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ORIGINAL PAPER

Nature of halogen bonding. A study based on the topological analysis of the Laplacian of the electron charge density and an energy decomposition analysis

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Abstract In this work we investigate the nature of the Cl···N interactions in complexes formed between substituted ammonium [$NH_n(X_{3-n})$ (with n=0, 1, 2, 3 and X=−CH_3, −F] as Lewis bases and F−Cl molecule as Lewis acid. They have been chosen as a study case due to the wide range of variation of their binding energies, BEs. Møller-Plesset [MP2/6-311+ +G(2d,2p)] calculations show that the BEs for this set of complexes lie in the range from 1.27 kcal/mol (in F −Cl···NF_3) to 27.62 kcal/mol [in F−Cl···$N(CH_3)_3$]. The intermolecular distribution of the electronic charge density and their $L(\mathbf{r})=-\frac{1}{4}\nabla^2\rho(\mathbf{r})$ function have been investigated within the framework of the atoms in molecules (AIM) theory. The intermolecular interaction energy decomposition has also been analyzed using the reduced variational space (RVS) method. The topological analysis of the $L(\mathbf{r})$ function reveals that the local topological properties measured at the (3,+1) critical point [in $L(\mathbf{r})$ topology] are good descriptors of the strength of the halogen bonding interactions. The results obtained from energy decomposition analysis indicate that electrostatic interactions play a key role in these halogen bonding interactions. These results allow us to establish that, when the halogen atom is bonded to a group with high electron-withdrawing capacity, the electrostatic interaction between the electron cloud of the Lewis base and the halogen atom unprotected nucleus of the Lewis acid produces the formation and determines the geometry of the halogen bonded complexes. In addition, a good linear relationship has been established between: the natural logarithm of the BEs and the electrostatic interaction energy between electron charge distribution of N atom and nucleus of Cl atom, denoted as $V_{e\text{-}n}$(N, Cl) within the AIM theory.

Keywords AIM · Charge density · Halogen bond · Laplacian · σ-hole

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Introduction

There has recently been an increasing interest in halogen bonds, XBs, because of their unique properties and their tremendous potential in the fields of molecular recognition, crystal engineering, supramolecular chemistry and the development of new pharmaceutical compounds. The study of the nature of halogen bonding interactions has turned out to be an important aspect of this topic. Studies of the electrostatic potentials of halogen-containing molecules show that the atoms of a halogen covalently bound often have a region of positive electrostatic potential on the outermost portion of the halogen atom, centered on the extension of the D−X bond [1–4]. Politzer et al. have attributed the formation of halogen bonds to the attractive electrostatic interaction between this positive potential and a lone pair of the acceptor. The presence of a region with positive electrostatic potential on a halogen indicates that noncovalent interactions between that halogen and a Lewis base should be highly

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electrostatic in nature. However, there are several studies showing that other components of the interaction energy can be decisive. Recently, Tomura [5] has studied the $H_{4-n}CCl_n \cdots \pi C_2H_2$ (with n=1, 2, 3, 4) systems by RVS method [6], finding that these complexes are mainly stabilized by the dispersion interaction while the electrostatic interaction also plays an important role in the attraction between acetylene and chloromethane molecules. Moreover, Riley et al. [7] have investigated the nature of the XBs using high-level computational methods, including the symmetry-adapted perturbation theory (SAPT) [8]. These authors have found that, the interactions between fluorinated and nonfluorinated halomethanes with formaldehyde (as well as with methanol) depend strongly on the electrostatic contributions as well as on the dispersion. However, in the interactions of substituted bromobenzenes and bromopyrimidines with acetone, only the electrostatic forces play the key role.

Alkorta et al. [9], in their theoretical study of the properties of the monomers, dimers, trimers, and tetramers of the inter halogen molecules (FCl, FBr, and ClBr) using the natural energy decomposition analysis (NEDA) [10] have found that the main source of the interaction energy corresponds to the polarization term. In addition, the study of the interactions between $F_nH_{3-n}CBr$ (with n=0, 1, 2, 3) and HMgH at the MP2/aug-cc-pVTZ level has revealed that the electrostatic interaction together with the charge transfer and polarization interactions, are responsible for the stability of these complexes [11].

