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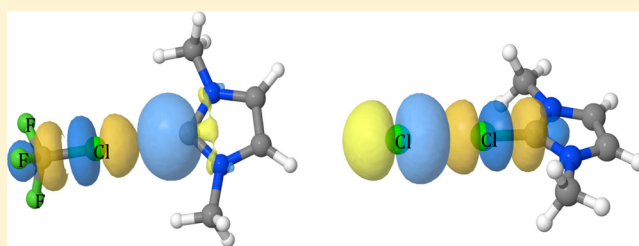
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S Supporting Information

ABSTRACT: A theoretical study of the halogen-bonded complexes ($A\cdots C$) formed between halogenated derivatives ($A-X$; $A = F, Cl, Br, CN, CCH, CF_3, CH_3, H$; and $X = Cl, Br$) and a nitrogen heterocyclic carbene, 1,3-dimethylimidazole-2-ylidene (MeIC) has been performed using MP2/aug'-cc-pVDZ level of theory. Two types of $A-X:MeIC$ complexes, called here type-I and -II, were found and characterized. The first group is described by long $C-X$ distances and small binding energies ($8-54 \text{ kJ}\cdot\text{mol}^{-1}$). In general, these complexes show the traditional behavior of systems containing halogen-bonding interactions. The second type is characterized by short $C-X$ distances and large binding energies ($148-200 \text{ kJ}\cdot\text{mol}^{-1}$), and on the basis of the topological analysis of the electron density, they correspond to ion-pair halogen-bonded complexes. These complexes can be seen as the interaction between two charged fragments: A^- and $^+[X-CIME]$ with a high electrostatic contribution in the binding energy. The charge transfer between lone pair $A(LP)$ to the σ^* orbital of $C-X$ bond is also identified as a significant stabilizing interaction in type-II complexes.



■ INTRODUCTION

Halogen bonding ($A-X\cdots B$) is a well-known noncovalent interaction that has been defined as “a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity”.¹ It plays an important role in many fields such as drug design, crystal engineering, and material sciences.²⁻⁸ This kind of noncovalent interaction can be explained in terms of electrostatic attraction between regions of positive electrostatic potential lying along the extension of the $A-X$ bond axis, the so-called σ -hole, of the group VII atoms and regions of negative electrostatic potentials on B (an electron rich species, i.e., a Lewis base).^{9,10} It should be mentioned that the contribution of the polarization and dispersion terms is not negligible in the stability of the $A-X\cdots B$ complexes.¹¹ In this sense, the $A-X\cdots B$ bond is highly directional, and the atoms are almost always linear or nearly so, giving rise to well-defined structures. The tendency to form halogen bonds with Lewis bases increases as X goes down in the periodic table group. The fluorine atom in general is unable to form halogen-bonded complexes, although it could be achieved under certain conditions.¹²⁻¹⁵ Among the more recurrent Lewis bases as halogen acceptors are found compounds containing O, N, halogens and S atoms.¹⁶⁻¹⁸ Singlet carbenes have not attracted too much attention as Lewis bases.

In general, carbenes are highly reactive species with short lifetimes; consequently, not many experimental studies of

complexes stabilized by either hydrogen bonding or halogen bonding involving carbenes are known.^{19,20} Some theoretical studies about intermolecular complexes stabilized by hydrogen-bonding containing carbenes are found in the literature,^{19,21,22} and to our knowledge, only a previous article deals with carbenes as the halogen acceptor in halogen-bonded $A-X\cdots C$ complexes is found.²²

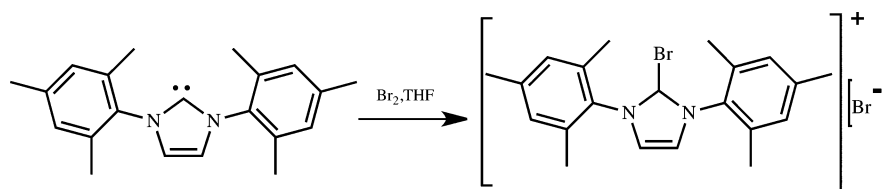
In 2000, Mohand et al.²³ published a review about stable cyclic carbenes, with about 50 N-heterocyclic carbenes (NHC)s that have been structurally characterized since 1991 when the first stable structure of this type of carbene was reported by Arduengo.²⁴ The NHCs are cyclic diaminocarbenes, particularly stable and strong σ -donors. They tend to bind more strongly to metal centers than most classical ligands.^{23,25-28} The study of steric and electronic factors on these compounds has been very important in order to gain more insights into the knowledge of their reactivity.^{23,29-31} The NHC-metal complexes are less sensitive to air and moisture and have proven remarkably resistant to oxidation.²⁷ The reactivity of NHCs with halogen derivatives is well documented. In this sense, Cole et al.³² reported the reaction between an NHC, 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene, and dibromine to produce the corresponding 1,3-bis(2,4,6-trimethylphenyl)-2-bromoimidazolium bromide as displayed in Scheme 1.

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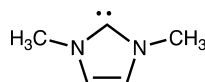
Scheme 1. Reaction between NHC and Bromine



Therefore, it could be interesting to evaluate the possibility of formation of prereactive complexes stabilized by halogen bonding as a previous step of the halogen addition reaction, as well as what role this interaction plays in the stabilization of the final product.

In the present article, the attention was pointed-out to the halogen-bonded A–X···C complexes formed between A–X (X = Cl, Br) and singlet nitrogen-heterocyclic carbenes, with A = F, Cl, Br, CN, CCH, CF₃, CH₃, and H as electron poor species and 1,3-dimethylimidazole-2-ylidene (MeIC) as electron rich species (see Scheme 2). The geometric, energetic, and electronic properties of the isolated monomers and the respective halogen-bonded AX:MeIC complexes will be characterized and discussed.

Scheme 2. Schematic Representation of the Carbene Used as Model of Halogen Acceptor [1,3-Dimethylimidazole-2-ylidene (MeIC)]



■ COMPUTATIONAL METHODS

The structures of the isolated monomers and complexes were optimized at second-order Møller–Plesset perturbation theory (MP2) using the aug'-cc-pVDZ basis set,^{33,34} which is derived from the Dunning aug-cc-pVDZ basis set by removing diffuse functions from H atoms. Frequencies were computed in order to establish that optimized structures correspond to equilibrium structures on their potential energy surfaces. Optimization and frequency calculations were performed using the Gaussian09 suite of programs.³⁵

The electron densities of the complexes were analyzed using the Atoms in Molecules (AIM) methodology, employing the AIMAll program.³⁶ The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density (ρ) maxima at the positions of the nuclei and saddle points that correspond to bond critical point (bcp). The zero gradient line that connects a bcp with two nuclei is the bond path. The electron density at bcp (ρ_{bcp}) and the Laplacian of the electron density at bcp ($\nabla^2\rho_{\text{bcp}}$) provide useful information for characterizing interactions within the complexes.^{37,38}

The areas of charge concentration in terms of the electron localization function (ELF)^{39,40} were calculated with the TOPMOD program.⁴¹ The ELF isosurfaces were visualized with the MOLEKEL program.⁴²

The natural bond orbital (NBO) method⁴³ has been used to analyze the stabilizing charge transfer interactions. The NBO-6 program⁴⁴ implemented in the Gaussian09 package was used for this purpose. The molecular electrostatic potentials (MEPs)

of the isolated MeIC, A–Cl, and A–Br monomers have been calculated with the Gaussian09 program. These were analyzed and represented on the 0.001 au electron density isosurfaces using the WFA program.⁴⁵

The binding energy, ΔE , of the complexes was calculated as the difference of the electronic energy between the sum of the isolated halogen-donor and -acceptor in their minima configuration and the A–X:MeIC complex.

