

Is there theoretical evidence for mutual influence between halogen and pnictogen-hydride bonds? An *ab initio* study

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Abstract. *Ab initio* MP2/6-311++G(d,p) level calculations have been carried out to investigate the interplay between the halogen and pnictogen-hydride bonds in $\text{NCX} \cdots \text{OPH}_3 \cdots \text{HMgY}$ complexes ($X = \text{F, Cl, Br}$; $Y = \text{F, Cl, Br, H}$). The results indicated that the cooperative effects are obvious in the target complexes. These effects were considered in detail in terms of electrostatic potential, energetic, geometric, charge-transfer and electron density properties of the complexes. The values of cooperative energy (E_{coop}) were ranging from -0.41 to -0.60 kJ/mol, -1.02 to -1.57 kJ/mol and -1.50 to -2.28 kJ/mol for $X = \text{F, Cl}$ and Br , respectively. Based on many-body analysis, two and three-body terms of interaction energies have a positive contribution to the total interaction energy. It was found that the amount of charge transfer in the triads is higher than that in the corresponding dyads. AIM analyses showed that the halogen and pnictogen-hydride bonds in the triads are amplified with respect to the dyads.

Keywords. Cooperativity; Pnictogen-hydride bond; halogen bond; *Ab initio* study.

1. Introduction

The importance of noncovalent interactions is due to their widespread applications in many fields such as, physical, chemical, and biological systems.¹ Although the hydrogen bond is probably the most important intermolecular interaction,^{2–5} interest has grown for other types of intermolecular interactions, such as halogen bond^{6–9} and lithium bond.¹⁰ A halogen bond is a short-range $\text{R-X} \cdots \text{B}$ interaction between a halogen atom (X) in one molecule (R–X) and a negative site in a donor of electron density B.¹¹ The term “ σ -hole” is a region of positive electrostatic potential on the outer surface of X along the bond axis that explains the stability of the X-bond.¹² The main origin of halogen bonding interaction is the electrostatic attraction between the σ -hole of halogen atom and the negative Lewis base.¹³ With increasing size of the halogen, $\text{Cl} < \text{Br} < \text{I}$, σ -hole becomes larger and more positive. However, σ -hole interactions have been perused extensively for halogen bonding (Group VII), and their incidence for Groups IV–VI is increasingly being identified.¹⁴

In recent years, pnictogen bond as a new type of intermolecular interaction has attracted much attention since

Hey-Hawking *et al.*,¹⁵ revealed in 2011 that it may act as a molecular linker in crystal materials.¹⁶ The pnictogen bond is a noncovalent interaction between a pnictogen atom in one molecule and an electron-rich site in another molecule. As mentioned in the previous paragraph, the formation of pnictogen bond can be described with the help of the σ -hole concept.^{17–23} Li *et al.*, predicted in 2012 that a pnictogen-hydride bond can exist in $\text{FH}_2\text{P} \cdots \text{HM}$ and $\text{FH}_2\text{As} \cdots \text{HM}$ ($\text{M} = \text{ZnH, BeH, MgH, Li, and Na}$) complexes.²⁴ In this different type of pnictogen bond, a metal hydride acts as the electron donor to form the pnictogen-hydride bond.

When the noncovalent interactions act simultaneously, reciprocally and mutually to enhance the strength, they are said to be acting cooperatively. The cooperativity, like the competition behavior, is another significant type of intermolecular interaction.^{25–28} Cooperativity effect plays an essential role in specifying the behavior in some biochemical and chemical systems.²⁹ The interplay between pnictogen-bond and halogen-bond in $\text{XCl} \cdots \text{FH}_2\text{P} \cdots \text{NH}_3$ ($X = \text{F, OH, CN, NC, and FCC}$) complex has recently been investigated by Li *et al.*³⁰ Their results indicate that both types of interaction enhance each other. The cooperative effects between $\text{F-H} \cdots \text{F}$ hydrogen bond and $\text{P} \cdots \text{N}$ pnictogen bond were studied by Alkorta *et al.*³¹ The cooperativity between