The topological description derived from the quantum theory of atoms in molecules (QTAIM) [12–14] has been extensively applied to study and characterizes the halogen bonding interactions [15–22]. Using this methodology, Zhang et al. [23] have recently studied the characteristics and nature of the halogen bonding in a series of B···XY [with B=H_2S, H_2CS, $(CH_2)_2S$ and XY=ClF, Cl_2, BrF, BrCl, Br_2] complexes. Their topological analysis has demonstrated that these halogen bonding interactions belong to weak interactions with an electrostatic nature. In a previous work, we have analyzed the Laplacian topology of the electronic charge density distribution in the aromatic halogen bonds D−X···πC_6H_6 (with D=−H, −CN, −F and X=F, Cl) [24]. The formation of these complexes results from the interaction between the charge density provided by the π-cloud (benzene molecule) and the charge density depletion region localized at the outer region of the halogen atom in the direction of the D−X bond.

In view of the existing information, it is clear that the nature of the XBs has not yet been elucidated. In order to make a contribution, in this work we investigate the nature of the bonding between chorine and nitrogen atoms in complexes formed by substituted ammonium [NH_nX_{3-n} (with n=0, 1, 2, 3 and X=−CH_3, −F] with F−Cl molecule. The intermolecular distribution of both the electronic charge density and the $L(\mathbf{r})$ function, has been examined within the framework of the AIM theory. These results are related to those obtained by the decomposition energy analysis.

Method and calculation details

The geometries of all the complexes and the corresponding isolated compounds were fully optimized using the Møller-Plesset second-order perturbation theory with the 6-311++G (2d,2p) basis set. The minimum energy nature of the optimized structures was verified using the vibrational frequency analysis. The binding energies were obtained at the same level of theory using the supermolecular approach that was calculated by subtracting the energies of the isolated compounds to the energy of the complex (the geometries of the isolated compounds corresponded to those in the complex). The basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi [25].

The weak interactions between closed-shell molecules usually decompose into several energy components including electrostatic (E_{ES}), exchange-repulsion (E_{EX}), polarization (E_{PL}), charge transfer (E_{CT}) and dispersion (E_{Disp}). In this work the total interaction energy (E_{Int}), of the complexes is defined as:

$$E_{Int} = E_{ES} + E_{EX} + E_{PL} + E_{CT} + E_{Disp}$$

The four terms, E_{ES}, E_{EX}, E_{PL} and E_{CT} were calculated according to the RVS method [6] at HF/6-311++G(2d,2p) level. The dispersion energy was estimated as the difference between the MP2/6-311++G(2d,2p) binding energy and the HF/6-311++G(2d,2p) binding energy. This is a standard practice in the literature [26]. AIM calculations were carried out using the wave functions generated from the B3LYP/6-311 G** calculations with the AIM2000 [27] and AIMAll [28] software. All calculations of electronic structure were carried out using the Gaussian 03 suite of programs [29].

Results

Geometrical and energetic parameters

Table 1 reports the values of the main parameters that describe the geometry of the studied systems and the interaction energies calculated at the MP2/6-311++G(2d,2p) level and corrected for basis set superposition error using the counterpoise procedure. It can be seen that in all the cases, Cl···N intermolecular distances are substantially shorter than the sum of the van der Waals radii [30] of the Cl and N atoms [r_{vdW}(Cl+N)=3.30 Å]. This is due to the mutual penetration of Cl and N atoms electronic densities. In

Table 1 Selected geometric parameters and binding energies calculated at the MP2/6-311++G(2d,2p) level and corrected by BSSE

Complexes	Structural parameters			ΔE_{MP2}
	d(X···N)	Δd(F–Cl)$_{Comp}$	∠ (F–Cl···N)	
FCl···N(CH$_3$)$_3$	2.0648	0.1575	179.99	−27.62
FCl···NH(CH$_3$)$_2$	2.0830	0.1447	179.15	−23.99
FCl···NH$_2$(CH$_3$)	2.1349	0.1199	178.77	−18.49
FCl···NH$_3$	2.2456	0.0818	179.99	−12.31
FCl···NH$_2$F	2.3038	0.0534	178.65	−7.65
FCl···NHF$_2$	2.5094	0.0209	178.85	−3.61
FCI···NF$_3$	2.7740	0.0055	179.96	−1.27

d(F–Cl)$_{Mon}$=1.6647 Å

d(Cl N): intermolecular distance.

Δd(F–Cl): is the change of F−Cl bond length upon complex formation

$-\Delta E_{MP2}$: binding energy.

