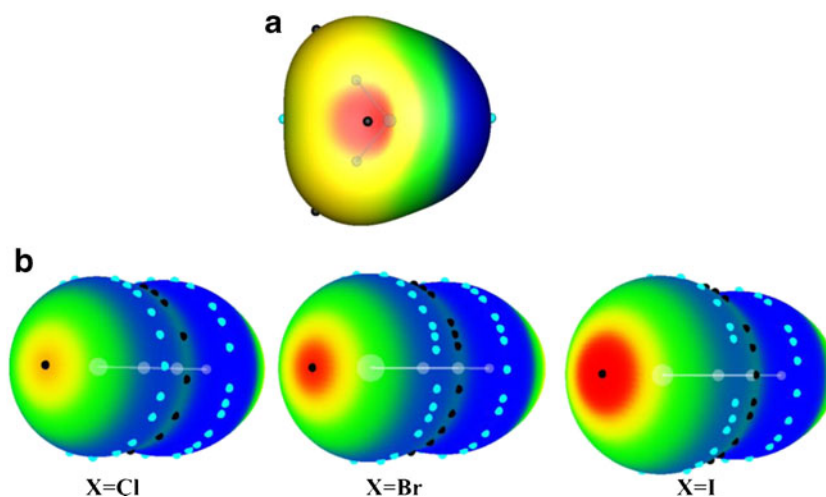


Table 1 Calculated halogen electrostatic potentials, $V_{S,max}$, and carbene–halogen intermolecular distances $r_{C\cdots X}$, for $CH_2\cdots X-CC-Y$ complexes ^{a,b}

X–CC–Y	$V_{S,max}$	$r_{C\cdots X}$
Cl–CC–H	21.9	3.16
Cl–CC–F	22.6	3.13
Cl–CC–COF	34.6	3.08
Cl–CC–COOH	29.2	3.11
Cl–CC–CF ₃	32.2	3.09
Cl–CC–NO ₂	37.1	3.06
Cl–CC–CN	36.0	3.07
Cl–CC–CH ₃	16.9	3.19
Cl–CC–OH	17.1	3.18
Cl–CC–NH ₂	14.7	3.19
Br–CC–H	27.5	3.11
Br–CC–F	28.7	3.08
Br–CC–COF	39.9	3.04
Br–CC–COOH	34.7	3.08
Br–CC–CF ₃	36.3	3.05
Br–CC–NO ₂	42.4	3.03
Br–CC–CN	41.4	3.04
Br–CC–CH ₃	22.7	3.14
Br–CC–OH	23.2	3.12
Br–CC–NH ₂	20.8	3.13
I–CC–H	35.8	2.97
I–CC–F	37.4	2.88
I–CC–COF	48.1	2.87
I–CC–COOH	43.7	2.91
I–CC–CF ₃	46.1	2.87
I–CC–NO ₂	51.8	2.80
I–CC–CN	49.4	2.84
I–CC–CH ₃	31.6	3.00
I–CC–OH	31.8	2.98
I–CC–NH ₂	29.4	3.00

^a All $V_{S,max}$ values in kcal mol^{−1}. ^b All intermolecular distances in Å

(1.10) [52]. The BrCCY and ClCCY molecules also form stable complexes with the carbene, with binding distances that are progressively greater as the size of the halogen decreases. For each case, the evaluated binding distances are smaller than the sum of vdW radii of the corresponding atoms, which supports the presence of the carbene–halogen interaction in these complexes. The binding distance is calculated to be 2.97 Å in the $CH_2\cdots ICCH$ complex. However, the presence of the electron-withdrawing groups makes a decrease of binding distance. More especially, the substitution of NO₂ and CN groups in the ICCY moiety makes a 0.16 and 0.13 Å decrease of the binding distance, respectively. On the other hand, for a given halogen atom, the substitution of an electron-donating group (e.g., Y=OH) results in a longer binding

distance. This trend consists with the earlier findings in other types of halogen bond [27–30].

It should be noted that for all complexes studied here, the carbene⋯halogen bonds are directional, and the angle θ_{C-X-C} ranges from 165–180°, similarly as what is found for normal halogen bonds [20–30]. This linear structure can be understood with the electrostatic potentials of CH_2 and XCCY. More specifically, Torii and Yoshida [53] reported that the atomic quadrupole moments on the halogen atoms play an essential role in determining the geometries of halogen-bonded complexes and the electrostatic interactions of the atomic quadrupole moments are the origin of the high directionality of the halogen bond. According to our results, halogen bonds involving iodine and bromine are sufficiently strong and highly directional, which indicates that the halogen bonds of iodine and bromine play important roles in controlling molecular recognition processes and crystal packing, as in the cases of hydrogen bonds. On the other hand, the directionality of halogen bonds involving chlorine is low.