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pnictogen bond and dihydrogen bond interactions in $\text{HMH} \cdots \text{HCN} \cdots \text{PH}_2\text{X}$ ($\text{M} = \text{Be}, \text{Mg}, \text{Zn}$; $\text{X} = \text{H}, \text{F}, \text{Cl}$) complexes was also studied by Eshrafi *et al.*³²

To the best of our knowledge, the interplay between the halogen and pnictogen-hydride bonds has not yet been investigated. In this regards, we designed some simple structures including halogen and pnictogen-hydride bonds. We carried out a theoretical study on the $\text{NCX} \cdots \text{OPH}_3 \cdots \text{HMgY}$ complexes ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{H}$) with the aim of investigating the mutual influence between halogen and pnictogen-hydride bonds. The properties and nature of interaction have also been understood with atoms in molecules (AIM),³³ natural bond orbital (NBO),³⁴ and molecular electrostatic potential (MEP).³⁵

2. Computational methods

All geometry optimizations were performed at MP2/6-311++G(d,p) level of theory using Gaussian 03 program.³⁶ Recently, it has been shown that MP2 method is able to accurately predict the interaction energies of the halogen-hydride interactions.³⁷ The vibrational frequency calculations were carried out at the same level to guarantee that the structures obtained corresponded to local minima on the potential energy surface. All the interaction energies were calculated at the same level as the difference of the total energy of the complexes and the sum of the isolated monomers, without any geometrical flexibility. To determine the corrected interaction

energy, the basis set superposition error (BSSE) correction was also calculated according to the counterpoise (CP) method proposed by Boys and Bernardi.³⁸

Molecular electrostatic potentials were computed with Wave Function Analysis–Surface Analysis Suite (WFA–SAS) developed by Politzer *et al.*³⁹ The AIM analysis was performed by means of the AIM2000 program,⁴⁰ using the MP2/6-311++G(d,p) wavefunction. The NBO calculations were performed at the MP2/6-311++G(d,p) level by means of the NBO 3.1 program.⁴¹

3. Results and Discussion

3.1 Molecular electrostatic potential

Molecular electrostatic potential (MEP) is a well-established tool for studying the nature of intermolecular interactions and interpreting and predicting noncovalent interactions. One of the real physical properties is electrostatic potential. It is experimentally determined by diffraction methods, and also with computational methods. Potential is one of the basic features of molecules that can determine many of its properties.^{42–45} The three dimensional MEP maps on the 0.001 electron/Bohr³ electron density isosurfaces of the monomers OPH_3 , NCBr and HMgBr and their complexes are depicted in Figure 1. As expected, there is a positive region of MEP outside the phosphorus atom along the extension of O–P bond and is surrounded by negative electrostatic