Distances in angstrom, angles in degrees and energies in kcal/mol

addition, Cl···N intermolecular distances decrease with the increase of the binding energy. On the other hand, all changes Δd(F–Cl) are positive, that is to say, the F–Cl bond is stretched as a result of complexation. The stretch of the F–Cl bond length correlates with the strength of the interaction [-ΔE_{MP2} Vs. Δd(F–Cl) R=0.994, Fig. S1 Supporting information]. In Table 1, it can also be observed that the equilibrium angle, ∠ F–Cl···N, is always close to 180°.

The results from Table 1 [MP2/6-311++G(2d,2p) calculations] indicate that all these complexes are stabilized as a consequence of the interaction between the halogen atom and the lone pair of the ammonia molecule. The substitution of hydrogen atom by fluorine atom and by methyl group has a big influence on the binding energy in this set of complexes. For example, the binding energy in F–Cl···N(CH$_3$)$_3$ complex is more than two times greater than in F–Cl···NH$_3$, while the binding energy of this one, is more than nine times greater than in F–Cl···NF$_3$ complex. It is also interesting to compare the BE of the F–Cl···N(CH$_{3-n}$)H$_n$ type complexes, for example: the F–Cl···N(CH$_3$)$_3$ complex is 1.15 times more stable than F–Cl···N(CH$_3$)$_2$H and it is 1.30 times greater than F–Cl···N(CH$_3$)H$_2$ while that the last one is 1.50 times more stabilized than the F–Cl···NH$_3$ complex. Then, the effect of addition of methyl groups on the nitrogen atom of the ammonia is mirrored by the increase of the strength or stability of the complexes formed, and this increase is slighter by the successive substitution of hydrogen atoms by methyl groups. Additionally as was expressed previously, the substitutions of hydrogen of the base by electron-withdrawing atoms, as the fluorine, produce a very important decrease of the stability of the complexes.

The analysis of the energies decomposition of the F–Cl···NH$_n$X$_{3-n}$ (with n=0, 1, 2, 3 and X=−CH$_3$, −F) complexes was performed to understand the origin of the Cl···N interactions and the results are summarized in Table 2. One of the most striking features of these data is the fact that the stabilities of the Cl···N halogen bonds are predicted to be attributable mainly to electrostatic forces and to a lesser extent to the charge transfer. The dispersive forces, which have been widely believed to be responsible for these types of interactions, play a smaller role in stabilizing these complexes, except in the FCl···NF$_3$ complex in which the dispersive force has a similar value to the electrostatic force. In addition, in Table 2 it is observed that all the components increase in magnitude with the intensification of the E_{int}, being the E_{ES} and E_{CT} components the most important ones.

The E_{Int} generally agree with those obtained at MP2/6-311++G(2d,2p) level. Figure 1 shows the interaction energy components for several points near the potential energy minimum of the FCl···NH$_3$ complex. One of the most interesting aspects of these data is the increasing contribution of the electrostatic interaction to the overall stability of the complex with the approach to equilibrium geometry. That is, for all the chlorine-nitrogen separation distances (Fig. 1a) and all the angles theta (Fig. 1b) the electrostatic component is dominant. In addition, in the equilibrium position of the FCl···NH$_3$ complex [r=2.25 Å in Fig. 1a and θ=0.00º in Fig. 1b], E_{ES} and E_{CT} are the dominant components. In other words the electrostatic interaction between the halogen atom and the nitrogen lone pair electrons, as well as, the charge transference between Lewis base and Lewis acid play a large role in determining the geometric structures and stability of these complexes.

Table 2 Energy decomposition analysis for the FCl···NH$_n$X$_{3-n}$ (n=0, 1, 2, 3 and X=−CH$_3$, −F) complexes

Complexes	E_{ES}	E_{EX}	E_{PL}	E_{CT}	E_{RES}	E_{Disp}	E_{Int}
FCl···N(CH$_3$)$_3$	−71.34	113.04	−19.22	−33.58	−4.39	−12.66	−28.15
FCl···NH(CH$_3$)$_2$	−67.45	105.69	−17.19	−31.21	−3.52	−10.69	−24.37
FCl···NH$_2$(CH$_3$)	−57.42	88.06	−13.10	−25.76	−2.31	−8.24	−18.77
FCl···NH$_3$	−40.99	59.60	−7.70	−17.00	−1.04	−5.34	−12.47
FCl···NH$_2$F	−27.62	41.97	−4.59	−11.46	−0.58	−5.58	−7.86
FCl···NHF$_2$	−10.85	16.96	−1.46	−4.47	−0.15	−3.83	−3.80
FCl···NF$_3$	−2.60	5.34	−0.42	−1.50	−0.01	−2.10	−1.29

