

On the strength of the halogen bonds: Mutual penetration, atomic quadrupole moment and Laplacian distribution of the charge density analyses

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ABSTRACT

Analyses of the atomic quadrupole moment and Laplacian distribution of the charge density were employed in the description of the strength of halogen bonds between ammonia as Lewis base and Lewis acids, D–X (with X = F, Cl, Br, I and D = –H, –CN, –F as halogen donor group). The geometries of all the complexes were fully optimized using the Møller–Plesset second-order perturbation theory with the 6-311++G(2d, 2p) basis set. For iodine atoms, an effective core potential (ECP) was used. Mutual penetration of electron charge densities, charge transference between Lewis base and Lewis acid, atomic dipole moment on nitrogen atom and change of atomic quadrupole moment on the halogen atom, were considered in this study. A significant charge density transference from the Lewis base to the Lewis acid is observed and the relation between the strength of the halogen bond and the amount of charge density transferred is explored. In addition, the analysis of the dipole moment at nitrogen atom in these complexes reflects the electronic rearrangement produced by the formation of the halogen bond and its strength. Moreover, we studied where the transferred electron charge is. We found that the Laplacian distribution and the atomic quadrupole moment on the halogen atom show that the electron density is not increased in the direction of the X···N bond, but it increases in the orthogonal direction to the bond forming (X···N). Finally, this work shows the important answers that the AIM analysis provides on the characteristics of the halogen bonds.

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1. Introduction

Halogen bonds (XBs) are primarily stabilizing electrostatic interactions between a polarizable halogen and an electron-rich Lewis base such as oxygen, nitrogen or sulfur atoms. In the XBs a halogen atom is shared between an atom, a group or a molecule that “donates” the halogen and another one that “accepts” it. In other words, a halogen atom X is shared among a donor D and an acceptor A. In halogen bonding, (like hydrogen bonding) the donor tends to be electron-withdrawing with high electronegativity [1]. It is not surprising that hydrogen (with partial positive charges) interacts attractively with electronegative atoms (such as N, O, S, F and Cl) but why halogen atoms (with partial negative charges) show a behavior similar to hydrogen atoms and can be attracted by other atoms with available lone pair. The explanation is simple: the halogen atoms are electron rich and the electron withdrawing group, bonded to them (D–X), produces an asymmetrical distribution of the halogen electrons and creates an electropositive region at the crown of the atom, sometimes referred to as a “ σ -hole” [2–5a,b] and more recently as “positive σ -hole” [6]. This

positive σ -hole acts as a Lewis acid to interact electrostatically with a Lewis base. These interactions, which are shorter than the sum of the atoms' van der Waals radii but longer than covalent bonds, are now known as XBs to emphasize their similarity to the more well-known hydrogen bonds (HBs). Moreover, the electronic structure of the halogen atom is quite different from that of the hydrogen atom. There must be some difference in the properties between the HBs and XBs. For example, the greater directionality of the XBs relative to the HBs can be understood by the analysis of the electron distribution using the quantum theory of atoms in molecules (QTAIMs) theory [7a–c]. From the topological analysis of the Laplacian distribution, our previous results show that the halogen-bonded complexes result from the interaction between the charge density provided by the lone pair of the donor atom of Lewis base (N, O, and S atoms or π -electron in aromatic halogen bonds (aXBs)) and the charge density depletion localized at the outermost portion of the X halogen atom centered on the D–X axis bonds (similar to the σ -hole in electrostatic potential) [8,9]. Such charge depletion on the X atom is due to electron density extraction produced on it by the D group. This generates a decrease of the charge density in the front part of the X atom, and this asymmetrical electron distribution increases with the capacity of deformation of the electron charge density on the X atom. In other

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words it increases with their polarizability. Also, from the theoretical and experimental electron charge density distribution, several studies point out the similarity between XBs and HBs as a lump-hole interaction [10].

The QTAIM and Natural Bond Orbital (NBO) analyses have been successfully applied in characterizing hydrogen bonds, halogen bonds [11–13] and chalcogen bonds [14] of different strengths in a wide variety of molecular complexes. Halogen–anion interactions [13] and halogen–cation interactions have not received as much attention as neutral halogen bonds. Such interactions, termed as charge-assisted halogen bonds, are indeed of vital importance in crystal engineering. The great potential of XBs interaction involving halogens as electron acceptors, in the design of new and high-value functional materials is now emerging clearly [15].

It is generally well accepted that the strength and effectiveness of halogen atoms (chlorine and also fluorine) in XBs formation depend on the nature of the halogen and of the halogen donor. As it is well known the halogen electronegativities increase and their polarizabilities decrease when going from iodine to fluorine. Then, if the halogen is bonded to an electronegative moiety, it is more likely to form stronger halogen bonds. Many works [2,16–20] have reported that the XBs are stronger than HBs; for example, we found that the XBs formed with ammonia and sulfide base are stronger than the HBs formed with these bases [9].

In addition, Grabowski [21] has studied different types of non-covalent interactions such as, halogen bond, hydrogen bond, and dihalogen bond in complexes of F_3Cl wherein the Cl–C bond can act as Lewis acid and as Lewis base. It was found that the change of *s*-character of the C hybrid orbital is connected with the strength of interaction, (the increase if C–Cl acts as the Lewis acid and the decrease if it acts as the Lewis base). Recently, similar dependencies between the *s*-parameter and the strength of interaction have also been found for hydrogen bond systems [22].

Between the halogen bonded complexes the case of fluorine is particularly interesting. It has been long pointed out that, the fluorine atom (the most compact and least polarizable atom) has no or little possibility to form XBs. Moreover, a recent work based on the Laplacian of the electron density and the topology of the valence shell charge concentration (VSCC) of the halogen atom was carried out by Eskandari and Zariny [10]. These authors reported that the fluorine atom, unlike the chlorine and bromine ones, is not able to form a XB because the “hole” is missing in its valence shell charge concentration. However, as it has been strongly established by Politzer et al. [6] and taking in consideration two very recent works of Metrangolo et al. (wherein computational and crystallographic evidence of XBs formed by fluorine atom was shown) the fluorine atom can certainly function as a XB donor and form complexes with lone-pair-containing neutral atoms and anions [23,24]. According to this information provided through molecular electrostatic potential and in disagreement with the requirement of the existence of the “hole” on the VSCC of halogen atom as a necessary condition in the formation of XBs, we believe that the inspection of the Laplacian topology can provide a good description of the XBs in halogen bonded complexes.

