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Ab initio study of weakly bound halogen complexes: RX···PH₃

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Abstract Ab initio calculations were employed to study the role of ipso carbon hybridization in halogenated compounds RX (R = methyl, phenyl, acetyl, H and X = F, Cl, Br and I) and its interaction with a phosphorus atom, as occurs in the halogen bonded complex type RX···PH₃. The analysis was performed using ab initio MP2, MP4 and CCSD(T) methods. Systematic energy analysis found that the interaction energies are in the range −4.14 to −11.92 kJ mol^{-1} (at MP2 level without ZPE correction). Effects of electronic correlation levels were evaluated at MP4 and CCSD(T) levels and a reduction of up to 27 % in interaction energy obtained in MP2 was observed. Analysis of the electrostatic maps confirms that the PhCl···PH₃ and all MeX···PH₃ complexes are unstable. NBO analysis suggested that the charge transfer between the moieties is bigger when using iodine than bromine and chlorine. The electrical properties of these complexes (dipole and polarizability) were determined and the most important observed aspect was the systematic increase at the dipole polarizability, given by the interaction polarizability. This increase is in the range of 0.7–6.7 u.a. (about 3–7 %).

Keywords Ab initio calculation · Halogen bonded complex · Molecular property · Interaction energy

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Introduction

An interesting type of intermolecular interaction that has been attracting attention recently is the halogen bonding, in which bridging between molecules is brought about by a halogen atom and an electronegative non-halogen atom [1–6]. An increasing variety of theoretical and experimental evidence confirms that non-covalent interactions such as –X···Y– (where X = F, Cl, Br, I, and Y = N, O, S, π) play similarly important roles as hydrogen bonds in crystal engineering, drug design and advanced materials, supramolecular chemistry and physical organic chemistry [7–10]. Due to its high electronegativity, fluoride is often categorized as a poor halogen bond donor. In fact, for most fluorinated molecules, the electrostatic potential on the fluorine surface is entirely negative. But when fluoride is bound to a strongly electronegative atom or group, its presents a positive spot that allows halogen bond formation centered on a fluoride atom [11, 12].

The nature of halogen bonds can be analyzed in terms of specific interactions between the atoms involved in bond formation and the anisotropic potential wall around the halogen atoms. It is known that electronegative atoms in various states of hybridization prefer to form contacts to halogens in the direction of the bond length C–X, at interatomic distances less than the sum of the van der Waals radii [4].

Politzer and collaborators have shown recently [5, 13–15] that halogen bonding has a high electrostatic character and can be analyzed in terms of the electrostatic potential near the X and Y atoms, and the so-called "sigma holes", which are regions of decreased electron density in the non-bonding side of the halogen atom [11]. These sigma holes depend on the level of sp_z hybridization of the halogen orbital accommodating the unshared pairs of electrons in the direction of the R–X bond. They also depend on the electronegativity of the radical attached to the halogen atom.

In addition to electrostatic effects, the attractive nature of halogen bonds also has contributions from polarization, charge transfer and dispersion interactions. Crystallographic studies that address the directionality of halogen bonds make no distinction between hybridization of the carbon atom bonded to the halogen and other atoms bonded to the carbon atom. The electronegativity of the sp^2 carbon is different from that expected for an sp^3 carbon. These differences play an important role in halogen bonding [16].

In a study of halogen···halide synthons, Twamley and co-workers [16] showed that the halogen···halide contacts ($I \cdots I^-$, $Br \cdots Br^-$ and $Cl \cdots Cl^-$) are more intense when the halogen is bonded to an sp^2 carbon and less intense when bonded to an sp^3 carbon. In fact, the calculated stabilization energy is calculated as a function of the ipso carbon hybridization and obeys the following order $sp > sp^2 > sp^3$. Thus, for $I \cdots I^-$ synthons, the interaction strength is -7.1 kJ mol^{-1} in iodomethane (sp^3), whereas for iodoacetylene (sp), it is -153.9 kJ mol^{-1} [16].

For halogen bonds, a behavior similar to that shown by halogen···halide synthons is expected as regards the hybridization of the ipso carbon, but in this case an electronegative atom replaces the halide. Indeed, most theoretical studies on halogen bonds have considered such atoms as being oxygen, nitrogen or sulfur. A possible (and much less explored) alternative is a halogen bond involving phosphorus, which can also bind to a halogen compound and form weakly bound complexes.