Symbols are explained in the text

All values in kcal/mol

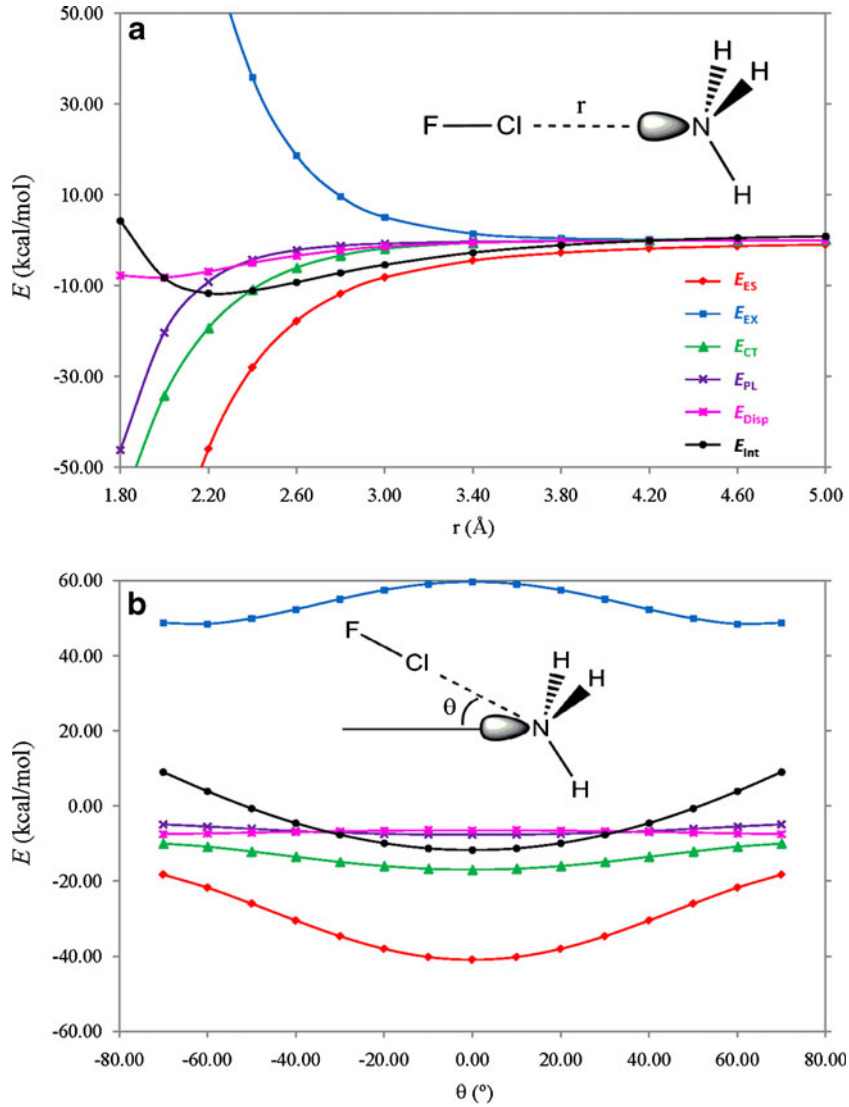

Fig. 1 Interaction energy components for FCl···NH_3 dimer. (**a**) As function of the chlorine-nitrogen separation distance. (**b**) As function of θ at r=2.25 Å

Topological analysis

The topological analysis of the electron charge density and its Laplacian function constitute a powerful tool to investigate the electronic properties of the molecular system and allows a deep examination of the interatomic interactions. Furthermore, this methodology has been successfully applied in the properties study of a variety of XBs [16, 23, 24, 31, 32]. Table 3 reports the selected topological properties of the XBs studied here. Calculated properties at the bond critical point, BCP, in ρ(**r**) topology are labeled with the subscript "b" and the calculated properties at the (3,+1) critical point (CP) of L(**r**) function are labeled with the subscript "hole".