With this in mind, we have chosen ammonia as Lewis base and different Lewis acids, to examine firstly, how the electronegativity difference ($\Delta\chi_{D-X}$) (between the halogen donor group and the halogen atom) affects the capacity of D–X Lewis acid to form halogen bonded complexes and subsequently how this affects the strength of the halogen bonds. Secondly, we would like to know if a relationship between the Laplacian topology in the VSCC at halogen atom and the strength of the XBs can be established; and thirdly, where the electron charge transferred from Lewis base is going to.

2. Methods and calculation details

For this study, halogen bonds formed between ammonia as Lewis base and D–X as Lewis acids, (with X = F, Cl, Br, I; and with D = –H, –CN, –F as halogen donor group) were selected. The geometries of all complexes were fully optimized using the Møller–Plesset second-order perturbation theory [25] with the 6-311++G(2d, 2p) basis set. For iodine atoms, an effective core potential (ECP) was used [26]. Geometrical variables were optimized using the Berny's analytical gradient method [27]. All stationary points were characterized as minimal energetic by calculating the Hessian matrix. The basis set superposition error (BSSE) was taken into account using the counterpoise method proposed by Boys and Bernardi [28]. The Natural Bond Orbital analysis was performed with the NBO 3.1 program [29], as implemented in the Gaussian 03. All these calculations were carried out using the Gaussian 03 suite of programs [30]. The calculations of local topological properties of the electron charge density at the critical points and the integrated atomic properties on the atomic basin, as well as the display of the molecular graphs were performed with the AIM2000 [31] and AIMAll [32] software, with the electron density obtained at B3LYP level [33,34] with the 6-311G(d, p) basis set.

3. Results

3.1. Geometrical and energetic parameters

In this work, all the optimized complexes have shown a C_{3v} symmetry wherein the D–X··N bond angle is near to 180°. Table 1 reports the selected structural and topological parameters in the halogen bonding complexes. The first properties reported in this table are: $d(X··N)$ halogen bond distance and the ($r(X) + r(N)$) van der Waals radii sum; and the second ones are the local topological properties calculated at D–X··NH₃ bond critical points (BCPs), these are the electron density $\rho(r_b)$, the Laplacian of the electron density $\nabla^2\rho(r_b)$, and the total electronic energy density $H(r_b)$. The binding energy corrected ($-\Delta E_{BSSE}$) by basis set superposition error (BSSE) is also given in Table 1.

As it can be seen in Table 1 through the binding energy analysis, the studied complexes display a significant range of strength from –0.65 (in H–Cl··NH₃ complex) to –15.78 kcal/mol, (in F–I··NH₃ complex) indicating that the halogen bonding interactions studied here are comparable in strength to the well-documented hydrogen bonding interactions [35]. These can be considered: weak, moderate and strong depending on the bridged halogen atom and more significantly on all the rest of the halogen donor molecule. In other words, fluorine is always weakly bonded to ammonia but the XB strength forming with Cl, Br, and I halogen atoms show a broad variation depending on the environment in which the halogen is covalently bonded. For example, the H–X··NH₃ (with X = Cl, Br, I) complexes are weak halogen bonds, $\Delta E_{BSSE} < \sim 4$ kcal/mol; NC–X··NH₃ are moderate halogen bonds, and $\sim 4 < \Delta E_{BSSE} < 10$ kcal/mol and F–X··NH₃ can be considered strong halogen bonds with $\Delta E_{BSSE} > 10$ kcal/mol. The results from Table 1 show that the intermolecular distances are lower than the van der Waals radii sum, with the exception of the H–Cl··NH₃ complex, wherein the $d(Cl··N)$ is slightly larger (by 0.01 Å). It is observed, in all the rest of the complexes, that the interpenetration between the electron cloud of the halogen atom and that of the nitrogen atom is significant. Likewise, the results reported by Amezcaga et al. have demonstrated that the distance of penetration electronic densities reaches the highest values in complexes formed with ammonia [9]. The results from Table 1 show that the interaction energy of F–Cl··NH₃ is 2.66 times greater than in NC–Cl··NH₃ complex, while the interaction energy of this one, is 2.32 times greater than

Table 1
Structural (in Å) and topological (in au) selected parameters, at the intermolecular region, in the complexes bonded by XBs. The interaction energies (in kcal/mol) corrected by BSSE is also given.

Complexes	Structural parameters		Topological parameters			ΔE_{BSSE}
	$d(\text{X} \cdots \text{N})$	$r(\text{X}) + r(\text{N})$	$\rho(\mathbf{r}_b)$	$\nabla^2 \rho(\mathbf{r}_b)$	$H(\mathbf{r}_b)$	
HF \cdots NH ₃	Not found					
NCF \cdots NH ₃	3.1380	2.90	0.0058	0.0231	0.0007	-1.01
FF \cdots NH ₃	2.6028	2.90	0.0170	0.0705	0.0020	-1.35
HCl \cdots NH ₃	3.3108	3.30	0.0078	0.0266	0.0009	-0.65
NCCl \cdots NH ₃	2.9734	3.30	0.0146	0.0481	0.0009	-3.93
FCl \cdots NH ₃	2.2456	3.30	0.0592	0.1588	-0.0060	-10.46
HBr \cdots NH ₃	3.2252	3.40	0.0108	0.0332	0.0007	-1.69
NCBr \cdots NH ₃	2.8928	3.40	0.0194	0.0588	0.0007	-5.56
FBr \cdots NH ₃	2.3488	3.40	0.0539	0.1347	-0.0068	-13.75
HI \cdots NH ₃	3.1717	3.53	0.0150	0.0408	0.0005	-2.89
NCI \cdots NH ₃	2.8734	3.53	0.0245	0.0651	-0.0001	-7.55
FI \cdots NH ₃	2.4802	3.53	0.0480	0.1182	-0.0060	-15.78

$d(\text{X} \cdots \text{N})$: Intermolecular distance; $r(\text{X}) + r(\text{N})$: sum of the van der Waals radii of X and N atoms.