In the present work, we consider both aspects simultaneously: the effect of ipso carbon hybridization, and the interaction with a phosphorus atom. To do so, we consider the specific interactions and electrical properties of type systems $RX \cdots PH_3$ (where R = methyl, phenyl, acetyl, H and X = F, Cl, Br and I). A three-dimensional (3D) molecular representation of these systems is given in Fig. 1.

Methods

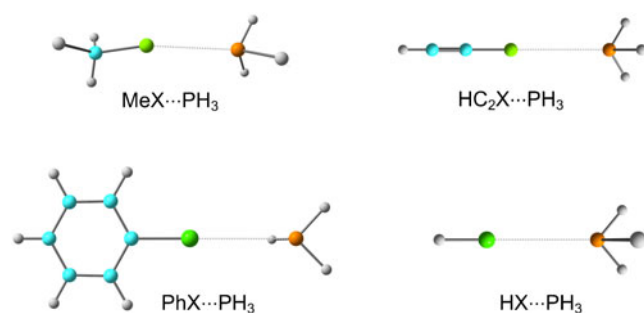Quantum chemistry calculations at second order perturbation theory (MP2) level were performed to obtain the geometries of $RX \cdots PH_3$ halogen bonded complexes (R = Ph, HC_2, H and X = F, Cl, Br, I). Geometry optimization was performed for the dimeric and monomeric species using the aug-cc-pVDZ basis set for all atoms except for iodine, for which the basis set aug-cc-pVDZ-PP [17] was used. Those basis sets and pseudopotential were tested in CCSD(T) calculations of several atomic properties, and in all cases the errors due to pseudopotential approximation were calculated to be nearly negligible [17].

Vibrational analysis was performed to ensure that the calculated structures are real minima of the potential energy surfaces, and also to obtain the zero point energy. The interaction energy was computed as the difference between the total energy of the halogen bonded complex and the sum of the total energy of the corresponding monomers. To analyze the role of electron correlation effects on the relative stability of the different heterodimers, single point calculations were performed at coupled cluster [CCSD(T)] and full-fourth-order MP4 levels. Basis set superposition error (BSSE) was taken into account in all values obtained for the interaction energies using counterpoise correction [18]. To gain insight into the electrostatic interaction between the halogen-containing molecules and PH_3 both the electronic density and the electrostatic potential were calculated using the MP2/aug-cc-pVDZ wave function. Natural bond orbital (NBO) [19] analysis was performed for all systems to highlight the changes in the electron density upon complexation. NBOs are a localized set of easily recognizable Lewis-like (σ and π bond, lone pair and core) and non-Lewis (σ^* and π^* antibond and Rydberg) orbitals, which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set. An important feature of the NBO method is that, unlike other charge partitioning schemes, the presence of diffuse functions in basis sets does not affect the results. All calculations presented in this study were performed using the Gaussian 03 package [20].

Results and discussion

Studies aiming to characterize the structural, energetic and spectroscopic characterization of hydrogen bond complexes involving PH_3 and halogen compounds have been reported [21–23]. However, in the context of halogen bonds, where the main interest is the $P \cdots X$ contact, very few results have been reported to date. To fill this gap we report here our results for the $RX \cdots PH_3$ complexes shown in Fig. 1. Our first finding, as expected, is the instability of the complex $MeX \cdots PH_3$, i.e., we found no bonded complex with the halogen attached to a sp^3 carbon in our calculations with halomethane. According to previous results, these complexes were expected to be less stable, and in fact our calculations show that it is not stable in all cases (X = F,

Fig. 1 $RX \cdots PH_3$ halogen bonded complexes. *RX* = halomethane (*MeX*), haloacetylene (*HC₂X*), halobenzene (*PhX*) and hydrogen halide (*HX*)

Cl, Br and I) showing slightly positive interaction energy. This is in accordance with the work of Politzer et al. [14], in which the authors show that haloalkanes have only a small sigma hole or none at all, leading to weak halogen bond or even no bond at all. Now, before considering the other complexes, let us discuss the monomers PH_3, HX, HC_2X and PhX.

Monomers

Halogen bonding is known to be an electrostatically driven interaction [24]. An interesting way to analyze the electrostatic interaction between halogen-containing molecules and PH_3 is to compute the molecular electrostatic potential of the isolated monomers on the molecular surface. The definition of molecular surface is not unique, but it is usual [13] to use the $\rho = 0.001\ e/a_0^3$ (au) electron isodensity surface proposed by Bader et al. [25]. In Figs. 2, 3, 4 and 5 we show such electrostatic potential maps for the PH_3, HX, HC_2X and PhX molecules. In all cases, both the electronic density and the electrostatic potential were calculated using the MP2/aug-cc-pVDZ wave function. The same color scale was used to represent the electrostatic potential in all cases.