The Laplacian of ρ(**r**) is related to the local components, kinetic G(**r**) and potential V(**r**) of the total energy via the local expression of the virial theorem [in au: $\nabla^2\rho(\mathbf{r})=2G(\mathbf{r})+V(\mathbf{r})$] [12–14]. The sign of $\nabla^2\rho(\mathbf{r})$ determines which of these two contributions to the total energy is in excess over its average virial ratio of 2:1. Thus, when the Laplacian is negative, the electronic charge is concentrated and the potential energy dominates. Additionally, when the Laplacian is positive, the electronic charge is locally depleted and the kinetic energy is in local excess. According to Bader and Essén [33], the first situation occurs in shared interactions, while the second situation is characteristic of closed-shell interactions. At Cl···N intermolecular BCP, shown in Table 3, the BCP localized between the N atom of the Lewis base and the Cl atom of the Lewis acid presents typical properties of closed-shell interactions: the value of electron density, $\rho(\mathbf{r}_b)$, is relatively low; the ratio of the perpendicular contractions of $\rho(\mathbf{r}_b)$ to its parallel expansion $|\lambda_1|/\lambda_3$ is<1, and the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r}_b)$, is positive.

According to the topological analysis of electron density distribution in the AIM theory, the electron density at the BCP, $\rho(\mathbf{r}_b)$, is used to describe the strength of a bond [12–14]. In general, the larger the value of $\rho(\mathbf{r}_b)$, the stronger the bond is. It can be seen from Table 3 that $\rho(\mathbf{r}_b)$

Table 3 Topological parameters calculated

Complexes	$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	$\lvert\lambda_1\rvert/\lambda_3$	$\rho(\mathbf{r}_{hole})$	$L(\mathbf{r}_{hole})$	$\lvert V_{e\text{-}n}(N,Cl)\rvert$	$\lvert V_{e\text{-}n}(Cl,N)\rvert$
$FCl\cdots N(CH_3)_3$	0.0552	0.4012	0.0663	0.1024	−0.0949	36.1945	29.1715
$FCl\cdots NH(CH_3)_2$	0.0526	0.3857	0.0602	0.1047	−0.0898	35.7753	28.9431
$FCl\cdots NH_2(CH_3)$	0.0479	0.3378	0.0663	0.1119	−0.0777	34.6809	28.3281
$FCl\cdots NH_3$	0.0397	0.2547	0.0741	0.1237	−0.0591	32.7186	27.0688
$FCl\cdots NH_2F$	0.0364	0.2228	0.0899	0.1333	−0.0474	29.5829	26.4564
$FCl\cdots NHF_2$	0.0253	0.1335	0.1107	0.1455	−0.0280	24.8441	24.4052
$FCl\cdots NF_3$	0.0144	0.0707	0.1173	0.1527	−0.0172	20.3580	22.1619

$\rho(\mathbf{r}_b)$: electron density at the Cl···N BCP

$\nabla^2\rho(\mathbf{r}_b)$: Laplacian of the electron density at the Cl···N BCP

$\lvert\lambda_1\rvert/\lambda_3$: ratio of the perpendicular contractions of $\rho(\mathbf{r}_b)$ to its parallel expansion at the Cl···N BCP

$\rho(\mathbf{r}_{hole})$: electron density at the (3,+1) critical point of the $L(\mathbf{r})$ function (sigma hole)

$L(\mathbf{r}_{hole})=-\frac{1}{4}\nabla^2\rho(\mathbf{r}_{hole})$ at the (3,+1) critical point of the $L(\mathbf{r})$ function (sigma hole)

$V_{e\text{-}n}(N,Cl)$: electrostatic interaction energy between total charge distribution of atom N and nucleus of atom Cl

$V_{e\text{-}n}(Cl,N)$: electrostatic interaction energy between total charge distribution of atom Cl and nucleus of atom N

$\rho(\mathbf{r}_b)$, $\nabla^2\rho(\mathbf{r}_b)$, $\rho(\mathbf{r}_{hole})$, $L(\mathbf{r}_{hole})$ and $V_{e\text{-}n}(N,Cl)$ are in atomic units, and $\lvert\lambda_1\rvert/\lambda_3$ is dimensionless

increases with the strength of the interaction. The electron density values range from 0.01 to 0.06 au, and the Laplacian of the electron density ranges from 0.07 to 0.40 au, which correlates fairly well with the values reported for similar interactions. The topological properties at the Cl···N BCP in the complexes analyzed here, show that their $\rho(\mathbf{r}_b)$ values are lower (as it is well-known) than the $\rho(\mathbf{r}_b)$ values found in covalent bonds (i.e., 0.264 au for the Cl–N BCP). However, they are on the same order of magnitude as those reported on other conventional H···LP interactions considered by Rozas et al. as hydrogen bonds of intermediate strength [i.e., 0.032 au for Me_2–(H)N···HCN complex and 0.038 au for Me_3N···HCN complex] [34].