The localized molecular orbital energy decomposition analysis (LMOEDA)⁴⁶ at the MP2 computational level was used in order to characterize the carbene···halogen interaction in A–X···C complexes in terms of meaning and physical components. Even though a number of decomposition analysis methods have been described in the literature and that the different term among them cannot be compared, the use of a single method for a series of compounds provides insight in the different mechanism of stabilization within the series of compounds considered.

On the basis of the LMOEDA methodology, the instantaneous electronic interaction energy (ΔE_{int}) between two fragments of the composite system can be decomposed into the terms indicated in eq 1:

$$\Delta E_{\text{int}} = E_{\text{elect}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (1)$$

where E_{elect} is the electrostatic term describing the classical Coulomb interaction between the occupied orbitals on one monomer and those on another, and $E_{\text{exch-rep}}$ is the repulsive exchange component resulting from the Pauli exclusion principle. E_{pol} and E_{disp} correspond to polarization and dispersion terms, respectively. LMOEDA is a simple and robust method to partition the instantaneous interaction energy on the basis of single determinant Hartree–Fock wave functions. It can be seen as a modification or extension from other decomposition schemes.^{47–49} The following stand out among the main features: (i) the electrostatic, exchange, and repulsion terms are separated; (ii) the polarization term is expressed as the orbital relaxation energy, and consequently, it is comparable to the sum of polarization, charge transfer, and the mixing terms in other schemes; and (iii) the dispersion terms can be expressed as the difference between the size-consistent electron correlation methods (e.g., MP2) and Hartree–Fock interaction energy. These calculations were carried out with the GAMESS program (version 2013-R1).⁵⁰

■ RESULTS AND DISCUSSION

Monomers. A priori, MeIC was considered as singlet electronic state since previous experimental and theoretical results indicate that singlet NHCs are more stable than the triplet states,²⁹ afterward, we found that the triplet-singlet energy separation in MeIC is 400 kJ·mol^{−1}.

A search in the CSD for NHC's not complexed with metals shows the presence of 54 crystals that provide 68 structures since in some cases more than one structure is present in the

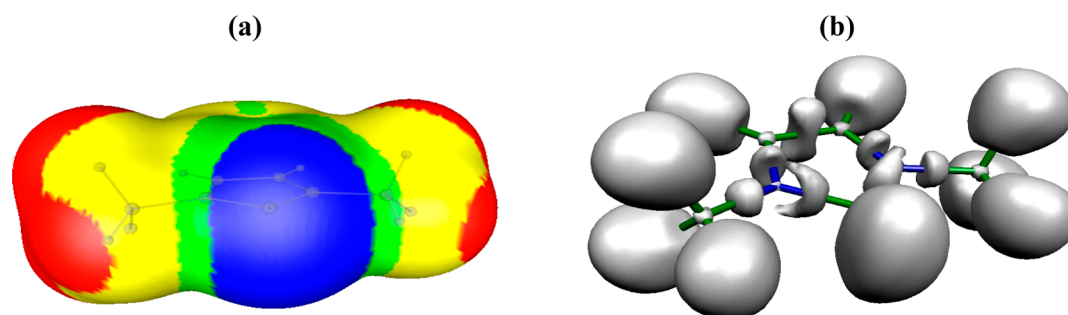


Figure 1. Computed electrostatic potential on the 0.001 au electron density isosurfaces of MeIC (a) and the ELF representation (calculated at the isosurface value $\eta = 0.7$) (b). The color code used for the electrostatic potential, in $\text{kJ}\cdot\text{mol}^{-1}$, is red > 84 > yellow > 42 > green > 0 > blue.

unit cell. The average value of the N–C bond and N–C–N angle is 1.364 Å and 102.6°, which are very close to the calculated values obtained by us for the MeIC molecule (1.377 Å and 101.3°).

The computed electrostatic potential on the 0.001 au electron density isosurface of MeIC (see molecular surface in Figure 1a) presents a patent region of negative potential corresponding to the lone pair on the divalent carbon center. Complementarily, the ELF analysis³⁹ revealed that the lone pair of the carbenoid carbon atom is localized in the molecular plane (σ -plane) as can be seen in Figure 1b. The integrated electron density of the basin corresponding to the lone pair accounts for 2.81 electrons.

In addition, the aromaticity of MeIC was also analyzed by nuclear independent chemical shifts (NICS) calculated at the MP2/aug'-cc-pVDZ level. The NICS have been widely used to evaluate systems exhibiting aromaticity. The NICS (0,1) values for the MeIC are −16.9 and −11.3 ppm at 0 Å (in the ring center) and 1 Å above the ring center, respectively. These values are slightly larger, in absolute value, than those obtained for the imidazole ring (−13.8 and −10.7 ppm, respectively), in conclusion, and on the basis of these data, singlet MeIC is more aromatic than imidazole.

The electronic properties of the halogen derivatives (A–X; A = F, Cl, Br, CN, CCH, CF₃, CH₃, H; and X=Cl, Br) have already been discussed⁵¹ and will be briefly mentioned. Regions of positive electrostatic potential along the extension of the covalent A–X bond were found in the set of molecules considered here, and their values are gathered in Table S1 of the Supporting Information. In general, as the electronegativity of A increases, the value of the MEP in the σ -hole becomes more positive.