Figure 2 shows that the electrostatic potential is negative at the phosphorous side of PH_3, which is expected due to the electronegativity difference between P and H. Now, the binding energy of the $RX\cdots PH_3$ complexes will depend greatly on the electrostatic potential at the halogen side of

Fig. 3 MP2/aug-cc-pVDZ electrostatic potential (au) map of *HX* molecules at the 0.001 au isodensity surface. X = F (*left top*), X = Cl (*left bottom*), X = Br (*right top*), X = I (*right bottom*)

the RX molecules, the more positive the electrostatic potential at the halogen site, the greater the binding energy.

Figures 3, 4, and 5 show that the electrostatic potential at the fluorine side is largely negative in HF and PhF, and is positive, although close to zero, in HC_2F. Therefore, RF molecules most probably do not form any halogen bonds with PH_3. For chlorine compounds, we observe that the Cl side is significantly positive in HC_2Cl, but less positive in HCl and even less in PhCl. Actually, there is only a small (green) spot of positive potential in the chlorine side in HCl near the intersection point between the symmetry axis and the molecular surface. This spot is even smaller in PhCl. This suggests a weak halogen bonding in the $HCl\cdots PH_3$ complex and even weaker in the $PhCl\cdots PH_3$, and that the binding energies might not be enough for the complexes to
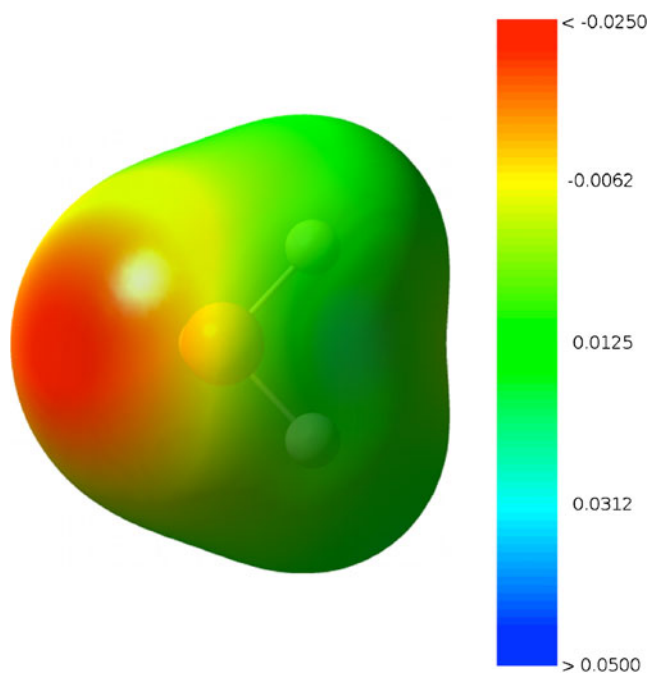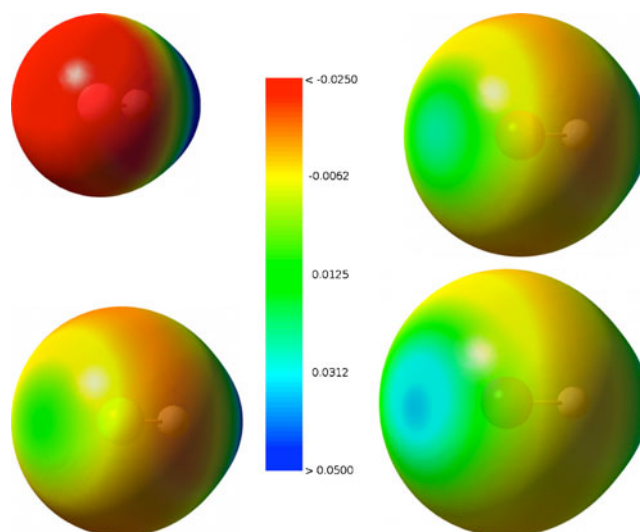

Fig. 2 MP2/aug-cc-pVDZ electrostatic potential (au) map of PH_3 at the 0.001 au isodensity surface

Fig. 4 MP2/aug-cc-pVDZ electrostatic potential (au) map of *HC_2X* molecules at the 0.001 au isodensity surface. X = F (*left top*), X = Cl (*left bottom*), X = Br (*right top*), X = I (*right bottom*)