In order to show how the electron charge density varies throughout the full range of halogen bonded complexes, in supporting information Fig. S2, we have represented the values of $-\Delta E_{MP2}$ versus $\rho(\mathbf{r}_b)$ [the energy is given in kilocalories per mole and $\rho(\mathbf{r}_b)$ is in atomic units]. The almost quadratic relationship obtained and the value of the correlation coefficient R=0.99 for XBs, show that $\rho(\mathbf{r}_b)$ is a good indicator of the bond strength. More interesting still, is the analysis along of the same series, of the $L(\mathbf{r})$ topology, as is commented more below.

The $L(\mathbf{r})=-\frac{1}{4}\nabla^2\rho(\mathbf{r})$ function is of particular interest to the present study due to that its topology shows the regions of the space where the electron density is locally concentrated or depleted [35]. The valence shell of an atom is divided into an inner region where $L(\mathbf{r})>0$ and an outer one where $L(\mathbf{r})<0$. The first one is called the valence shell charge concentration (VSCC). Thus, a local maximum (or minimum) in $L(\mathbf{r})$ signifies a local concentration (or depletion) of electron density. From a topological view point, the extremes or CPs in the distribution of the $L(\mathbf{r})$ function easily provide the precise localization of different reactivity zones. In this way, a (3, −3) CP corresponds to a local maximum in $L(\mathbf{r})$ [with $\nabla^2\rho(\mathbf{r})<0$] and indicates a local electronic charge concentration (CC), while a (3,+3) CP corresponds to a local minimum in $L(\mathbf{r})$, [with $\nabla^2\rho(\mathbf{r})>0$] and indicates a local depletion of the electronic charge (CD). On the other hand, (3,−1) and (3,+1) CPs are saddle points.

In the field of the halogen bonded complexes, many researchers attributed the formation of halogen bonds to the attractive electrostatic interaction between the region of positive electrostatic potential on the outermost portion of the halogen atom and the lone pair of the acceptor [1–4]. However, this concept fails in some special situations, for example in the CH_3Cl molecule. The chlorine atom in this molecule does not have a positive electrostatic potential on its surface and consequently should not be able to form XBs. However, Riley et al. [7] showed that this molecule is able to form a stable XB with OCH_2. For this reason we consider it more appropriate to analyze the CPs of the $L(\mathbf{r})$ topology, where the electrostatic contribution and also the other contributions, due to the electron re-distribution (polarization and charge transfer) are considered. (The electron redistribution within monomers of the complex is related to the electron polarization contribution and the redistribution between the monomers is due to the electron charge transfer from the Lewis base to the Lewis acid). The analysis of the distributions of the $\nabla^2\rho(\mathbf{r})$ [or of the $L(\mathbf{r})$ function] show the presence of a depletion of electron density in the direction of the interaction (in the direction of the positive sigma-hole of Politzer). As a consequence, more negative values of $L(\mathbf{r}_{hole})$ were found in complexes formed with three-methyl ammonia [$L(\mathbf{r}_{hole})$=–0.0949 au, see Table 3].

It is worth stressing that this conclusion is based on a real physical property of the system: the electron charge density that

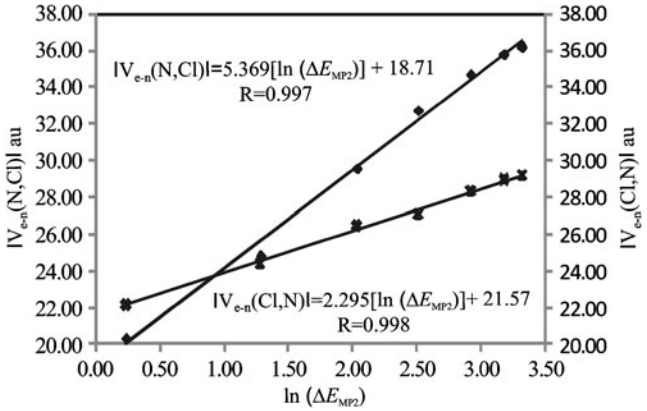

Fig. 2 Correlation between $|V_{e\text{-}n}(N,Cl)|$ and $|V_{e\text{-}n}(Cl,N)|$ with the natural logarithm of the binding energies