Interaction energies

As already mentioned in literature, the stabilities of halogen-bonded complexes depend primarily upon both the magnitudes of the $V_{S,max}$ and $V_{S,min}$ that give rise to the σ -hole bonding and also upon any existing or potential secondary interactions [9, 16, 24–30]. Table 2 lists the evaluated interaction energies for different carbene–halogen complexes using M06-2X, MP2 and CCSD(T) methods. According to 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 −1.5 and −9.8 kcal mol^{−1}. 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 (less negative) by about 0.1–0.8 kcal mol^{−1} than those at the MP2 levels. The performance of M06-2X versus MP2 and CCSD(T) for the halogen-bonded complexes shows that it is not sufficient to include only the “medium-range” electron correlation which M06-2X are said to capture.

From Table 2, it is evident that for a given Y substitution and for a given level of theory, the strength of the carbene⋯halogen bond increases in the Cl<Br<I order. This can be confirmed with electrostatic potentials. The same trend is also valid for other halogen bonds and is illustrated by the increase of the magnitude of the electrostatic potential of a σ -hole of a relevant halogen atom [27–30]. This finding indicates qualitatively that the electrostatic interaction plays a significant role in the formation of the carbene–halogen interaction. Figure 3 indicates plots of M06-2X interaction energies versus halogens $V_{S,max}$ for the title complexes. One of the most pronounced patterns is

Table 2 Calculated interaction energies and EDA results of $\text{CH}_2 \cdots \text{X}-\text{CC}-\text{Y}$ complexes^a

X-CC-Y	E_{int}^{M06-2X}	$E_{\text{int}}^{\text{MP2}}$	$E_{\text{int}}^{\text{CCSD}(T)}$	E_{elst}	$E_{\text{exch-rep}}$	E_{pol}	E_{disp}	$E_{\text{elst}}/E_{\text{disp}}$
Cl-CC-H	-2.2	-2.2	-2.1	-4.5	7.1	-1.6	-3.2	1.4
Cl-CC-F	-2.3	-2.2	-2.0	-4.8	7.6	-1.6	-3.4	1.4
Cl-CC-COF	-3.5	-3.4	-3.1	-6.6	8.9	-2.0	-3.8	1.7
Cl-CC-COOH	-3.0	-2.9	-2.5	-5.7	8.1	-1.8	-3.6	1.6
Cl-CC-CF ₃	-3.3	-3.2	-2.8	-6.2	8.5	-1.9	-3.7	1.7
Cl-CC-NO ₂	-3.8	-3.6	-3.2	-7.1	9.3	-2.1	-3.9	1.8
Cl-CC-CN	-3.7	-3.6	-3.2	-6.8	9.1	-2.1	-3.8	1.8
Cl-CC-CH ₃	-1.7	-1.8	-1.6	-3.7	6.5	-1.4	-3.0	1.2
Cl-CC-OH	-1.7	-1.8	-1.6	-3.8	6.7	-1.4	-3.2	1.2
Cl-CC-NH ₂	-1.5	-1.6	-1.4	-3.5	6.5	-1.4	-3.1	1.1
Br-CC-H	-3.7	-3.6	-3.2	-7.4	11.1	-2.9	-4.5	1.6
Br-CC-F	-3.9	-3.8	-3.4	-8.0	12.0	-3.1	-4.8	1.7
Br-CC-COF	-5.2	-5.0	-4.5	-9.9	13.5	-3.6	-5.2	1.9
Br-CC-COOH	-4.6	-4.4	-4.2	-10.4	13.9	-2.8	-5.3	2.0
Br-CC-CF ₃	-4.9	-4.8	-4.5	-9.6	13.3	-3.5	-5.1	1.9
Br-CC-NO ₂	-5.6	-5.3	-4.8	-10.4	13.9	-3.9	-5.3	2.0
Br-CC-CN	-5.4	-5.3	-4.7	-10.0	13.4	-3.7	-5.1	2.0
Br-CC-CH ₃	-3.1	-3.1	-2.9	-6.5	10.4	-5.0	-4.4	1.5
Br-CC-OH	-3.2	-3.2	-2.8	-6.8	10.9	-2.7	-4.6	1.5
Br-CC-NH ₂	-3.0	-2.9	-2.6	-6.5	10.7	-2.7	-4.5	1.4
I-CC-H	-6.7	-6.2	-5.5	-15.9	23.3	-6.8	-7.4	2.2
I-CC-F	-7.5	-6.8	-6.0	-18.4	29.7	-10.2	-8.5	2.2
I-CC-COF	-8.9	-8.2	-8.0	-22.4	31.3	-8.0	-9.8	2.3
I-CC-COOH	-8.0	-7.4	-7.2	-22.6	31.6	-7.3	-9.7	2.3
I-CC-CF ₃	-8.6	-8.0	-7.6	-22.2	31.0	-7.6	-9.9	2.2
I-CC-NO ₂	-9.8	-8.8	-8.5	-23.9	31.7	-7.9	-9.7	2.5
I-CC-CN	-9.3	-8.6	-8.3	-22.9	33.1	-7.4	-12.1	2.4
I-CC-CH ₃	-6.3	-6.1	-6.0	-13.5	21.0	-7.2	-6.6	2.1
I-CC-OH	-6.4	-6.2	-6.1	-13.5	21.3	-7.7	-6.5	2.0
I-CC-NH ₂	-6.1	-6.0	-5.7	-13.7	21.1	-6.9	-6.6	2.1