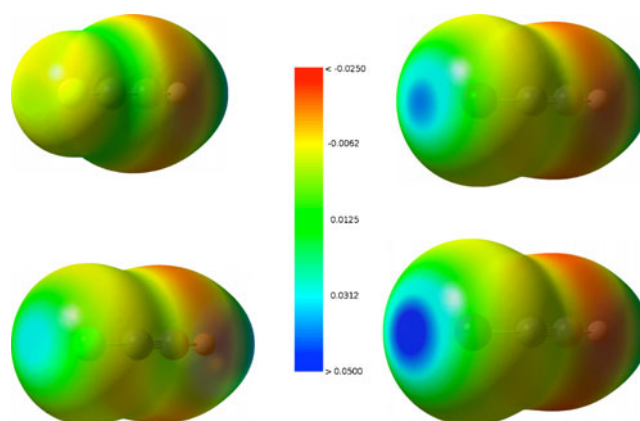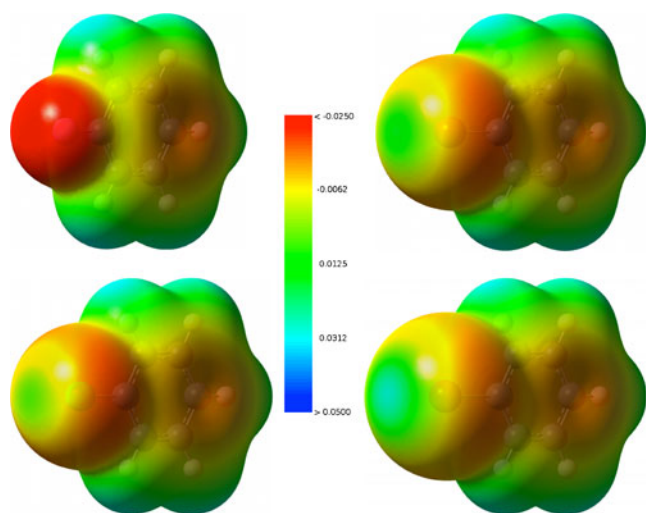**Fig. 5** MP2/aug-cc-pVDZ electrostatic potential (au) map of *PhX* molecules at the 0.001 au isodensity surface. $X = F$ (*left top*), $X = Cl$ (*left bottom*), $X = Br$ (*right top*), $X = I$ (*right bottom*)

be stable. The same small positive spot is observed in the electrostatic map of PhBr.

In order to have a numerical reference for those electrostatic potential analyses, Table 1 lists the values of electrostatic potential near the halogen atoms, in the intersection point between the symmetry axis of the molecules and the molecular surfaces. These values are also the maximum values of the electrostatic potential on the molecular surface at the halogen side. That is, on the surface, moving outwards from the intersection point, the electrostatic potential becomes less positive and even negative, as shown in Figs. 3, 4 and 5. The exceptions to this general behavior are HF and PhF, for which the potential immediately becomes a little more negative but then starts increasing. Therefore, except for HF and PhF, there is generally a

positive region in the external side of the halogen atom and a negative belt around it. Thus, the best (electrostatic) contact point for the P atom is along the C–X (or H–X) direction.

Considering that the electrostatic interaction is mainly responsible for halogen bonding between the PH_3 and RX compounds, such a characteristic enforces some directionality and linearity of the halogen bond, as pointed out by Politzer et al. [14].

Now, according to the analysis of the electrostatic maps and the values in Table 1, we could predict that $RF\cdots PH_3$ complexes must be unstable. As for the other complexes, the binding energies would probably follow the sequence of increasing electrostatic potential on the halogen site.

Complexes

Analysing the $RX\cdots PH3$ complexation, we found that, indeed, for $X = F$, the complexes are not stable, presenting negative binding energy, confirming the repulsive interaction suggested by the negative electrostatic potential on both P and F. For the other PhX, HC_2X and HX complexes with PH_3, we found that the $PhCl\cdots PH_3$ complex is also not stable, presenting a very low interaction energy that was not enough to overcome the zero point vibrational energy (ZPE) correction. This is in accord with the fact that PhCl presented the least positive electrostatic potential in the halogen outermost region (see Table 1 and Fig. 5). Thus, the results for $PhCl\cdots PH_3$ and all $MeX\cdots PH_3$ complexes are not listed here.