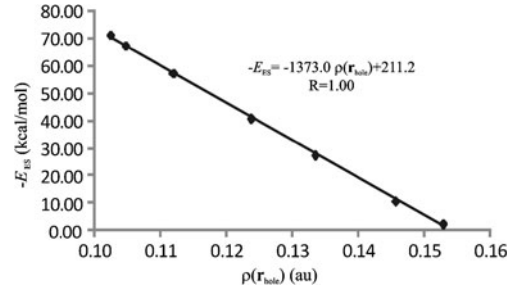

Fig. 4 Correlation between $\rho(\mathbf{r}_{hole})$ and the electrostatic component of the E_{int} in halogen bonding complexes

can be obtained experimentally or by computational methods. Indeed, it is important to consider (in contraposition to the electrostatic potentials) that the quantum theory of atoms in molecules (QTAIM) proposed by Bader is very consistent and physically supported because the electronic density is pondered while the quantum-mechanical observable.

In addition, in the context of the electron charge density distributions provide by QTAIM, we have calculated the electrostatic interaction energy between the electron cloud of the Lewis base and the nucleus of the halogen atom of the Lewis acid (these values are shown in Table 3). It is observed that $|V_{e\text{-}n}(N,Cl)|$ and also $|V_{e\text{-}n}(Cl,N)|$ increase with the module of the binding energy.

It is interesting to note that in most complexes $|V_{e\text{-}n}(N,Cl)|>|V_{e\text{-}n}(Cl,N)|$ whereas only in the FCl···NF_3 complex $|V_{e\text{-}n}(N,Cl)|<|V_{e\text{-}n}(Cl,N)|$. This is probably due to the fact that in the FCl···NF_3 complex the dispersive force has a value similar to electrostatic force (see Table 2). In addition, Fig. 2 shows a good correlation between $|V_{e\text{-}n}(N,Cl)|$ and $|V_{e\text{-}n}(Cl,N)|$ with the natural logarithm of the binding energies. Therefore, the electrostatic interaction between the electron cloud of the Lewis base and the nucleus of the halogen atom of the Lewis acid, plays a key role in stabilizing these halogen bonding interactions.

Figure 3 undoubtedly shows that the formation of the studied complexes results from the interaction between a maximum in $L(\mathbf{r})$ [(3,−3) CP] with a minimum (or saddle) in $L(\mathbf{r})$ [(3,+3) or (3,+1) CP]. Clearly, the molecules are oriented so that the lumps in the valence shell charge concentration (VSCC) of the nitrogen atom of the Lewis base are aligned with the hole in the VSCC of the chlorine atom of the Lewis acid.

Another important result is obtained comparing the envelopes of the $L(\mathbf{r})$ function (Fig. 3). Interestingly enough, the extension of the charge depletion region localized over the chlorine atom and facing the lone pair of the Lewis base increases in the order FCl···NF_3<FCl···NH_3<FCl···$N(CH_3)_3$; that is to say, following the order of the strength of the interaction. In addition, Table 3 shows that $\rho(\mathbf{r}_{hole})$ and $L(\mathbf{r}_{hole})$ values decrease in the order FCl···NF_3>FCl···NHF_2>FCl···NH_2F>FCl···NH_3>FCl···$NH_2(CH_3)$>FCl···$NH(CH_3)_2$>FCl···$N(CH_3)_3$; that is, in reverse order to the strength of the interaction. In other words, the strength of interaction increases with depletion of electronic charge density over the σ-hole. We believe that the electronic charge density depletion localized over the chlorine atom allows the electrostatic interaction between the halogen atom nucleus and the Lewis base. Resuming up, the decrease of $\rho(\mathbf{r}_{hole})$ at (3,+1) CP is connected with the