^aAll interaction energies and energy terms in kcal mol⁻¹

the relationship between interaction energies and halogens $V_{\text{S,max}}$ values: Higher $V_{\text{S,max}}$ (more positive σ -holes) result in complexes that are more strongly bound.

Energy decomposition analysis

Although decompositions of the various halogen-bonding interactions have already been investigated, none of these decompositions has been done for carbene \cdots halogen interactions. Thus, for all complexes investigated here, the interaction energies were analyzed in terms of electrostatic, exchange-repulsion, polarization and dispersion energies. However it may be noted that there is no rigorous basis for defining such energy terms [54], since they are not physical observable quantities. Furthermore, the energy components are not independent of each other, no matter what procedure is used. For example, polarization is an intrinsic part of the electrostatic interaction (unless only

point charges are involved) [35]. Accordingly, it is not surprising that the various procedures that have been proposed for decomposing interaction energies sometimes lead to contradictory conclusions. For instance, based on perturbation theory, the formation of $\text{F}_3\text{C}-\text{Cl}\cdots\text{O}=\text{CH}_2$, $\text{F}_3\text{C}-\text{Br}\cdots\text{O}=\text{CH}_2$ and $\text{F}_3\text{C}-\text{I}\cdots\text{O}=\text{CH}_2$ complexes, are attributed primarily to the electrostatic and dispersion effects [2]. While the method proposed by Palusiak [34], for exactly the same interactions, concludes that charge transfer and polarization dominate, with electrostatics contributing only “slightly”. On the other hand, Politzer et al. [35] indicated, on the basis of binding energy decomposition of halogen-bonded complexes, that the formation and observed properties of the resulting noncovalent complexes can be fully explained in terms of electrostatics/polarization plus dispersion as the driving forces. Even considering these limitations, however, it is possible to estimate the electrostatic and the dispersion portions of noncovalent interaction energies [36].