$\rho(\mathbf{r}_b)$: Electron density; $\nabla^2 \rho(\mathbf{r}_b)$: Laplacian of the electronic density; $H(\mathbf{r}_b)$: local electronic energy density. All measured in BCP X \cdots N.

in H-Cl \cdots NH₃ complex. It is also interesting to compare the interaction energies of the NC-X \cdots NH₃ type complexes, for example: the NC-I \cdots NH₃ complex is 1.36 times more stable than NC-Br \cdots NH₃ and it is 1.41 times greater than NC-Cl \cdots NH₃, while that the last one is 3.89 times more stabilized than the NC-F \cdots NH₃ complex. Additionally, the H-F \cdots NH₃ complex will not be formed. The capacity of D-X compounds to act as Lewis acid in front of ammonia as Lewis base was examined and the results obtained allow us to say that the “acid capacity” [36] of D-X as Lewis acid (for a same halogen atom, X) depends on the halogen donor group and increases in the order: H-X < NC-X < F-X, while for a same halogen donor, D, the “acid capacity” increases in the order D-F \cdots NH₃ < D-Cl \cdots NH₃ < D-Br \cdots NH₃ < D-I \cdots NH₃, that is to say, following the polarizability of the halogen atom.

3.2. Relationship between the strength of XBs and the electronegativity differences in the (D-X) halogen donor molecule

As a consequence of the foregoing, the difference of electronegativity, $\Delta\chi_{\text{D-X}}$, between the halogen atom and the halogen donor, (-H, -CN, -F) was taken into account in order to evaluate and quantify the “acid capacity” of the Lewis acids and their relationship with the halogen bonds strength.

In Fig. 1, ΔE_{BSSE} vs. the Paulings electronegativity difference between the halogen atom and the halogen donor group bonded to them, is displayed (the energy is given in kcal/mol and χ is dimen-

sionless). As it can be seen in Fig. 1, the $\Delta\chi_{\text{D-X}} \leq 0$ values always correspond to binding energy values <4 kcal/mol; consequently there are “weak XBs”. For $\Delta\chi_{\text{D-X}} > 0$ the binding energy values span from 4 to 16 kcal/mol therefore there are “moderate and strong XBs”. This allows us to define the three regions indicated in the Fig. 1. Additionally, an exponential correlation ($R = 0.97$) between the binding energy and the Paulings electronegativity difference, $\Delta\chi_{\text{D-X}}$, was found in the set of the studied complexes.

The results shown in the exponential correlation are indicative of the two effects indicated above (i) the polarizability of the halogen atom and (ii) the difference between the halogen atom electronegativity and the donor group electronegativity bonded to it. Consequently, the results obtained show that, for the same halogen, the enhance of $\Delta\chi_{\text{D-X}}$ values reflect in direct mode the strengthening of the halogen bonds (i.e. -0.65, -3.93 and -10.46 kcal/mol for H-Cl \cdots NH₃, NC-Cl \cdots NH₃ and F-Cl \cdots NH₃, respectively). Apparently, fluorine is a better electron-withdrawing group than cyano group and this fact defines their strength. It is interesting to highlight that, in a previous paper on aromatic halogen bonds, (aXB), we have found that the binding energy decreases following the order: NC-Cl \cdots $\pi\text{C}_6\text{H}_6$ > F-Cl \cdots $\pi\text{C}_6\text{H}_6$ > H-Cl \cdots $\pi\text{C}_6\text{H}_6$ [8]. These results are interesting because these situations show a difference between both XBs types (depending on the Lewis base). In other words, these reflect the different XBs nature (mainly electrostatic force in complexes engaged with ammonia and dispersion force in aXBs).

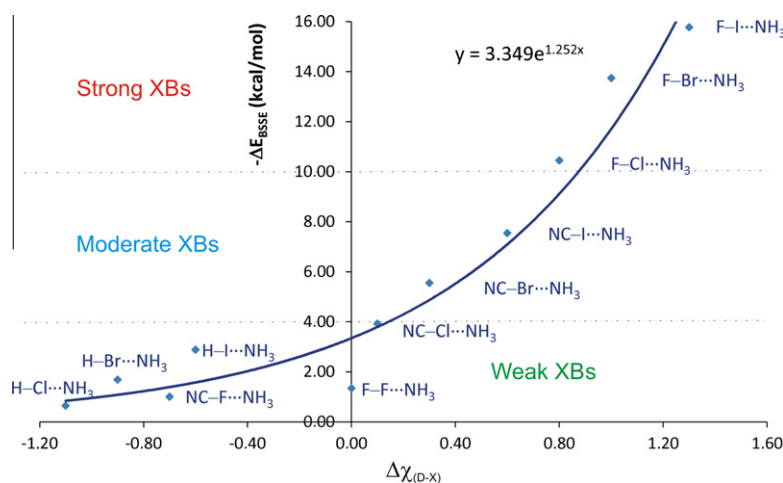


Fig. 1. Exponential correlation between the binding energy in D-X \cdots NH₃ complexes (with D = -H, -CN, -F and X = F, Cl, Br, I) and the Paulings electronegativity difference (between the halogen atom and the electron-withdrawing group bonded to it). The coefficient correlation is included.

3.3. AIM and NBO analyses

3.3.1. Local topological properties at the X...N BCPs

As it is well known, to characterize HBs in a rigorous manner within the QTAIM Caroll and Bader [37] and Koch and Popelier [38] proposed a set of criteria indicative of these interactions. These criteria comprise a set of local topological properties of the electron density and a set of integrated atomic properties on the bridge hydrogen atom. These criteria have been recently used to characterize halogen bonds [9,39]. Then, for the different complexes studied in this work we have used these criteria to evaluate, as these properties can be seen as different indicators of halogen bonds strength.

The topological characteristics at the intermolecular BCP, represented in Table 1, show typical properties of closed-shell interactions: the value of electron density, $\rho(\mathbf{r}_b)$, is relatively low and the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r}_b)$, is positive. Clearly, the values reported are within reasonable limits. The electron density values ranging from 0.0058 to 0.0592 au and the Laplacian values range from 0.0231 to 0.1588 au, which correlates fairly well with the values reported for similar interactions [9]. It is also interesting that these interactions lead to low and positive values of the $H(\mathbf{r}_b)$; however, in stronger complexes formed between ammonia and F–Cl, F–Br, NC–I and F–I compounds the values of $H(\mathbf{r}_b)$ are low and negative.