AX:MeIC Complexes: Energetic and Geometric Aspects. Table 1 shows the binding energy ΔE in $\text{kJ}\cdot\text{mol}^{-1}$, the distance between interacting halogen and carbenoid carbon center, $R(\text{X}–\text{C})$ in Å, and the internal angle of the five-membered ring of the MeIC carbene, $a\text{N}–\text{C}–\text{N}$, for all the halogen-bonded complexes. The geometry and total energies of all the complexes were gathered in Figure S1 of the Supporting Information. They are divided into two main groups depending on the binding energy values. Traditional A–X:MeIC halogen-bonded complexes will be referred to as type-I, with those nontraditional as type-II. The latter complexes are similar to those designated as ion-pair halogen-bond complexes by Del Bene and co-workers for the FCl:CNX,^{52,53} H₂XP:ClF, and H₂XP:Cl₂ complexes.⁵⁴ Other groups have recently described similar cases for other systems.^{55,56}

It is interesting to notice that the NC–Cl:MeIC complex exhibited the two types of halogen-bonds as minima. In the

Table 1. Binding Energy ΔE (in $\text{kJ}\cdot\text{mol}^{-1}$), Carbenoid-Halogen Distances $R(\text{C}–\text{X})$ (in Å), and Bond Angle of NHC $a\text{N}–\text{C}–\text{N}$ (in Degrees) for All Complexes Calculated at the MP2/aug'-cc-pVDZ Level of Theory

complex	ΔE	$R(\text{C}–\text{X})$	$a\text{N}–\text{C}–\text{N}$
Traditional Halogen-Bonded Complexes, type I			
H ₃ C–Cl:MeIC	6.6	3.373	101.3
H–Cl:MeIC	9.2	3.304	101.3
HCC–Cl:MeIC	22.0	3.056	101.5
F ₃ C–Cl:MeIC	22.6	3.042	101.5
NC–Cl:MeIC	32.5	2.949	101.6
H ₃ C–Br:MeIC	17.0	3.137	101.5
H–Br:MeIC	19.9	3.154	101.5
HCC–Br:MeIC	38.4	2.884	101.8
F ₃ C–Br:MeIC	38.5	2.861	101.9
NC–Br:MeIC	53.3	2.746	102.2
Ion-Pair Halogen-Bonded Complexes, type II			
Br–Cl:MeIC	148.6	1.719	107.6
Cl–Cl:MeIC	169.0	1.718	107.5
F–Cl:MeIC	196.5	1.745	106.7
Br–Br:MeIC	163.1	1.937	106.5
Cl–Br:MeIC	178.8	1.928	106.5
F–Br:MeIC	200.5	1.953	105.8
NC–Cl:MeIC	−41.3	1.758	107.2

case of the type-I minimum, it shows a binding energy of 32.5 $\text{kJ}\cdot\text{mol}^{-1}$, while the type-II complex minimum presents a negative binding energy of −41.3 $\text{kJ}\cdot\text{mol}^{-1}$ with respect to the separate monomers. The computed binding energy in the type-II complex from the ionic species, NC[−] and ⁺[Cl–MeIC], provides a binding energy value of 306.7 $\text{kJ}\cdot\text{mol}^{-1}$. The variation of the total energy along the C(carbene)⋯Cl distance of the NC–Cl:MeIC system is shown in Figure 2. Notice that the profile is associated with the interconversion of type-II into type-I complex. The former corresponds to a metastable minimum with a small barrier (1.7 $\text{kJ}\cdot\text{mol}^{-1}$) that evolves favorably toward type-I minimum.

With the purpose to find some explanations on what factors could be used to predict the formation of one type of halogen bond or the other, we calculated the bond dissociation energy (BDE) of all A–Cl(Br) molecules using G3 methodology.⁵⁷ Table 2 collects the computed and experimental BDE values. The computed BDEs are quite close to the experimental data.

We noted that calculated BDE values in the range of 192.9 and 252.5 $\text{kJ}\cdot\text{mol}^{-1}$ correspond to the weakest A–X bond, which tend to yield halogen-bonded complexes type-II, while BDE in the range of 292.0 and 441.0 $\text{kJ}\cdot\text{mol}^{-1}$ tend to form traditional halogen-bonded complexes or type-I. In this sense,

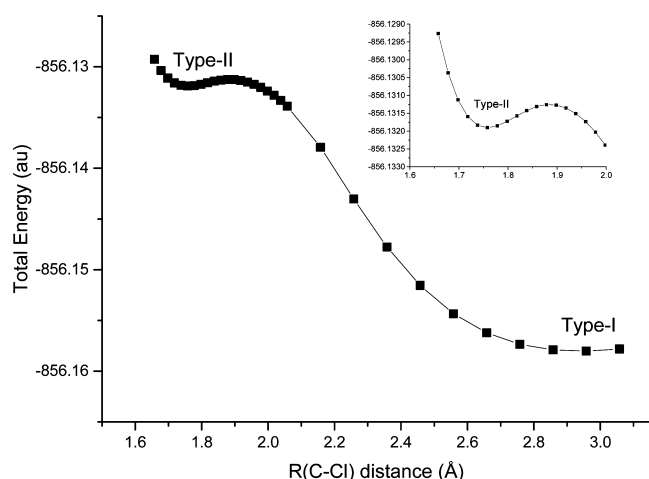


Figure 2. Total energy along the C(carbene)···Cl distance of the NC-Cl:MeIC system. The inset shows in detail the energetic values surrounding the type-II minimum. The location of the two minima is indicated.

Table 2. Computed and Experimental Bond Dissociation Energies (BDE) of A-Cl(Br), Computed Were Obtained Using G3Methodology; All Values Are Given in $\text{kJ}\cdot\text{mol}^{-1}$

halogen derivatives	computed BDE	exptl BDE ⁵⁸
Yield to Complexes, type-I		
H ₃ C-Cl	344.7	350.2 ± 1.7
H-Cl	430.5	431.361 ± 0.013
HCC-Cl	441.0	435.6 ± 8.4
F ₃ C-Cl	365.5	365.3 ± 3.8
NC-Cl	433.9	422.6 ± 8.4
H ₃ C-Br	292.0	294.1 ± 2.1
H-Br	365.9	366.16 ± 0.020
HCC-Br	408.0	410.5
F ₃ C-Br	300.0	296.2 ± 1.3
NC-Br	380.4	364.8 ± 4.2
Yield to Complexes, type-II		
Br-Cl	216.9	219.32 ± 0.05
Cl-Cl	237.6	242.580 ± 0.004
F-Cl	252.5	260.83
Br-Br	192.9	193.859 ± 0.120
Cl-Br	216.9	219.32 ± 0.05
F-Br	248.3	230.04 ± 0.25

type-II complexes correspond to electronegative A substituents (A = F, Cl, Br), as the substituents become more electronegative; thus, a weak A-X bond interacts with NHC. Note that the respective binding energies are between 148.6 and 200.5 $\text{kJ}\cdot\text{mol}^{-1}$ (excepting for NC-Cl:MeIC where ΔE is negative in relation to the separated neutral monomers) and are more stable than halogen-bonded complexes type-I, where ΔE is in the range of 6.6 and 53.3 $\text{kJ}\cdot\text{mol}^{-1}$.