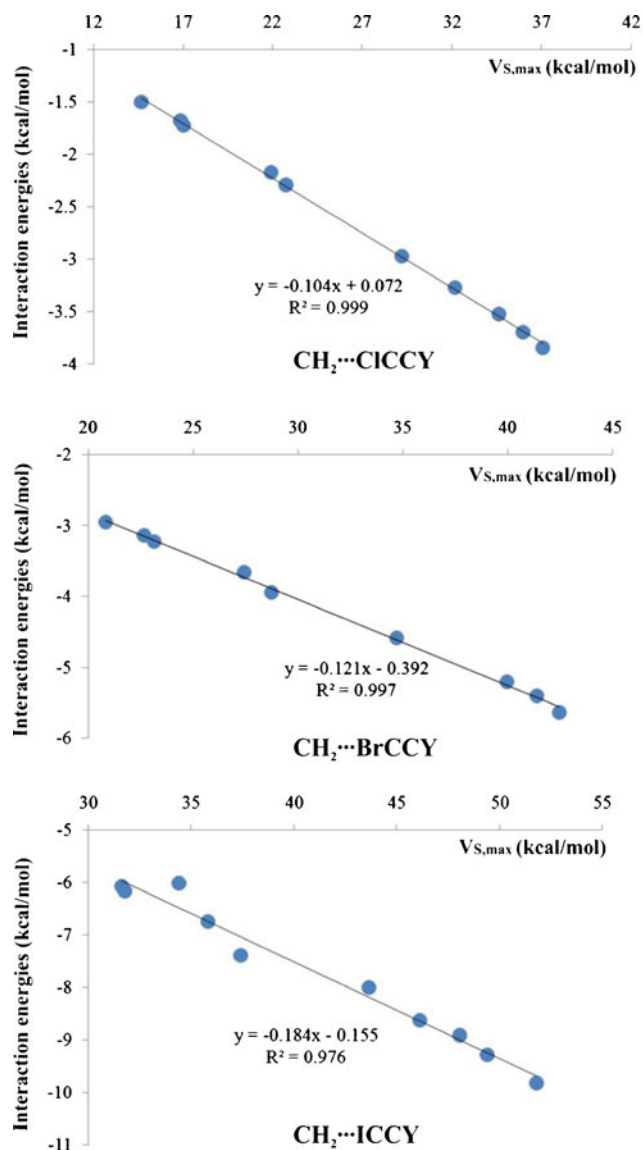


Fig. 3 Correlation between M06-2X interaction energies and magnitudes of halogen's $V_{S,max}$ in $CH_2 \cdots XCCY$ complexes

It is evident that for the all complexes considered here, the electrostatic term (E_{elst}) is slightly larger (*i.e.*, more negative) than the dispersion term (E_{disp}) and the changes in the electrostatic interactions are mainly responsible for the enhancement of the halogen bond. It is the most evident for complexes with the $Y=CN, NO_2, COF$ groups; however, even for a complex with $Y=NH_2$, the electrostatic can be 1.12–2.06 times larger than the dispersion term. In particular, the large value of E_{elst} ($-23.9 \text{ kcal mol}^{-1}$) shows that electrostatic interactions are the major source of the attraction in the $CH_2 \cdots ICCNO_2$ complex. For the weakest carbene–X bonded systems studied here (*i.e.*, those with $Y=CH_3, OH$ and NH_2), the dispersive term either has only a somewhat lower value than E_{elst} or is even clearly dominant among all attractive terms. One can see that

increasing the size and positive nature of a halogen's σ -hole markedly enhances the strength of the electrostatic component of the halogen-bonding interaction. More especially, halogens with larger, more positive σ -holes tend to exhibit weaker dispersion interactions, which is attributed to the lower local polarizabilities of the larger σ -holes [36].

According to the EDA results, it is also found that electrostatic effects account for about 48 %, 50 % and 53 % of the overall attraction in the $CH_2 \cdots ClCCY, CH_2 \cdots BrCCY$ and $CH_2 \cdots ICCY$ complexes, respectively. By comparison, the polarization component of these interactions represents about 18 %, 20 % and 23 % of the total attractive forces, while dispersion contributes 34 %, 30 % and 25 % to the stability of these complexes, respectively. Consequently, it can be noted that the $CH_2 \cdots XCCY$ interaction is remarkably dependent on both electrostatic and dispersion forces, with electrostatic playing the largest role in their stability. Comparing the data for the chlorine, bromine and iodine substituted $CH_2 \cdots XCCY$ systems, it can be seen that the polarization and electrostatic contribution to the interaction energies increases with increasing halogen size. Interestingly, there is a larger increase in the electrostatic component, going from chlorine to iodine, than in the polarization. The increase in the E_{pol} can be attributed to the more evident distortion of the electron cloud of CH_2 by the electric field of the $X-CC-Y$ in the complex. For the same type of complex, the $E_{exch-rep}$ becomes more positive in the order $Cl < Br < I$, maybe this is due to the increased overlap between the orbitals of the two monomers. The results reported herein suggest that the nature of the carbene-halogen interaction is related to the nature of the σ -hole donor and acceptor.

Conclusions

Within this work, the halogen bond interactions between the carbene and $XCCY$ molecule have been investigated, where $X=Cl, Br$ and $I; Y=H, F, COF, COOH, CF_3, NO_2, CN, NH_2, CH_3, OH$. We found a good correlation between halogen's $V_{S,max}$ and evaluated binding distances. It is shown that for a given Y substitution, the magnitude of $V_{S,max}$ associated with the halogen atoms of the system tends to increase as the size of the halogen increases. According to interaction energies results, all the CCSD(T), MP2 and M06-2X methods indicate the presence of a relatively weak halogen-bonding interaction due to the interaction energies between -1.50 and $-9.81 \text{ kcal mol}^{-1}$. In general, the M06-2X method provides slightly larger stabilization energy relative to the CCSD(T) values. Our calculations indicated that increasing the size of a halogen's σ -hole enhances the strength of the electrostatic component of

the $\text{CH}_2 \cdots \text{XCCY}$ interaction. This can be attributed to the lower local polarizabilities of the larger σ -holes.

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