Generally, it has been observed that the electron charge density and its Laplacian at HB BCP, gives an easy indication of HB strength [40]. Also, in several previous works [41,42a–c] it was found that the topological properties at the BCP in intermolecular interaction reflect the strength of the interaction, in an improved mode, with respect to other parameters (i.e. geometrical parameters). However, recently Mo [43] has reported that in intramolecular resonance-assisted hydrogen bonds (RAHBs) systems the estimate of HB strengths based on the QTAIM topological properties is imperfect. He has made a computational study on a series of typical RAHB systems using the block-localized wave function (BLW) method [44,45] combined with QTAIM analysis to examine the correlation between the electron density topological parameters and hydrogen bonding strengths in these systems. He found out that while the deactivation of the π resonance in these RAHB systems by the use of the BLW method has considerably weakened the hydrogen bonding strength, little change on the topological properties of electron densities at hydrogen bond BCPs has been observed.

Consequently, we have explored the relationship between the strength of the different bonds and the topological characteristics at the intermolecular BCP. From Table 1, comparing the values of the (\mathbf{r}_b) in the F–X...NH₃ complexes, it can be seen that the density increases following the order F...N \ll I...N < Br...N < Cl...N, and on the other hand, the binding energies of the interactions increase following the order F–F...NH₃ < F–Cl...NH₃ < F–Br...NH₃ < F–I...NH₃. In other words, for the F–X...NH₃ subset of our studied halogen bonded complexes no correlation between $\rho(\mathbf{r}_b)$ and ΔE_{BSE} was found. However, a fairly good linear relationship was found between ΔE_{BSE} and $\rho(\mathbf{r}_b)$ at X...N BCP; for example: $R = 0.98$; $R = 0.99$ and $R = 1.0$ for chlorine, bromine, and iodine bonded complexes, respectively (graphics not shown). Therefore, the comparison of stabilization energy or binding energy with the charge density at the intermolecular BCP must be restricted to structures of complexes in which the same pairs of atoms are interacting.

3.3.2. Mutual penetration and their relationship with binding energy

In the context of the AIM theory, it is said that an atom is penetrated when its bonded radius (r_X), defined as the distance from its nucleus to a BCP, becomes smaller than its non-bonded radius,

Table 2

Mutual penetration of the halogen and the nitrogen atoms (in Å).

Complexes	Lewis bases		Lewis acids			Total $\Delta r_N + \Delta r_X$
	r_N	Δr_N	r_X^0	r_X	Δr_X	
NCF...NH ₃	1.73	0.26	1.56	1.41	0.15	0.41
FF...NH ₃	1.45	0.54	1.52	1.16	0.36	0.90
HCl...NH ₃	1.68	0.31	1.94	1.62	0.32	0.63
NCCL...NH ₃	1.51	0.48	1.87	1.47	0.40	0.88
FCI...NH ₃	1.14	0.85	1.80	1.11	0.69	1.54
HBr...NH ₃	1.60	0.39	2.04	1.62	0.42	0.81
NCBr...NH ₃	1.44	0.55	1.98	1.45	0.53	1.08
FBr...NH ₃	1.19	0.80	1.91	1.16	0.75	1.55
HI...NH ₃	1.52	0.47	2.22	1.65	0.57	1.04
NCI...NH ₃	1.39	0.60	2.16	1.49	0.67	1.27
FI...NH ₃	1.23	0.76	2.08	1.25	0.83	1.59

$r_N^0 = 1.99 \text{ \AA}$.

Symbols are explained in the text.

(r_X^0), defined as the distance from the nucleus to a given value of its electronic density contour. Generally, 0.001 au is chosen because it corresponds to atomic sizes in molecules that agree with the van der Waals radii measured in gas-phase experiments. Then, the extent of the penetration is being measured by the difference between two values ($\Delta r_{X,N} = r_{X,N}^0 - r_{X,N}$). The results of radii calculations for the atoms involved in the complexes studied are given in Table 2.

As expected, it is established that the values of charge density at the BCP between each pair of bonded atoms increase with their mutual penetration [38]. An exponential correlation between the mutual penetration and the binding energy with a correlation coefficient higher to 0.94 was found in these complexes.

When comparing the halogen penetration distance in the D–X...NH₃ complexes, for a same halogen donor group, it is observed that Δr_X , augments following the order: F < Cl < Br < I, that is, it increases following the order of the halogen atom polarizability. On the other hand, comparing Δr_X when the same X atom is bonded to a different halogen donor group, it can be observed that the penetration distance increases in the order: –H < –CN < –F. In other words, the penetration distance increases with the increase of the “electron-withdrawing power” of the halogen donor group; it agrees with the electronegativity values: $\chi_{(-H)} = 2.1 < \chi_{(-CN)} = 3.3 < \chi_{(-F)} = 4.1$ [46]. A similar tendency is observed on the nitrogen atom, that is: Δr_N (H–X...NH₃) < Δr_N (NC–X...NH₃) < Δr_N (F–X...NH₃). However, a difference can be verified when –F is the halogen donor group, i.e. $\Delta r_N = 0.54$; 0.85; 0.80; and 0.75 for F...N, Cl...N, Br...N, and I...N, respectively. These results show that the “polarizability of the halogen atom” and the “electron-withdrawing power of the halogen donor group” define the mutual penetration of the electron cloud of the atoms involved and the strength of the halogen bonds studied in this work.

It is important to remark that according to Koch and Popelier criteria, the mutual penetration of the electron density of the bonded atoms is the necessary and sufficient condition for the presence of a HB, because it has never been violated in general hydrogen bonding systems [38,7].(b) Based in the similarity of criteria applied for XBs in the set of complexes analyzed, wherein $\Delta r_X > 0$ and $\Delta r_N > 0$, we can establish with certainty that XBs can also be formed with fluorinated compounds, (i.e.; D–F with D = –CN, –F but it is not formed with D = –H).

3.3.3. Integrated atomic properties

Table 3 shows the changes in the integrated atomic properties for the halogen atoms involved in the XBs. Such properties are the electronic population, $N(\Omega)$, the total energy of the atom, $E(\Omega)$, the dipole moment, $Mu(\Omega)$, the atomic quadrupole moment,

Table 3
Variations of integrated atomic properties on the basin halogen atoms involved in the halogen bonding complexes. Values of $Q_{zz}(\Omega_X)$ in the complexes, are also included.