In the traditional halogen-bonded complexes (type-I) studied here, the Cl-C and Br-C distances are shorter than the sum of the van de Waals radii⁵⁹ of the respective atoms, i.e., 3.45 and 3.55 Å for Cl-C and Br-C, by 2–15% and 8–23%, respectively. The angle of interaction A-X···C is usually close to linearity, which implies no significant presence of secondary interactions. The angle N-C-N is quite similar to that in the isolated nitrogen heterocyclic carbene, 101.3°. It can also be noted that halogen-bonds become stronger as the substituent A

tends to increase its electron withdrawing power; this fact has already been pointed-out by several authors.^{60–63}

In the halogen-bonded complex type-II (or ion-pair type), Cl-C and Br-C distances are similar to the Cl-C and Br-C covalent bond lengths, i.e., 1.790 and 1.966 Å,⁶⁴ respectively. Concomitantly, the A-Cl(Br) distances are substantially longer, in the range of 2.05–2.83 Å, than those found in complexes type-I (1.29–1.95 Å). The angle A-X···C is also close to linearity. However, in contrast with the traditional halogen bonding complexes, the angle N-C-N increases with respect to the one in the isolated carbene between 4.5 and 6.3° revealing a stronger interaction as it can be seen by high values of ΔE . Politzer and Murray have attributed this strong interaction to two factors: a highly positive electrostatic potential on the halogen atom, σ -hole, and the presence of electron donating group in the Lewis base, which help to increase the electronic charge and polarizability on the donor atom.^{9,65,66}

In order to gain insight into the contributions of the different terms of the instantaneous interaction energy (ΔE_{int}) in the complexes, the LMOEDA methodology was applied; Table 3

Table 3. ΔE_{int} and Its Contributions for Halogen-Bonded Complexes; All Values Are Given in $\text{kJ}\cdot\text{mol}^{-1}$

complex	ΔE_{int}	E_{elect}	$E_{\text{exch-rep}}$	E_{pol}	E_{disp}
Traditional Halogen-Bonded Complexes, type-I					
H ₃ C-Cl:MeIC	-8.0	-6.7	18.4	-5.9	-13.8
H-Cl:MeIC	-10.1	-12.6	20.1	-5.9	-11.7
HCC-Cl:MeIC	-23.5	-33.1	38.9	-12.1	-17.2
F ₃ C-Cl:MeIC	-25.1	-36.4	41.4	-13.8	-16.3
NC-Cl:MeIC	-34.4	-51.9	53.1	-17.6	-18.0
H ₃ C-Br:MeIC	-16.3	-27.2	47.3	-13.8	-22.6
H-Br:MeIC	-19.2	-32.2	43.1	-12.1	-18.0
HCC-Br:MeIC	-38.0	-72.0	90.0	-28.0	-28.0
F ₃ C-Br:MeIC	-39.3	-78.7	99.2	-32.6	-27.2
NC-Br:MeIC	-54.8	-111.7	133.5	-45.6	-31.0
Ion-Pair Halogen-Bonded Complexes, type-II					
Br-Cl:MeIC	-307.5	-349.8	154.4	-79.9	-32.2
Cl-Cl:MeIC	-321.0	-367.8	166.5	-90.4	-29.3
F-Cl:MeIC	-399.0	-497.9	306.8	-189.4	-18.5
Br-Br:MeIC	-347.7	-418.8	254.8	-140.6	-43.1
Cl-Br:MeIC	-362.0	-440.6	268.2	-151.9	-37.7
F-Br:MeIC	-457.4	-607.7	437.7	-271.8	-15.6
NC-Cl:MeIC	-319.0	-404.6	243.5	-116.4	-41.5

contains the four terms of the ΔE_{int} as it is described in eq 1. The LMOEDA for type-II systems was performed by taking the interaction between two charged subunits or ion-pair, the negative A⁻ and positive ⁺[X-MeIC], which agrees with the NBO analysis of the natural charges where all complexes type-II showed this feature. Consequently, for the complexes with configuration type-II, the attractive term E_{elect} is always higher than repulsive term $E_{\text{exch-rep}}$ as well as other attractive terms (E_{pol} and E_{disp}); it corresponds to the dominant contribution to the interaction energy. Among the three attractive terms (E_{elect} , E_{pol} and E_{disp}), the E_{elect} provides between 68 and 76%, the polarization (which is defined as the orbital relaxation energy including charge transfer and mixing terms) corresponds between 17 and 30%, and the MP2 dispersion term is only 2–7% of the total attractive energy for the halogen-bonded complexes type-II.

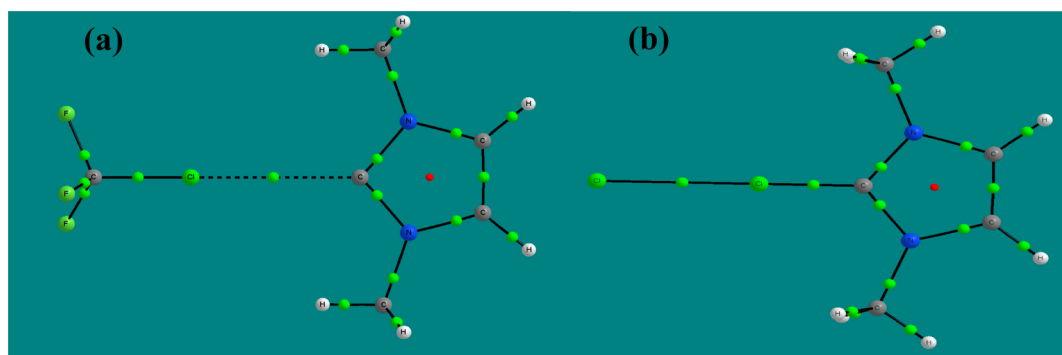


Figure 3. Electron density molecular graphs of the two types of complexes: (a) the traditional, $F_3C-Cl:MeIC$ (I) and (b) the ion-pair halogen bond complex, $Cl-Cl:MeIC$ (II). The green dots localized between atoms represent the location of the bond critical points of the electron density, and the lines connecting the atoms indicate the bond paths.