Figure 6 is a schematic representation of the $RX\cdots PH_3$ complex and shows the main geometrical parameters involved in the halogen bonding. The calculated values for these parameters are listed in Table 2. We observed that the covalent bond $d_{R–X}$ suffered a slight elongation upon complexation in all cases. This elongation ($\Delta d_{R–X}$) varies in the range of 0.001–0.012 Å and depends on the halogen size at the bond; the bigger the halogen, the larger the elongation. This is consistent with the increasing positive electrostatic potential verified for bigger halogens, leading to an increased interaction energy as discussed below.

Our vibrational analysis shows that the stretching mode related to this elongation presents a modest red shift, ranging from −2 to −24 cm^{-1}. The intermolecular distances vary

Table 1 Electrostatic potential (au) near the halogen atom, in the intersection point between the symmetry axis and the molecular surface (see text and Figs. 2, 3, 4 and 5). The potential near the P atom in PH_3 is also shown

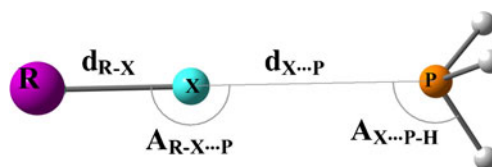| Molecule	Potential
PH_3	−0.026
HF	−0.030
HCl	0.012
HBr	0.023
HI	0.037
HC_2F	0.000
HC_2Cl	0.033
HC_2Br	0.042
HC_2I	0.054
PhF	−0.024
PhCl	0.008
PhBr	0.015
PhI	0.026

Fig. 6 General structure of $RX\cdots PH_3$ complexes showing the main geometric parameters. See Table 2

Table 2 Main geometric parameters of the studied complexes. Distances in Å and angles in degrees. See the labels of the columns in Fig. 6

Complexe	d_{R-X}	Δd_{R-X}	$d_{X\cdots P}$	$A_{R-X\cdots P}$	$A_{X\cdots P-H}$
PhBr···PH$_3$	1.903	0.001	3.610	170.9	132.5
PhI···PH$_3$	2.111	0.003	3.667	179.8	122.6
HC$_2$Cl···PH$_3$	1.659	0.002	3.618	180.0	121.5
HC$_2$Br···PH$_3$	1.807	0.005	3.506	180.0	122.1
HC$_2$I···PH$_3$	2.014	0.012	3.517	180.0	121.4
HCl···PH$_3$	1.289	0.001	3.638	149.3	170.4
HBr···PH$_3$	1.422	0.002	3.699	171.5	132.2
HI···PH$_3$	1.614	0.005	3.753	179.7	123.1

from 3.506 Å (HC$_2$Br···PH$_3$) to 3.753 Å (HI···PH$_3$). Analysis in terms of van der Waals radii reveals that all halogen bond distances, $d_{X\cdots P}$, are less than the sum of the radii for the atoms participating in the bond, except bonds involving the chlorine, which are slightly larger, implying very weak interactions. The angles $A_{R-X\cdots P}$ and $A_{X\cdots P-H}$ give an indication of the relative orientation of the phosphine in relation to the halogenated compound. $A_{R-X\cdots P}$ is associated directly with halogen bond directionality and varies slightly from linearity, with the exception of the HCl···PH$_3$ complex for which the angle $A_{R-X\cdots P}$ is about 150°. The angle $A_{X\cdots P-H}$ provides a gross vision of the orientation of the plane formed by the phosphine hydrogen atoms, so when that the R–X bond is orthogonal to this plane, the angle $A_{X\cdots P-H}$ is 122.2°. Thus, for almost all complexes, the phosphine molecule maintains a position that orients the phosphorus lone pair to the halogen atom. The notable exception is, again, the HCl···PH$_3$ complex, for which this angle is 170.4, which reflects its weak interaction energy. This is consistent with the small electrostatic potential in the outer region of Cl in HCl, as shown in Table 1.

A systematic analysis of the interaction energies (Table 3) of the different complexes can be carried out in the light of

Table 3 Calculated counterpoise corrected interaction energies (kJ mol^{-1}) of the dimers. ΔZPE Zero point energy difference between the complex and the separated parts obtained using MP2/aug-cc-pVDZ