Complexes	$\Delta N(\Omega_X)$	$\Delta \nu(\Omega_X)$	$\Delta M(\Omega_X) $	$\Delta E(\Omega_X)$	$Q_{zz}(\Omega_X)$	$\Delta Q_{zz}(\Omega_X)$
NCF...NH ₃	-0.0058	0.5875	-0.0459	0.0046	0.4263	0.0008
FF...NH ₃	-0.0022	-3.1678	-0.1215	0.0184	1.9030	0.0557
HCl...NH ₃	-0.0241	-1.7162	-0.1106	0.0099	4.3444	0.5326
NCl...NH ₃	-0.0349	-1.4884	-0.1974	0.0167	4.9156	0.5937
FCl...NH ₃	0.0777	-9.1614	0.5817	-0.0036	7.2058	0.9955
HBr...NH ₃	-0.0291	-5.6616	-0.1720	0.0174	6.5672	0.7643
NCBr...NH ₃	-0.0294	-4.5768	0.0911	0.0199	7.0747	0.5835
FBr...NH ₃	0.0612	-10.7272	0.7357	-0.0046	9.2319	1.2632
HI...NH ₃	-0.0300	-8.1290	-0.3059	0.0124	10.8294	1.5714
NCI...NH ₃	-0.0181	-12.5374	0.2983	0.0114	11.8491	1.8999
FI...NH ₃	0.0334	-10.2956	0.7538	-0.0075	13.7745	2.3060

All the values in au.

$Q_{zz}(\Omega_X)$ and the atomic volume, $\nu(\Omega)$. In addition, the $Q_{zz}(\Omega_X)$ values for isolated molecules and complexes are shown. The changes ($\Delta P(\Omega)$) were calculated subtracting the property value of the atom ($P(\Omega)$) in the isolated monomer to the value of the corresponding property in the complex. The accuracy of the integration was assessed by the magnitude of the $L(\Omega)$ function, which in all cases is less than 10^{-5} au for H atoms and 10^{-4} au for other atoms.

The criteria for HB, based on the integrated properties of the hydrogen atom, involves loss of electron population ($\Delta N < 0$), energetic destabilization ($\Delta E > 0$), decrease of dipole polarization ($\Delta Mu < 0$), and decrease of the hydrogen atoms volume ($\Delta \nu < 0$) [38]. In the halogen bonded complexes studied here, we observed that the criterion of loss of electron population, energetic destabilization and the decrease of the dipole polarization of the bridge halogen atom from the halogen donor, were not always satisfied. For example, in the strongest complexes bonded by halogen (in FCl...NH₃, FBr...NH₃, and FI...NH₃ complexes) an increase of electron population, an energetic stabilization and an increase of the dipole polarization on bridge halogen atom were observed as a consequence of the complex formation. In all complexes, the criterion of decrease of the halogen atom volume is always satisfied with the exception of a weaker fluorine bonded complex (NCF...NH₃ complex) perhaps due to the high compactness of the fluorine atom. However, it should be highlighted that the criterion of mutual penetrations is always verified (see Table 2).

3.3.4. Atomic dipole moment at nitrogen atom and its relationship with binding energy

Beyond the change of the dipole polarization on the halogen atom in the complex, we can analyze the change due to the elec-

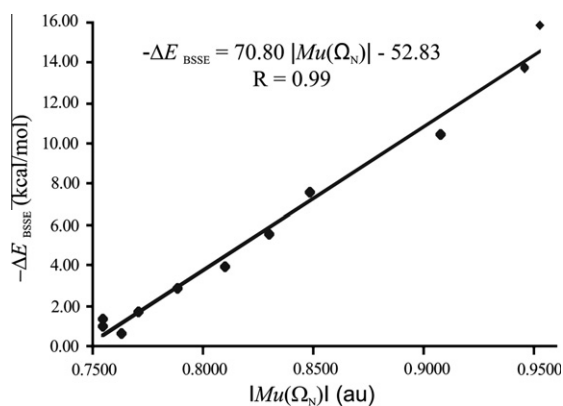


Fig. 2. Linear correlation between the binding energy and magnitude of atomic dipole moment on nitrogen atom in D-X...NH₃ complexes (with D = -H, -CN, -F and X = F, Cl, Br, I). The correlation coefficient is shown.

tron redistribution. In fact, although the halogen bond is an weaker interaction than a covalent interaction, it causes rearrangement in electronic density distribution on all the atoms forming the complex. From integrated atomic properties these deformations of electronic density distribution or electronic redistribution are shown by the atomic dipole moment, $Mu(\Omega)$. For example, upon complexes formation an increase of dipole moment is observed on the nitrogen atom of the Lewis base.

Fig. 2 shows the relationship between the magnitude of the electric dipole moment on nitrogen atom, $|Mu(\Omega_N)|$ and the ΔE_{BSSSE} in the D-X...NH₃ complexes. There is a good correlation between these parameters for all complexes considered here ($R = 0.99$) as it can be seen in the same figure. This indicates that the deformation of the electron density at the Lewis base measured by $|Mu(\Omega_N)|$ is a good indicator of the strength of the interactions studied here. We might consider that a similar relationship can exist between the strength of these interactions and $|Mu(\Omega_X)|$. However, this is not observed. The correlation coefficient between $|Mu(\Omega_X)|$ and ΔE_{BSSSE} is 0.75 (figure not shown).

3.3.5. Atomic quadrupole moment

The atomic quadrupole moment in a particular direction (i.e. along the z-axis Q_{zz}) is a measure of the deviation of electron density from spherical symmetry. That is to say, a spherical electron density distribution results in a value of zero for Q_{zz} . This component measures how the electron density is elongated or compressed along the z-axis relative to a direction perpendicular to z. Thus, if this diagonal component is negative the electron density is concentrated along this axis and consequently the electron distribution is prolate with respect to the z-axis [7a–c]. Similarly, when the component Q_{zz} is positive, the electron distribution is oblate. This property of Q_{zz} allows us to quantify the deformation experienced by the electron density on the halogen atom basin in the XBs. As it has been pointed by Popelier [7b], the magnitude of the atomic quadrupole moment is invariant with respect to the choice of the axis system and can therefore be used to compare atoms in different chemical environments without worrying about the molecular interaction.