Table 4. Electron Density ($C-X$ and $A-X$) and Laplacian ($C-X$) at the Bond Critical Point for All Halogen-Bonded Complexes (in au); NBO Second-Order Stabilization Energy $E(2)$ (in $\text{kJ}\cdot\text{mol}^{-1}$) Due to the Charge Transfer from $C(LP)$ toward the $\sigma^* A-X$ Orbital and from $A(LP)$ toward $\sigma^* C-X$ Orbital in Type-I and -II Complexes, respectively

complex	$E(2)$			
Traditional Halogen-Bonded Complexes, type-I	$\rho_{bcp}(C-X)$	$\nabla^2\rho_{bcp}(C-X)$	$\rho_{bcp}(A-X)$	$C(LP)-\sigma^*(A-X)$
$H_3C-Cl:MeIC$	0.0079	0.0224		5.3
$H-Cl:MeIC$	0.0088	0.0259		8.6
$HCC-Cl:MeIC$	0.0137	0.0424		16.9
$F_3C-Cl:MeIC$	0.0144	0.0430		17.6
$NC-Cl:MeIC$	0.0169	0.0515		23.5
$H_3C-Br:MeIC$	0.0141	0.0392		21.3
$H-Br:MeIC$	0.0135	0.0385		21.5
$HCC-Br:MeIC$	0.0222	0.0612		47.0
$F_3C-Br:MeIC$	0.0237	0.0625		54.7
$NC-Br:MeIC$	0.0293	0.0741		72.9
Ion-Pair Halogen-Bonded Complexes, type-II				$A(LP)-\sigma^*(C-X)$
$Br-Cl:MeIC$	0.2110	-0.2832	0.0319	66.2
$Cl-Cl:MeIC$	0.2155	-0.2843	0.0364	72.9
$F-Cl:MeIC$	0.2012	-0.2325	0.0751	140.3
$Br-Br:MeIC$	0.1459	-0.0249	0.0436	162.4
$Cl-Br:MeIC$	0.1482	-0.0259	0.0485	167.7
$F-Br:MeIC$	0.1410	0.0040	0.0878	252.5

It is also interesting to note that for the complexes type-I the absolute value of the $E_{\text{exch-rep}}$ term is the largest one. The E_{elect} is a dominant attractive term only in the strongest halogen bonding complexes, providing up to 59% of the total attractive energy, while in the weakest complexes its contribution reaches only 25%. The polarization contribution lies between 19 and 24%, and after the E_{elect} component, E_{pol} term is the second main contribution, only in the two strongest complexes ($F_3C-Br:MeIC$, and $NC-Br:MeIC$). Finally, the MP2 dispersion term contributes by about 16% in all attractive terms for the strongest complexes and increases its contribution, reaching 52% in the weakest complex ($H_3C-Cl:MeIC$) where it is the most important attractive term.

Electronics Aspects: Results of AIM and NBO Analyses. The electronic structure of $A-X:MeIC$ complexes type-I and -II will be analyzed using AIM and NBO procedures.

The molecular graphs of two representative complexes of type-I and -II are shown in Figure 3a,b, respectively, while those for other $A-X\cdots C$ halogen-bonded complexes are collected in Figure S1 of the Supporting Information. Table 4 reports the electron density features of interest for all halogen-bonded complexes such as the electron density at $C-X$ and $A-X$ bond

critical points, and the sign of the Laplacian at $C-X$ bond. The Laplacian, the second order derivative of the electron density, $\nabla^2\rho$, provides useful information for characterizing the nature of the chemical interaction by examining its sign; this parameter indicates where electron density is accumulated or depleted. While a negative value could be classified as shared shell, a positive value is classified as a closed shell interaction. Shared shell interactions usually are found between covalently bonded atoms; closed shell interactions usually correspond to ionic or weak interactions (hydrogen bonds, halogen bonds, van der Waals complexes, etc.).

In complexes type-II, the electron density at $C-X$ bcp is between 0.141 and 0.201 au being similar to those found in the covalent $C-Cl$ and $C-Br$ bonds, while the electron density at $C-X$ bcp in complexes type-I lies between 0.0079 and 0.0293 au, which are quite similar to those found in weak interaction but stronger than van der Waals contacts. In addition, the values of the electron density at the bcp along $A-X$ interaction in ion-pair halogen-bonded complexes are in the range of 0.0319–0.0878 au, which agrees with typical closed-shell interactions. Figure 4a shows an excellent exponential relationship of the electron density at $C-X$ bond critical point, ρ_{bcp} , as

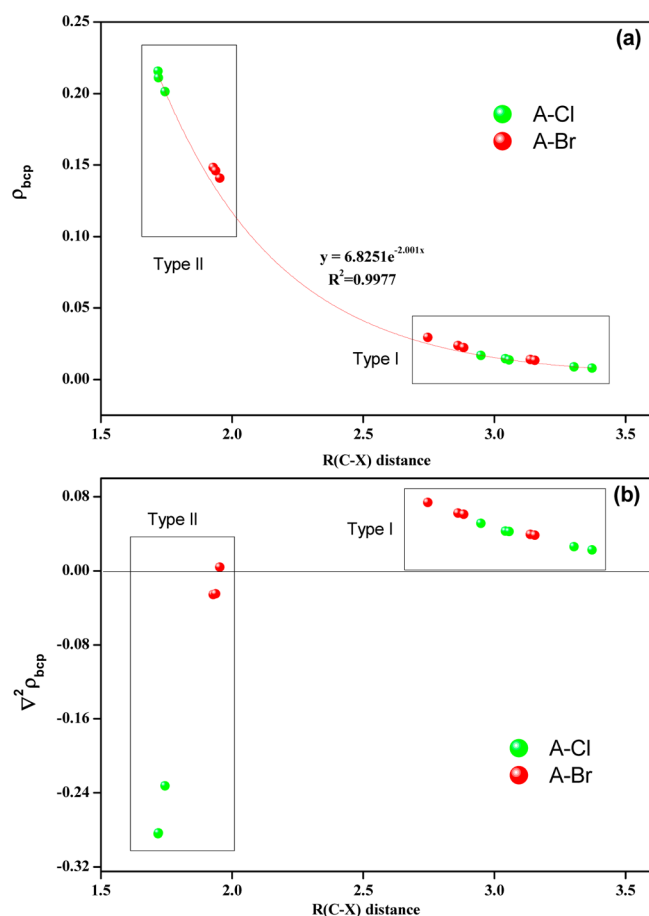


Figure 4. Electron density (a) and Laplacian (au) (b) at the C–X bcp vs R(C–X) interatomic distance (Å).

a function of the interatomic C–X distance. Similar correlations have been found for pnictogen bonds and other noncovalent interactions.^{67–69} Figure 4b shows that the evolution of the Laplacian against the interatomic distance is similar to those described for other interatomic contacts in the whole range of distances.⁷⁰

As can be seen in Table 4 and Figure 4b, the Laplacians at the C–X bcp, $\nabla^2 \rho_{\text{bcp}}$, change sign as the halogen bond type is changed from traditional to ion-pair. In addition, the values of the total energy, H , at the C–X bcp show negative values for all the complexes of type-II, with small and positive for those of type-I, which agrees with the important covalent character of the C–X bond in the first ones and not in the second ones. The

evolution of the total energy, H , at the C–X bcp vs. the interatomic distance is shown in Figure S2 of the Supporting Information.

The NBO analysis was used with the purpose to identify possible intermolecular interactions between the halogenated derivatives and a nitrogen heterocyclic carbene. In this scheme the electronic wave function is partitioned into a set of occupied Lewis-type and unoccupied non-Lewis-type orbitals, which gives rise to interpret the electronic interactions as charge transfer between the filled (donors) and the empty (acceptors) natural orbitals. This was evaluated by the second-order stabilization energy $E(2)$. Figure 5 shows the two orbitals involved in the charge transfer for two complexes, $\text{F}_3\text{C}-\text{Cl}:\text{MeIC}$ (panel a) and $\text{Cl}-\text{Cl}:\text{MeIC}$ (panel b), which are classified as type-I and -II, respectively.