	HF	MP2	MP4	CCSD(T)	ΔZPE
PhBr···PH$_3$	4.77	−4.14	−3.47	−3.01	1.46
PhI···PH$_3$	2.30	−11.55	−10.71	−10.17	1.46
HC$_2$Cl···PH$_3$	0.67	−5.31	−4.69	−4.39	2.43
HC$_2$Br···PH$_3$	0.75	−7.82	−6.69	−6.32	1.17
HC$_2$I···PH$_3$	−2.13	−11.92	−10.21	−9.71	2.55
HCl···PH$_3$	2.47	−2.76	−2.13	−2.01	2.47
HBr···PH$_3$	2.55	−3.68	−2.93	−2.76	2.97
HI···PH$_3$	0.42	−9.62	−8.70	−8.41	3.47

results obtained using highly correlated methods. In general, we found that the interaction energies are relatively low, ranging from −4.14 to −11.92 kJ mol^{-1} (at MP2 level without ZPE correction) and that for each type of complex, the interaction energy increases with the size of the halogen atom. Previous studies on the interaction between neutral molecules and halogen compounds indicate that the magnitude of these interactions is the same as that found here. Complexes between formaldehyde and halobenzene, for example, have X···O interaction energy for of −4.81 e −7.28 kJ mol^{-1} for X = Br and I, respectively [26]. PhBr···M complexes (M = NH$_3$, H$_2$O and SH$_2$) have interaction energies of −8.99, −6.77 and −6.36 kJ mol^{-1}, respectively [26]. For halogen-bonded complexes with hydrogen halides, Yu and colleagues found values in the interval from −1.56 to −7.11 kJ mol^{-1} [27]. In short, these data suggest that halogen complexes involving PH$_3$ are sufficiently stable, having interaction energies comparable to those of hydrogen bonding [28].

As is well known, electron correlation is critical for the accurate evaluation of molecular energies. We can verify this by analyzing our HF results, which indicate unbounded states to almost all systems investigated. The CCSD(T) and MP4 results give a clear picture of the role of electron correlation effects on the relative interaction energies. We observed that the MP2 values are consistently higher than the corresponding MP4 and CCSD(T) values. For the latter, the interaction energy is reduced by up to 27 % (for PhBr···PH$_3$ and HCl···PH$_3$ complexes). The MP4 results are also reduced in relation to the MP2 results, in this case by at most 23 % (HCl···PH$_3$). In any case, this difference can be crucial to the evaluation of the stability of a weakly bound complex. However, we observed here that all correlated methods indicate the formation of stable complexes.

Now, applying the ΔZPE correction (which was calculated at MP2 level) to the MP2 interaction energies, we still find bonded complexes, but the interaction energies of the HCl···PH$_3$ and HBr···PH$_3$ complexes become almost negligible, and therefore it is not possible to infer anything about their stability, even at low temperatures.

Although atomic charges are not physical observables and are inherently dependent on the method of calculation, the charge distribution provides interesting qualitative information on the electrostatic of the systems. Thus, the charge distributions of the halogen-bonded complexes were examined in terms of NBO analysis. Figure 7 presents the difference in atomic charges between the complex and separated species. Overall, the magnitude of the difference is in the range 1–20 me. We can observe that, upon formation of a halogen bond, there is a charge rearrangement with a decrease in electron density at the halogen site and a slight increase in the phosphorus atom for all cases. We also observe that, in all cases, NBO analysis suggests that the
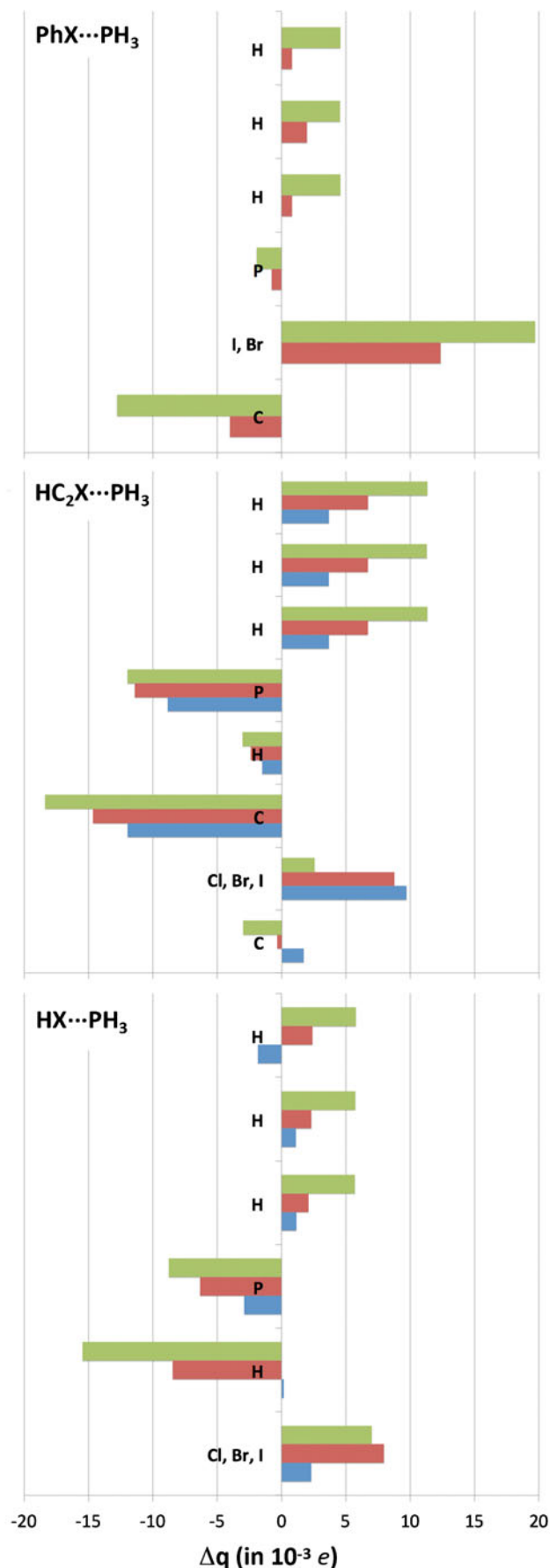
◀ **Fig. 7** Difference in atomic charge (in 10^{-3} e) between the complex and separated species, obtained using natural bond orbital (NBO) analysis. *Blue*, *red* and *green* represents the RCl···PH₃, RBr···PH₃ and RI···PH₃ complexes, respectively. Some halobenzene atoms (C and H), with minor charge variations, are not shown for clarity