In Table 3, the atomic quadrupole moment values calculated on the basin halogen atom, that is $Q_{zz}(\Omega_X)$ measured in the direction of the interaction X...N (in the complexes and in the isolated molecule) are reported. The results show that all halogens have a positive value of this property, in the complex studied and in isolated Lewis acid, indicating that in this direction an electron charge density depletion is present. This allows the interaction of the Lewis base with the halogen atom. On the other hand and according to what was expected, the $Q_{zz}(\Omega_N)$ values, measured in the direction of the X...N interaction are all negative, indicating that in this direction an accumulation electron density is produced (date not shown).

It is further noted that $Q_{zz}(\Omega_X)$ increase in the sense $Q_{zz}(\Omega_F) < Q_{zz}(\Omega_{Cl}) < Q_{zz}(\Omega_{Br}) < Q_{zz}(\Omega_I)$, indicating that in this direction the depletion on the halogen atom electron charge density increases. These results follow the same trend as the stability of the halogen bonds when this depends only on the bridge halogen atom; that is, for a same halogen donor group (for example, in the $F-X \cdots NH_3$ complexes, with $X = F, Cl, Br, I$), the strength of the halogen bond interaction depends on the bridge atom and follows the order: $F < Cl < Br < I$ (see Table 1).

3.3.6. Anisotropic charge concentration distribution in the VSCC of the halogen atom

It was also interesting to examine in detail the structure exhibited by the Laplacian distribution of the halogen bonded complexes. The Laplacian of the electron density ($\nabla^2\rho(r)$) plays a central role in AIM theory and yields valuable information on bonding through its topology, especially via the critical points in $L(\mathbf{r})$ function, ($L(\mathbf{r}) = -1/4\nabla^2\rho(\mathbf{r})$). It has been demonstrated that the maxima, denoted by (3, -3), in the $L(\mathbf{r})$ distribution can be considered as the physical expression to the electron pairs of the Lewis model [47]. Indeed, the analysis of $L(\mathbf{r})$ provides insight into many features of atoms within molecules and atoms in molecules forming complexes as well (i.e. $D-X \cdots NH_3$). For example, in a previous work about complexes attached by aromatic halogen bonds, we demonstrate that the dual character, as a nucleophile as well as an electrophile of the halogen atoms, is well described by the Laplacian topology of the electronic charge density [8].

Fig. 3 summarizes the results for the $H-Cl \cdots NH_3$, $NC-Cl \cdots NH_3$ and $F-Cl \cdots NH_3$ complexes. At the top of this figure contour maps of $L(\mathbf{r})$ for these complexes are displayed in a plane containing the $D-Cl$ molecule and an $N-H$ bond of ammonia molecule. The anisotropic charge distribution on the chlorine atom can also be clearly seen. That is, in the halogen donor molecules, the equatorial region at the halogen atoms is a site that exhibits the highest concentration of charge. The maxima of charge concentration in the valence shell charge concentration (VSCC) of the chlorine atom are located on both sides (right and left) to the internuclear axis direction. In contraposition, the axial region along the $D-X$ direction is a site of charge depletion (where the previously mentioned hole is found). This same feature is clearly displayed at the envelope graph at $L(\mathbf{r}) = 0.0875$ au for $H-Cl \cdots NH_3$, $NC-Cl \cdots NH_3$ and $F-Cl \cdots NH_3$ where a hole on the isosurface of the chlorine atom at the halogen donor bond is shown (Fig. 3 bottom). The molecules are oriented so that the lumps in VSCC of the nitrogen atom of the Lewis base is aligned with the (3, +1) CP corresponding to the hole in the VSCC of the chlorine atom of the Lewis acid. The bond paths (grey lines) and BCP (red circles) in $\rho(\mathbf{r})$ topology are also shown.

It can be observed in Fig. 3 top that the zone or domain of this CP (the hole on the reactive surface to $L(\mathbf{r}) = 0$) is noteworthy in $F-Cl$. On the contrary in $NC-Cl$ and $H-Cl$ Lewis acids a thinness of the VSCC in the axial direction is merely observed.

This effect can be seen notably augmented by observation of the envelope at $L(\mathbf{r}) = 0.0875$ au, wherein the extension of the charge depletion region (or the “size hole”) in the $F-Cl \cdots NH_3$ complex (localized over the chlorine atom and facing the N atom) is greater than in the $NC-Cl \cdots NH_3$ and $H-Cl \cdots NH_3$ complexes. This is probably the reason why the first complex has a higher binding energy than the other two. This observation agrees with what was expected, due to the relative electronegativities of the donor groups (that is following the order: $-H < -CN < -F$). In addition, the distances between the nitrogen atom and the intermolecular BCP ($R_{N \cdots BCP}$) also decrease following the order $H-Cl \cdots NH_3 > NC-Cl \cdots NH_3 > F-Cl \cdots NH_3$. These and other previously discussed features show the role of the donor groups in the strength of the XBs. In other words, we can see that the chlorine atom in $F-Cl$ exhibits a great region of charge depletion in its valence shell. Sub-