In complexes type-I, the interaction between the lone pair on the divalent carbon atom, C(LP) with the σ^* of the A–X bond, is the main stabilizing interaction within these complexes based on the NBO analysis. The second-order stabilization energy due to this intermolecular interaction varies between 5.3 and 72.9 $\text{kJ}\cdot\text{mol}^{-1}$ as can be seen in Table 4, even a rough correlation between $E(2)$ and total stabilization energy ($R^2 = 0.90$) was found.

Finally, in complexes type-II, the interaction between lone pair of the A, A(LP) toward σ^* of the C–X bond, can be considered as a significant stabilizing interaction. The $E(2)$ values are between 66.2 and 252.5 $\text{kJ}\cdot\text{mol}^{-1}$ where the values of the complexes of the bromine derivatives are higher than those of the analogous chlorine ones. It is important to emphasize that the NBO analysis helps to obtain detailed information about the main intermolecular interactions that are accounted for in the polarization term in the LMOEDA method for the instantaneous interaction energy.

A search in the CSD for NHCs presenting an interaction between the carbenoid atom and a halogen one with interatomic distances shorter than 3.0 Å provides 11 crystals with 15 structures. The refcodes for these structures have been included in Table S2 of the Supporting Information. Four structures show four C–Cl bonds with an interatomic distance of approximately 1.69 Å, three C–Br between 1.84 and 1.88 Å, and eight C–I interactions, which expand between 2.04 and 2.75 Å. All of these cases can be considered as ion-pair halogen-bonded complexes. No structure has been found with C–Cl/Br distances between 3.0 and 4.0 Å, which will correspond to traditional XB interactions in the CSD.

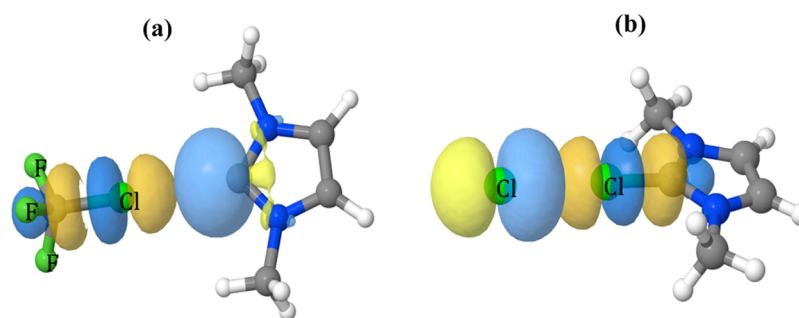


Figure 5. NBO orbitals involved in the stabilizing charge transfer. (a) Lone pair of the MeIC carbene C(LP) and the C–Cl σ^* orbitals in $\text{F}_3\text{C}-\text{Cl}:\text{MeIC}$ (I) and (b) lone pair of the Cl, Cl(LP), and C–Cl σ^* orbitals in $\text{Cl}-\text{Cl}:\text{MeIC}$ (II).

CONCLUSIONS

A theoretical study of the complexes between a halogen derivatives (A–X) and a singlet NHC, MeIC, has been carried out using MP2/aug'-cc-pVDZ level. Two halogen-bond type complexes were found and characterized. The first one (type-I) presents the traditional behavior of systems containing halogen-bonding interaction. Thus, the longest C–X distances, low binding energies (between 8 and 54 kJ·mol⁻¹), and electron density values at C–X bond critical points are quite similar to those found in closed shell interactions, and the main NBO stabilizing intermolecular interaction accounted as charge transfer is from C(LP) toward σ^* A–X orbital.

The second complex series (type-II) presents short C–X distances and longer A–X distances and high binding energies (between 148 and 200 kJ·mol⁻¹). The topological analysis of electron density in C–X bonds showed similar characteristics to shared shell interactions. These complexes can be considered as the interaction between two charged fragments, A⁻ and ⁺[X–CIME], with a high electrostatic contribution to the binding energy. These complexes are always more stables than the type-I; the NBO analysis on these complexes allow to identify a charge transfer from A(LP) toward σ^* orbital of C–X bond and recognize this as a significant stabilizing interaction, which is accounted for in the polarization term of the instantaneous interaction energy of the LMOEDA methodology.

ASSOCIATED CONTENT

Supporting Information

σ -hole values for the halogenated derivatives; molecular graphs, Cartesian coordinates, and MP2 energies of the A–X...C halogen-bonded complexes, refcodes for the halogen-bonded NHCs found in CSD, and evolution of the total energy, *H*, at the C–X bcp vs the interatomic distance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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REFERENCES

- (1) Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Definition of the Halogen Bond (IUPAC Recommendations 2013). *Pure Appl. Chem.* **2013**, *85*, 1711–1713.
- (2) Politzer, P.; Murray, J. S. Halogen Bonding: An Interim Discussion. *ChemPhysChem* **2013**, *14*, 278–294.
- (3) Troff, R. W.; Makela, T.; Topic, F.; Valkonen, A.; Raatikainen, K.; Rissanen, K. Alternative Motifs for Halogen Bonding. *Eur. J. Org. Chem.* **2013**, *2013*, 1617–1637.