charge transfer between moieties is greater when using iodine than with bromine or chlorine. The bigger charge transfer occurs for the HC₂I···PH₃ complex, in which the PH₃ molecule becomes ~21 me more positive.

An interesting point is that the interaction energy of the complexes, shown in Table 3, does not correlate strictly with the positive electrostatic potential on the outside of the halogen atoms shown in Table 1. For example, PhI would have been predicted to have significantly smaller interaction energy than HC₂I and even HI. Nevertheless, we observe, from Table 3, that PhI···PH₃ has significantly larger inter-action energy than HI···PH₃ and almost as large as in HC₂I···PH₃. This can be explained by considering the po-larizability of the monomers (shown in Table 4) and the difference in atomic charges in Fig. 7. Upon complexation with PH₃, the RX molecule is polarized, that is, it suffers an internal charge transfer in which a portion of electron den-sity will migrate to the R moiety and the nucleus of the X atom will be less screened, resulting in larger sigma holes than in the isolated situation. Now, the PhX molecules are much more polarizable then the HC₂X molecules, which are in turn much more polarizable than the HX molecules. Therefore the halogen atoms become much more positive in PhX than in HC₂X or HX as shown in Fig. 7. This is accompanied by an influx of negative charge to the C or H atom attached to X due to the internal charge transfer.

Our results show also that the PhBr molecule forms a more stable complex with PH₃ than HBr, corroborating that polarization is an important mechanism behind stabilization of a halogen bond.

The electrical properties of these complexes are also presented in Table 4. There seems to be no clear dependence of the dipole moment in relation to the size of the halogen. For complex HC₂X···PH₃ a clear increase in dipole moment is observed following the order Cl < Br < I but, for the other complexes, no systematic behavior is observed. Although we found no experimental results for the dipole moment of the complexes, the values calculated here for the isolated species are in very good agreement with experimental val-ues [29]. Dipole polarizability is related to the volume of the electronic cloud. This fact can be seen here, since the larger complexes (such as PhI···PH₃) have higher polarizability than the smaller complex (e.g., HCl···PH₃). In fact, a sys-tematic increase in the value of polarizability is obtained as the size of the halogen complex increases. No experimental values could be found for the polarizability of the complex, but the calculated values for the monomers are in good agreement with experimental values [29]. We also evaluated

Table 4 MP2/aug-cc-pVDZ calculated dipole moment, μ (D) and polarizabilities, α (au), for complexes and monomers. Interaction polarizabilities (see text) are in parenthesis. Experimental values are taken from [30]