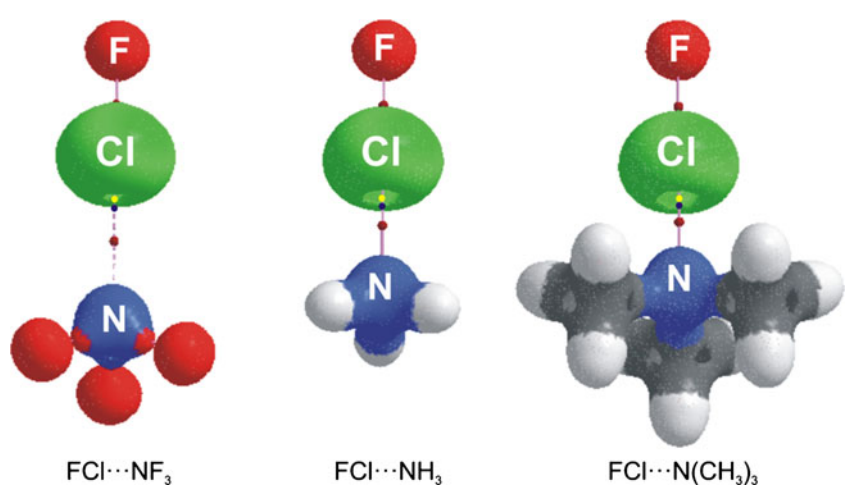

Fig. 3 Envelops at $L(\mathbf{r})$=0.00 au. The molecules are oriented so that the lumps in the valence shell charge concentration (VSCC) of the nitrogen atom of the Lewis base are aligned with the holes in the VSCC of the chlorine atom of the Lewis acid. In addition, the bond critical points of $r(\mathbf{r})$ at F–Cl and Cl···N (in red), and (3,+1) CPs (in yellow) and the (3,+3) CPs (in blue) of the $L(\mathbf{r})$ function are shown

decrease of the accumulation of charge density; likewise, the greater decrease of $\rho(\mathbf{r}_{hole})$ [from 0.1527 au in F–Cl···NF_3 to 0.1024 au in F–Cl···$N(CH_3)_3$ complexes] is connected with the greater strength of the interaction. See in supporting information Fig. S3 [-ΔE_{MP2} Vs. $\rho(\mathbf{r}_{hole})$] and Fig. S4 [-ΔE_{MP2} Vs. $\nabla^2\rho(\mathbf{r}_{hole})$].

On the other hand, the binding energy electrostatic contribution, E_{ES}, is the result of the interaction between the undistorted electron distribution of the monomer (F–Cl) and that of the monomer (substituted ammonium). This contribution includes the interactions of all permanent charges and multipoles, such as dipole-dipole, dipole-quadrupole, etc. Figure 4 shows a good correlation between the electron charge density at the (3,+1) CP of the $L(\mathbf{r})$ function, $\rho(\mathbf{r}_{hole})$, and binding energy electrostatic contribution, E_{ES}. In other words, the electrostatic force of the Cl···N interaction increases with the decrease of the electron density at (3,+1) CP of the $L(\mathbf{r})$ function.

Conclusions

This work, carried out on a set of complexes within a wide range of variation of binding energy (from 1.27 to 27.62 kcal/mol), highlights the utility of the topological analysis of the charge density and of the $L(\mathbf{r})$ function, in conjunction with energy decomposition analysis as a methodology to investigate the nature of the halogen bonds. Based on the energy decomposition analysis, we have found that the electrostatic and the charge transference (in minor measure) components have the most significant contributions to the total interaction energy -*in all ranges of strength*- of the complexes analyzed here and play a substantial role in determining the optimal geometry of the complexes.

The local properties at (3,-1) CPs in $\rho(\mathbf{r})$ and (3,+1) CPs in $L(\mathbf{r})$ topologies are good descriptors of the strength of these complexes. The local properties at (3,+1) CPs in $L(\mathbf{r})$ topology reveal that, the strength of interaction increases with depletion of electronic charge density over the σ-hole. Moreover, the topological analysis of the $L(\mathbf{r})$ function reveals that the electronic density measured at the (3,+1) CP of the $L(\mathbf{r})$ function is a good descriptor of the electrostatic component. Furthermore, a good lineal correlation was established between the $\rho(\mathbf{r}_{hole})$ and E_{ES}. In addition, a lineal relationship was established between the $|V_{e\text{-}n}(N,Cl)|$ values and the natural logarithm of the binding energy. These findings suggest that, the electrostatic interaction between the lone pair of N atom and nucleus of Cl atom plays a key role in stabilizing these halogen bonding interactions.

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