- (4) Aakeröy, C. B.; Chopade, P. D.; Desper, J. Establishing a Hierarchy of Halogen Bonding by Engineering Crystals without Disorder. *Cryst. Growth Des.* **2013**, *13*, 4145–4150.
- (5) Aakeröy, C. B.; Panikkattu, S.; Chopade, P. D.; Desper, J. Competing Hydrogen-Bond and Halogen-Bond Donors in Crystal Engineering. *CrystEngComm* **2013**, *15*, 3125–3136.
- (6) Cavallo, G.; Metrangolo, P.; Pilati, T.; Resnati, G.; Sansotera, M.; Terraneo, G. Halogen Bonding: A General Route in Anion Recognition and Coordination. *Chem. Soc. Rev.* **2010**, *39*, 3772–3783.
- (7) Metrangolo, P.; Resnati, G.; Pilati, T.; Biella, S. Halogen Bonding in Crystal Engineering. In *Halogen Bonding: Fundamentals and Applications*; Metrangolo, P., Resnati, G., Eds.; Springer: New York, 2008; Vol. 126, pp 105–136.
- (8) Meyer, F.; Dubois, P. Halogen Bonding at Work: Recent Applications in Synthetic Chemistry and Materials Science. *CrystEngComm* **2013**, *15*, 3058–3071.
- (9) Politzer, P.; Murray, J. S. Halogen Bonding: An Important and Widely-Occurring Example of Sigma-Hole Interactions. In *Abstracts of Papers of the American Chemical Society*; American Chemical Society: Washington, DC, 2009; Vol. 238.
- (10) Politzer, P.; Murray, J. S.; Clark, T. Halogen Bonding and Other Sigma-Hole Interactions: a Perspective. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178–11189.
- (11) Riley, K. E.; Murray, J. S.; Fanfrlik, J.; Rezac, J.; Sola, R. J.; Concha, M. C.; Ramos, F. M.; Politzer, P. Halogen Bond Tunability II: the Varying Roles of Electrostatic and Dispersion Contributions to Attraction in Halogen Bonds. *J. Mol. Model.* **2013**, *19*, 4651–4659.
- (12) Metrangolo, P.; Murray, J. S.; Pilati, T.; Politzer, P.; Resnati, G.; Terraneo, G. Fluorine-Centered Halogen Bonding: A Factor in Recognition Phenomena and Reactivity. *Cryst. Growth Des.* **2011**, *11*, 4238–4246.
- (13) Metrangolo, P.; Murray, J. S.; Pilati, T.; Politzer, P.; Resnati, G.; Terraneo, G. The Fluorine Atom As a Halogen Bond Donor, viz. a Positive Site. *CrystEngComm* **2011**, *13*, 6593–6596.
- (14) Nayak, S. K.; Reddy, M. K.; Row, T. N. G.; Chopra, D. Role of Hetero-Halogen (F...X, X = Cl, Br, and I) or Homo-Halogen (X...X, X = F, Cl, Br, and I) Interactions in Substituted Benzanilides. *Cryst. Growth Des.* **2011**, *11*, 1578–1596.
- (15) Esraili, M. D.; Mohammadian-Sabet, F.; Esmailpour, P.; Solimannejad, M. Cooperativity between Fluorine-Centered Halogen Bonds: Investigation of Substituent Effects. *J. Mol. Model.* **2013**, *19*, 5625–5632.
- (16) Legon, A. C. The Interaction of Dihalogens and Hydrogen Halides with Lewis Bases in the Gas Phase: An Experimental Comparison of the Halogen Bond and the Hydrogen Bond. In *Halogen Bonding: Fundamentals and Applications*; Metrangolo, P., Resnati, G., Eds.; Springer: New York, 2008; Vol. 126, pp 17–64.
- (17) Grabowski, S. J. Cooperativity of Hydrogen and Halogen Bond Interactions. *Theor. Chem. Acc.* **2013**, *132*, 1347.
- (18) Riley, K. E.; Hobza, P. Strength and Character of Halogen Bonds in Protein-Ligand Complexes. *Cryst. Growth Des.* **2011**, *11*, 4272–4278.
- (19) Alkorta, I.; Rozas, I.; Elguero, J. Non-Conventional Hydrogen Bonds. *Chem. Soc. Rev.* **1998**, *27*, 163–170.
- (20) Conejero, S.; Paneque, M.; Poveda, M. L.; Santos, L. L.; Carmona, E. C–H Bond Activation Reactions of Ethers That Generate Iridium Carbenes. *Acc. Chem. Res.* **2010**, *43*, 572–580.
- (21) Alkorta, I.; Elguero, J. Carbenes and Silylenes as Hydrogen Bond Acceptors. *J. Phys. Chem.* **1996**, *100*, 19367–19370.
- (22) Li, Q.; Wang, Y.; Liu, Z.; Li, W.; Cheng, J.; Gong, B.; Sun, J. An Unconventional Halogen Bond with Carbene As an Electron Donor: An Ab Initio Study. *Chem. Phys. Lett.* **2009**, *469*, 48–51.
- (23) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable Cyclic Carbenes and Related Species beyond Diaminocarbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849.
- (24) Arduengo, A. J.; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