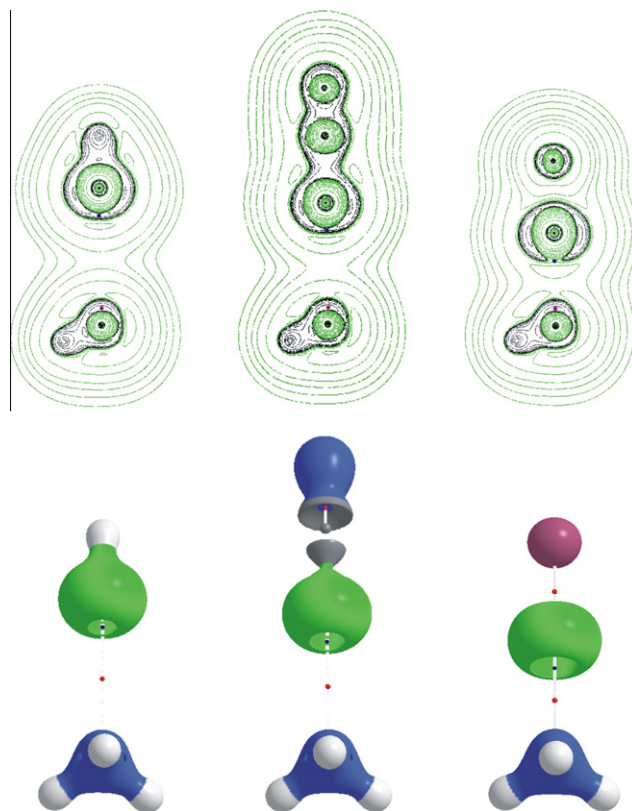


Fig. 3. (Top) Contour maps of $L(\mathbf{r})$ for $H-Cl \cdots NH_3$, $NC-Cl \cdots NH_3$ and $F-Cl \cdots NH_3$ complexes in a plane containing the Lewis acid and a N–H bond of ammonia molecule. Black contours denote negative values of $\nabla^2\rho$, this is $[L(\mathbf{r}) > 0]$ and green contours positive values of $\nabla^2\rho$ [$L(\mathbf{r}) < 0$]. Starting at a zero contour, contour values change in steps of $\pm 2.10n$, $\pm 4.10n$, $\pm 8.10n$ with n beginning at -3 and increasing in steps of unity. Note the anisotropic distribution of the charge concentration in the VSCC of the Cl atom. The maxima are located on the VSCC of chlorine atom, in perpendicular direction to the bond direction $D-Cl$ in $D-Cl \cdots NH_3$ complexes, on the contrary, the minimum or r -CP is localized on the VSCC of chlorine atom in front of nitrogen atom of the Lewis base. (bottom) envelope at $L(\mathbf{r}) = 0.0875$ au for $H-Cl \cdots NH_3$, $NC-Cl \cdots NH_3$ and $F-Cl \cdots NH_3$. The molecules are oriented so that the lump in the valence shell charge concentration (VSCC) of the nitrogen atom of the Lewis base is aligned with the (3, +1) CP corresponding to the hole in the VSCC of the chlorine atom of the Lewis acid. Also, the bond paths (grey lines) and BCP (red circles) in ρ topology are shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sequently, we can inform that the chlorine atom in the $F-Cl \cdots NH_3$ complex has (in the direction of its hole) an increased capability to act as an electrophile towards the lump of the Lewis base on the valence shell surface. More significantly, we believe that the nature of this interaction is primarily electrostatic due to an electrostatic attraction between the “slightly shielded nuclei” of the chlorine atom in the interaction direction, and the charge density accumulated on the valence shell of the nitrogen atom of the Lewis base.

3.3.7. Interactions between donor–acceptor orbital

In previous works we have shown the importance of the AIM studies in conjunction with the Natural Bond Orbitals (NBOs) analysis of charge transference in weak, moderate and strong HBs [48a–c] and as well as in XBs [9]. Both methodologies provide a good complement in the understanding of the intermolecular interactions. Subsequently, we have also calculated the charge transferred from the lone pair orbital, n_N , (electron donor) towards the $\sigma^*(D-X)$ antibonding orbital (electron acceptor).

The amount of charge transferred, Δn_N , which takes place during the interaction Lewis base with a Lewis acid is presented in Table 4. As a result, the stabilizing interaction (2 orbitals-2

Table 4

Population change of donor and acceptor orbitals, interaction energy between orbitals ($\Delta E^{(2)}$) and charge transference (CT_{AIM}) between Lewis base and Lewis acid are included.

Complexes	n_N	Δn_N	$\Delta[\sigma^*_{(D-X)}]$	$E^{(2)}_{n(N) \rightarrow \sigma^*_{(A-X)}}$	CT_{AIM}
NCF...NH ₃	1.99343	-0.00159	0.00053	0.28	0.0067
FF...NH ₃	1.93904	-0.05598	0.05811	4.50	0.0303
HCl...NH ₃	1.98521	-0.00981	0.00760	1.26	0.0049
NCCL...NH ₃	1.97201	-0.02301	0.01827	3.64	0.0194
FCl...NH ₃	1.78304	-0.21198	0.19648	41.73	0.1710
HBr...NH ₃	1.97802	-0.01700	0.01487	2.47	0.0087
NCBr...NH ₃	1.95236	-0.04266	0.03456	6.89	0.0316
FBr...NH ₃	1.79784	-0.19718	0.18200	40.06	0.1556
HI...NH ₃	1.96329	-0.03173	0.02767	4.76	0.0136
NCI...NH ₃	1.92886	-0.06616	0.05313	11.25	0.0410
FI...NH ₃	1.82045	-0.17457	0.15718	36.90	0.1207

n_N : Occupation numbers for nitrogen. Occupation number for isolated nitrogen $n_{N(isolated)} = 1.9950e$.

Δn_N represents the change in population of donor atom lone pair of Lewis base.

$\Delta\sigma^*_{D-X}$ denote the change in population of σ^*_{D-X} antibonds respect to the isolated compound.

CT_{AIM} denote charge transference between Lewis base and Lewis acid in au.

Energy values are in kcal/mol and electronic populations are in electron.

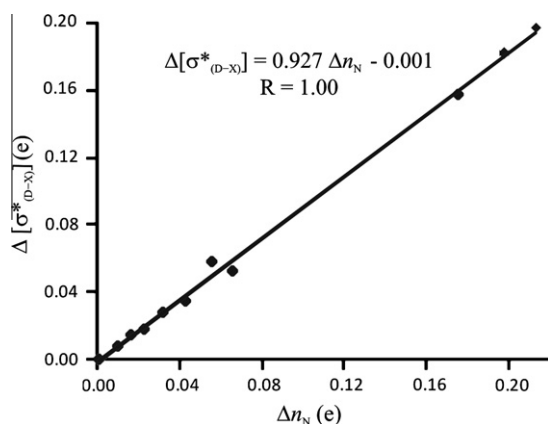


Fig. 4. Linear correlation between the change of the electron population at lone pair of N atom of the Lewis base, Δn_N , vs. the change of the electron population of the antibonding orbital, $\Delta\sigma^*_{D-X}$, from Lewis acid.

electrons) between the n_N donor orbital and a $\sigma^*_{(D-X)}$ acceptor orbital is analyzed. The donor acceptor interaction energy due to the $n_N \rightarrow \sigma^*_{(D-X)}$ interaction, ($\Delta E^{(2)}$) can be estimated by the second order perturbation theory. The $\Delta E^{(2)}$ and the charge transference values are also indicative of weak, moderate and strong interactions in the XBs. If Δn_N donor < 0 and $\Delta\sigma^*_{(D-X)}$ acceptor > 0 , the charge flows from the lone pair of the Lewis base to the D–X antibonding orbital at Lewis acid. The observation of the results given in Table 4 shows that upon complexes formation, the $\sigma^*_{(D-X)}$ antibonds electron population increases in a broad range, as indicated by the values of $\Delta\sigma^*_{(D-X)}$, which ranged from 0.00053 (in NC–F...NH₃ complex) to 0.19648e (in F–Cl...NH₃ complex). Moreover, as reflected in the Δn_N donor vs. $\Delta\sigma^*_{(D-X)}$ acceptor plots, all the charge that the donor orbital had lost was consequently gained by the acceptor orbital (see Fig. 4).