Complex	μ (calc)	μ (exp)	α (calc)	α (exp)
PhBr···PH$_3$	1.022	–	126.8 (4.4)	–
PhI···PH$_3$	0.414	–	143.2 (6.7)	–
HC$_2$Cl···PH$_3$	0.561	–	69.2 (2.8)	–
HC$_2$Br···PH$_3$	0.987	–	77.1 (4.1)	–
HC$_2$I···PH$_3$	1.648	–	91.4 (6.0)	–
HCl···PH$_3$	1.438	–	47.0 (0.7)	–
HBr···PH$_3$	0.436	–	53.6 (1.5)	–
HI···PH$_3$	0.683	–	66.7 (2.5)	–
Monomer	μ(calc)	μ (exp)	α (calc)	α (exp)
PH$_3$	0.6342	0.57	30.3	32.7
PhBr	1.7495	1.7	92.1	99.2
PhI	1.9354	1.7	106.2	104.6
CH$_2$Cl	0.4467	0.4441	36.2	41.0
CH$_2$Br	0.276	0.2296	42.7	49.9
CH$_2$I	0.1262	0.0252	55.1	–
HCl	1.1846	1.1086	16.0	17.7
HBr	0.9162	0.8272	21.8	24.4
HI	0.5566	0.4480	33.9	36.7

the so-called interaction polarizability [30], which is defined as the difference between the polarizability of the halogen bonded complex and the sum of the polarizabilities of its separate monomers.

The calculated values of interaction polarizability for all complexes shown in parenthesis in Table 4 are in the range of 0.7–6.7 au, suggesting that the dipole polarizability of the halogen bonded system is approximately additive. Usually this amount is small, about 0.5–2.5 % of the total polarizability for small hydrogen bonded complexes [30]. In the case of the halogen-bonded complexes investigated here, the interaction polarizability is significantly higher (3–7 %, with the exception of the most weakly bound HCl···PH$_3$ complex). This larger relative variation is due primarily to the atoms involved in halogen bonding, having atomic polarizability much larger than H, O and N atoms, which normally appear in hydrogen bonds. The HC$_2$I···PH$_3$ complex, for example, has an interaction polarizability of 6.0 au, implying an increase of 7 % in relation to the sum of the polarizability of the separated HC$_2$I and PH$_3$ monomers.

Conclusions

In this work, we evaluated the role of ipso carbon hybridization in RX (R = methyl, phenyl, acetyl, H and X = F, Cl, Br, I) and its interaction with a phosphorus atom, as it occurs in the halogen bonded complex type RX···PH$_3$. This analysis was performed using ab initio MP2, MP4 and CCSD(T) methods. We found that MeX···PH$_3$ and PhCl···PH$_3$ are not stable, both types presenting positive interaction energies. For other systems, all bonded, we observed that the R–X covalent bond suffered a slight elongation after complexation (0.001–0.012 Å depends on the halogen size) in all cases. This deformation is correlated directly with the intensity of the interaction energy.

We conducted a systematic energy analysis and found that the interaction energies are in the range −4.14 to −11.92 kJ mol^{-1} (at MP2 level without ZPE correction). These values are comparable to those found in halogen bonds involving neutral molecules such as NH$_3$, H$_2$O and SH$_2$, making it stable enough to be detected, at least at low temperatures. Effects of electronic correlation levels were evaluated in MP4 and CCSD(T) levels and a reduction of up to 27 % in interaction energy obtained in MP2 was observed. After applying the ZPE correction at MP2 level, bonded complexes were still found, but the interaction energies of the HCl···PH$_3$ and HBr···PH$_3$ complexes become almost negligible, and therefore it is not possible to infer anything about their stability, even at low temperatures.

We computed the molecular electrostatic potential of the isolated monomers on the molecular surface to gain insight into the electrostatic interaction between the halogen-containing molecules and PH$_3$. According to analysis of the electrostatic maps, the PhCl···PH$_3$ and all RF···PH$_3$ complexes are unstable. Nevertheless, we found that stability of the complexes is not only determined by the electrostatic interaction between monomers, but the polarization of the molecules upon complexation is also an important ingredient that must be taken into account for the formation and stabilization of halogen bonds.

Finally, we calculated the electronic properties of these complexes, and the most important aspect observed was the systematic increase of the dipole polarizability, given by the interaction polarizability. This increase is in the range of 0.7–6.7 au (about 3–7 %) for all complexes and is significantly greater than the observed increase in hydrogen bonded complexes, where this increase is approximately 0.5–2.5 %.

The values reported here for structure, interaction energies and electric properties can be useful for the detection and characterization of halogen bonded complexes involving PH$_3$, as the Lewis base ought to be observable experimentally in the gas phase, certainly at low temperature.

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