- (25) Li, X.; Curran, D. P. Insertion of Reactive Rhodium Carbenes into Boron-Hydrogen Bonds of Stable N-Heterocyclic Carbene Boranes. *J. Am. Chem. Soc.* **2013**, *135*, 12076–12081.
- (26) Matsuoka, S.-I. Recent Progress in N-Heterocyclic Carbene Chemistry: Application to Polymer Synthesis. *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 659–660.
- (27) Hitzel, S.; Faerber, C.; Bruhn, C.; Siemeling, U. Reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with Nitron and with the "Enders Carbene": Access to Ruthenium(III) NHC Complexes. *Organometallics* **2014**, *33*, 425–428.
- (28) Emsermann, J.; Arduengo, A. J., III; Opatz, T. Synthesis of Highly Substituted 2-C-13-Imidazolium Salts and Metal NHC Complexes for the Investigation of Electronic Unsymmetry by NMR. *Synthesis-Stuttgart* **2013**, *45*, 2251–2264.
- (29) Dixon, D. A.; Arduengo, A. J. Electronic-Structure of a Stable Nucleophilic Carbene. *J. Phys. Chem.* **1991**, *95*, 4180–4182.
- (30) Pérez, P.; Chamorro, E. Global and Local Reactivity of N-Heterocyclic Carbenes with Boron and Phosphorus Atoms: An Analysis Based on Spin Polarized Density Functional Framework. *THEOCHEM* **2010**, *943*, 110–114.
- (31) Pinter, B.; Nagels, N.; Herrebout, W. A.; De Proft, F. Halogen Bonding from a Hard and Soft Acids and Bases Perspective: Investigation by Using Density Functional Theory Reactivity Indices. *Chem.—Eur. J.* **2013**, *19*, 518–529.
- (32) Cole, M. L.; Jones, C.; Junk, P. C. Studies of the Reactivity of N-Heterocyclic Carbenes with Halogen and Halide Sources. *New J. Chem.* **2002**, *26*, 1296–1303.
- (33) Woon, D. E.; Dunning, T. H. Gaussian-Basis Sets for Use in Correlated Molecular Calculations. 5. Core-Valence Basis Sets for Boron through Neon. *J. Chem. Phys.* **1995**, *103*, 4572–4585.
- (34) Dunning, T. H. Gaussian-Basis Sets for Use in Correlated Molecular Calculations. 1. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *103*, 4572.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al., *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
- (36) Keith, T. A. *AIMAll*, 13.11.04; TK Gristmill Software: Overland Park, KS, 2013; <http://aim.tkgristmill.com> (accessed Dec 1, 2013).
- (37) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.
- (38) Popelier, P. L. A. *Atoms in Molecules: An Introduction*. Prentice Hall PTR: Upper Saddle River, NJ, 2000.
- (39) Becke, A. D.; Edgecombe, K. E. A Simple Measure of Electron Localization in Atomic and Molecular Systems. *J. Chem. Phys.* **1990**, *92*, 5397–5403.
- (40) Silvi, B.; Savin, A. Classification of Chemical Bonds Based on Topological Analysis of Electron Localization Functions. *Nature* **1994**, *371*, 683–686.
- (41) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *TopMod Package*; Texas A&M: College Station, TX, 1997.
- (42) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.0*; J. Swiss Center for Scientific Computing: Manno, Switzerland, 2000.
- (43) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular Interactions from a Natural Bond Orbital, Donor-Acceptor Viewpoint. *Chem. Rev.* **1988**, *88*, 899–926.
- (44) Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO-6*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2013.
- (45) Bulat, F.; Toro-Labbé, A.; Brinck, T.; Murray, J.; Politzer, P. Quantitative Analysis of Molecular Surfaces: Areas, Volumes, Electrostatic Potentials and Average Local Ionization Energies. *J. Mol. Model.* **2010**, *16*, 1679–1691.
- (46) Su, P.; Li, H. Energy Decomposition Analysis of Covalent Bonds and Intermolecular Interactions. *J. Chem. Phys.* **2009**, *131*, 014102.
- (47) Kitaura, K.; Morokuma, K. A New Energy Decomposition Scheme for Molecular Interactions within the Hartree-Fock Approximation. *Int. J. Quantum Chem.* **1976**, *10*, 325–340.
- (48) Ziegler, T.; Rauk, A. Carbon Monoxide, Carbon Monosulfide, Molecular Nitrogen, Phosphorus Trifluoride, and Methyl Isocyanide As Sigma Donors and Pi Acceptors. A Theoretical Study by the Hartree-Fock-Slater Transition-State Method. *Inorg. Chem.* **1979**, *18*, 1755–1759.
- (49) Hayes, I. C.; Stone, A. J. An Intermolecular Perturbation Theory for the Region of Moderate Overlap. *Mol. Phys.* **1984**, *53*, 83–105.
- (50) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; et al. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (51) Del Bene, J. E.; Alkorta, I.; Elguero, J. An Ab Initio Study of Cooperative Effects in Ternary Complexes $\text{X}:\text{CNH}:\text{Z}$ with $\text{X}, \text{Z} = \text{CNH}, \text{FH}, \text{ClH}, \text{FCl}$, and HLi : Structures, Binding Energies, and Spin-Spin Coupling Constants across Intermolecular Bonds. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13951–13961.
- (52) Del Bene, J. E.; Alkorta, I.; Elguero, J. Do Traditional, Chlorine-Shared, and Ion-Pair Halogen Bonds Exist? An Ab Initio Investigation of $\text{FCl}:\text{CNX}$ Complexes. *J. Phys. Chem. A* **2010**, *114*, 12958–12962.
- (53) Del Bene, J. E.; Alkorta, I.; Elguero, J. Do Nitrogen Bases Form Chlorine-Shared and Ion-Pair Halogen Bonds? *Chem. Phys. Lett.* **2011**, *508*, 6–9.
- (54) Alkorta, I.; Elguero, J.; Del Bene, J. E. Characterizing Traditional and Chlorine-Shared Halogen Bonds in Complexes of Phosphine Derivatives with ClF and Cl_2 . *J. Phys. Chem. A* **2014**, *118*, 4222–4231.
- (55) Li, Q.; Ma, S.; Liu, X.; Li, W.; Cheng, J. Cooperative and Substitution Effects in Enhancing Strengths of Halogen Bonds in $\text{FCl}\cdots\text{CNX}$ Complexes. *J. Chem. Phys.* **2012**, *137*, 084314.
- (56) Politzer, P.; Murray, J. S. Halogen Bonding and Beyond: Factors Influencing the Nature of $\text{CN}-\text{R}$ and $\text{SiN}-\text{R}$ Complexes with $\text{F}-\text{Cl}$ and Cl_2 . *Theor. Chem. Acc.* **2012**, *131*, 1114.
- (57) Mó, O.; Yáñez, M.; Eckert-Maksić, M.; Maksić, Z. B.; Alkorta, I.; Elguero, J. Periodic Trends in Bond Dissociation Energies. A Theoretical Study. *J. Phys. Chem. A* **2005**, *109*, 4359–4365.
- (58) Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.
- (59) Bondi, A. Van der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, *68*, 441–451.
- (60) Alkorta, I.; Sanchez-Sanz, G.; Elguero, J.; Del Bene, J. E. Exploring $(\text{NH}_2\text{F})(2)$, $\text{H}_2\text{FP}:\text{NFH}_2$, and $(\text{PH}_2\text{F})(2)$ Potential Surfaces: Hydrogen Bonds or Pnictogen Bonds? *J. Phys. Chem. A* **2013**, *117*, 183–191.
- (61) Grabowski, S. J. Non-Covalent Interactions: QTAIM and NBO Analysis. *J. Mol. Model.* **2013**, *19*, 4713–4721.
- (62) Riley, K. E.; Hobza, P. The Relative Roles of Electrostatics and Dispersion in the Stabilization of Halogen Bonds. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17742–17751.
- (63) Riley, K. E.; Rezac, J.; Hobza, P. Competition Between Halogen, Dihalogen and Hydrogen Bonds in Bromo- and Iodomethanol Dimers. *J. Mol. Model.* **2013**, *19*, 2879–2883.
- (64) Haynes, W. M. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*; CRC Press: Boca Raton, FL, 2011.
- (65) Shields, Z. P.; Murray, J. S.; Politzer, P. Directional Tendencies of Halogen and Hydrogen Bonds. *Int. J. Quantum Chem.* **2010**, *110*, 2823–2832.
- (66) Clark, T.; Murray, J. S.; Politzer, P. Role of Polarization in Halogen Bonds. *Aust. J. Chem.* **2013**, *67*, 451–456.
- (67) Alkorta, I.; Elguero, J.; Del Bene, J. E. Pnictogen-Bonded Cyclic Trimers $(\text{PH}_2\text{X})(3)$ with $\text{X} = \text{F}, \text{Cl}, \text{OH}, \text{NC}, \text{CN}, \text{CH}_3, \text{H}$, and BH_2 . *J. Phys. Chem. A* **2013**, *117*, 4981–4987.
- (68) Alkorta, I.; Sanchez-Sanz, G.; Elguero, J.; Del Bene, J. E. Pnictogen Bonds Between $\text{X} = \text{PH}_3$ ($\text{X} = \text{O}, \text{S}, \text{NH}, \text{CH}_2$) and Phosphorus and Nitrogen Bases. *J. Phys. Chem. A* **2014**, *118*, 1527–1537.

(69) Alkorta, I.; Elguero, J.; Solimannejad, M. Single Electron Pnictogen Bonded Complexes. *J. Phys. Chem. A* **2014**, *118*, 947–953.

(70) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. From Weak to Strong Interactions: A Comprehensive Analysis of the Topological and Energetic Properties of the Electron Density Distribution Involving X–H...F–Y Systems. *J. Chem. Phys.* **2002**, *117*, 5529–5542.