3.3.8. Analysis of the electron charge density transference by AIM

Beyond the charge transferred between orbitals provided by NBO analysis, we can estimate the total charge density transferred from the base Lewis, in the context of the AIM theory, and relate this to the strength of the halogen bond. As it was shown before, a remarkable characteristic of the halogen bonds is the gain of electron population on all the atoms of the Lewis acid and their subsequent stabilization. The total electron charge density transferred, CT_{AIM} , is calculated as the Lewis base electron charge density loss

during the formation of the complex. In this way, the atomic population in all the atoms of the NH₃ was calculated using Bader's partition. Therefore, the difference between the total electron population of the ammonia upon the complexation and the isolated ammonia ($\Delta N_{Lewis\ base}$) has been considered. Similarly to the NBO analysis, in the AIM analysis, if $\Delta N_{Lewis\ base} < 0$, then the electronic charge density will flow from the base to the acid. In other words $\Delta N_{Lewis\ base}$ represents the fractional number of electrons transferred from the electron donor unit (base) to the electron acceptor unit (acid) in the complexes, expressed in electron numbers. The values of CT_{AIM} are reported in Table 4 and the variation of atomic electron population, that is, the electron density gained and lost upon the complexation is represented in Fig. S1a–c of the Supporting Information, where it can be seen that $\Delta N(\Omega_H)$ proportionally diminishes in relation to the strengthening of the halogen bond formed. In other words, we found that the electron population of hydrogen atoms of ammonia decreases in the complexes. This indicates that the hydrogen atoms bonded to the nitrogen atom, also provide electron charge density to the Lewis acid. Summing up, all atoms of the Lewis base play an electron donating role in the formation of halogen bonded complexes.

The total charge transferred calculated by AIM from the ammonia to the different acids shows a similar tendency to the charge transferred between orbitals. The maximum amount of charge transferred, takes place from ammonia towards the F–Cl Lewis acid, and considering NC–X as Lewis acids, it varies following the order NC–I $>$ NC–Br $>$ NC–Cl \gg NC–F. In addition, the minimum amount of transferred charge flows between ammonia and H–Cl. From the data in Table 4, it can be observed that the magnitude of the CT_{AIM} lies in a broad range of variation (from 0.0049 to 0.1710e). Furthermore, a good relationship between the CT_{AIM} and the binding energy is found in the complexes between ammonia and D–X acids (with D = –H, –CN) ($R = 0.994$). These results have demonstrated that the charge transfer interaction plays an important role in the formation of these halogen bonded complexes. However, a different behavior is observed when the electron charge transference is very high (in the F–X_(F,Cl,Br,I)...NH₃ complexes). In these complexes the CT_{AIM} values range from 0.0303 to 0.1710e and the relationship between CT_{AIM} and the binding energies is not satisfied. Moreover, it is interesting to analyze where the transferred charge density goes.

3.3.9. Where the charge density has been transferred to

As it has been established above, the existence of a “hole” on the surface of the halogen atom valence shell in the D–X molecules is indicative of a local deficiency in electrons. These data have induced us to believe that this region of charge depletion on the valence shell surface outside the bonding region could be filled by the electron density provided by a Lewis base as ammonia. The results obtained mainly by atomic quadrupole moment analysis have demonstrated us that this conjecture is not correct because the Q_{zz} values are higher (more positive values) in the complexes than in D–X isolated. From the Laplacian study it is also evident that the hole on the halogen atom is not diminished by the charge density transference. In contraposition, the results show that the electron charge lost by the ammonia is distributed on the whole Lewis acid and that the charge density values at nb-CP on the bridge halogen atom is augmented as a consequence of the complexes formation (i.e. 0.2946 au in FCl and 0.2951 au in FCl...NH₃).

4. Conclusions

In this work a systematic theoretical study at MP2/6-311++G (2d, 2p) level was carried out in the description of the strength of halogen bonds (in a wide range from –0.65 to –15.78 kcal/

mol) between ammonia as Lewis base and Lewis acids, D–X (with X = F, Cl, Br, I and with D = –H, –CN, –F as halogen donor group). From the topological analysis of the Laplacian of the electron charge density we have shown that the formation of the studied complexes is due to the electrostatic interaction between the charge density provided by the lone pair (ammonia molecule) and the charge density depletion region localized at the outset region of the halogen atom in the direction of the D–X bond. The localization of the thinning of the electron density in the VSCC of halogen atom which makes the halogen nucleus less shielded in the interaction direction and more prone to interact electrostatically with the accumulation charge density on N atom, determines the geometry of the D–X...NH₃ complexes. The existence of this thinning of the electron density in the VSCC of halogen atom is a necessary condition in the formation of halogen bonds. This fact is also present in the VSCC of fluorine atom; consequently the F atom can also form XBs. A great charge density transference from the base Lewis to the acid Lewis was observed when ammonia is bonded to F–Cl, F–Br and F–I compounds; in general the amount transferred is in relation to the strength of the halogen bond in D–X...NH₃ complexes (with X = F, Cl, Br, I; and with D = –H, –CN). In addition, the analysis of the dipole moment at nitrogen atom in these complexes reflects the electronic rearrangement produced by the formation of the halogen bond and its strength.

The Laplacian topology as well as the analysis of the atomic quadrupole moments have showed the anisotropic distribution of the charge density at the halogen atom in the halogen bonded complexes and this has allowed us to understand where the electronic charge was transferred to. We have found that the electron density is not increased in the direction of the X...N bond, but increases in the orthogonal direction to the bond forming (X...N). In addition, relationships between the strength of the XBs with (i) the acid capacity of the Lewis acid calculated as the electronegativity differences between the halogen atom and the halogen donor group; with (ii) the mutual penetration of electron density of the atoms that interact; and with (iii) the dipole moment on the nitrogen atom, were established.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2012.07.019>.

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