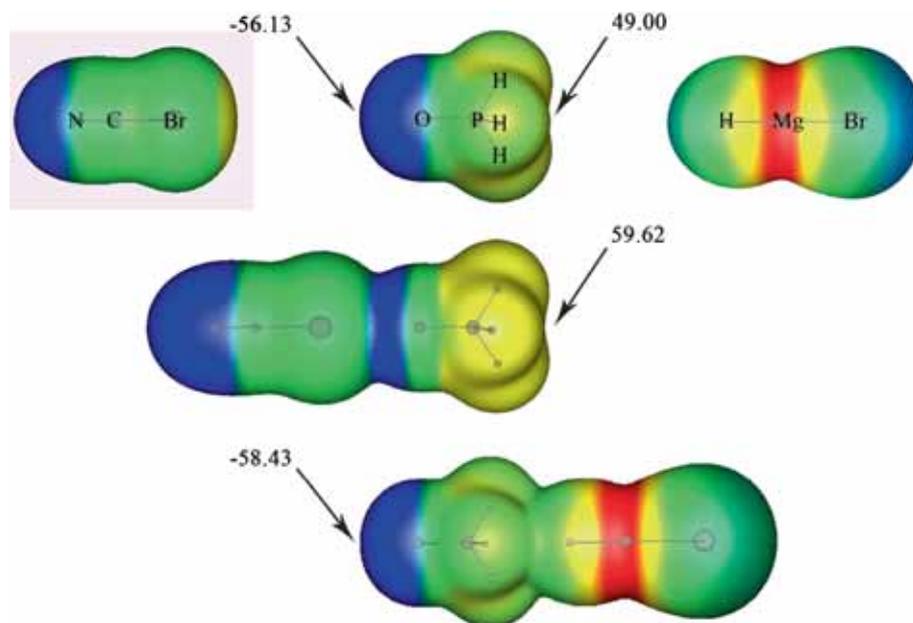


Figure 1. Electrostatic potential maps on the 0.001 (electron/Bohr³) electron density isosurfaces of isolated NCBr , OPH_3 , and HMgBr and their binary complexes. Color ranges, in kcal mol⁻¹: red > 60 > yellow > 20 > green > -15 > blue.

potential, which corresponds to the σ -hole. Except for the positive MEP region outside the phosphorus atom, there is also a negative potential $V_{S,\min}$ associated with the oxygen atom along the extension of O–P bond.

The most positive ($V_{S,\max}$) and most negative ($V_{S,\min}$) electrostatic potentials are shown in Table 1. According to Table 1, $V_{S,\min}$ value is -56.13 kcal/mol for the O atom and $V_{S,\max}$ on the P atom is 49.00 kcal/mol in OPH_3 monomer. For NCX , the positive region of MEP exists outside the X atom along the extension of C–X bond. The $V_{S,\max}$ values, 33.03 kcal/mol, 41.34 kcal/mol, 48.93 kcal/mol, increase in the order $\text{NCF} < \text{NCCl} < \text{NCBr}$. Therefore, $\text{NCX} \cdots \text{OPH}_3$ ($X = \text{F}, \text{Cl}, \text{Br}$) dyads could be formed by the $\text{X} \cdots \text{O}$ halogen bond. As is clear from the Table 1, with the formation of the $\text{X} \cdots \text{O}$ halogen bond, the $V_{S,\max}$ values outside the P atom in $\text{NCX} \cdots \text{OPH}_3$ dyads become larger than that in OPH_3 monomer, along the sequence of $Y = \text{F}, \text{Cl}, \text{Br}$. For HMgY ($Y = \text{F}, \text{Cl}, \text{Br}, \text{H}$), there is a negative region of MEP outside the hydrogen atom along the extension of H–Mg bond, that become increasingly more negative in the order $\text{HMgF} < \text{HMgCl} < \text{HMgBr} < \text{HMgH}$. So, OPH_3 and HMgY ($Y = \text{F}, \text{Cl}, \text{Br}, \text{H}$) can form $\text{P} \cdots \text{H}$ pnictogen–hydride bond, that is Group V σ -hole interaction. When OPH_3 forms the pnictogen–hydride bond with HMgY , $V_{S,\min}$ on the O atom becomes more negative, which demonstrates that the complexes are better electron donors than those of the corresponding monomers. From Table 1, with the formation of the $\text{P} \cdots \text{H}$ pnictogen–hydride bond, the $V_{S,\min}$ values outside the oxygen atom in the bimolecular complexes $\text{OPH}_3 \cdots \text{HMgY}$ become more negative than in OPH_3 monomer, along the sequence of $Y = \text{F}, \text{Cl}, \text{Br}, \text{H}$, which demonstrates that the complexes are stronger electron donors than the corresponding monomers. According to Table 1, the $V_{S,\min}$ values outside the oxygen atom in $\text{OPH}_3 \cdots \text{HMgF}$, $\text{OPH}_3 \cdots \text{HMgCl}$, $\text{OPH}_3 \cdots \text{HMgBr}$ and $\text{OPH}_3 \cdots \text{HMgH}$ are -58.32 , -58.36 , -58.43 and -60.72 kcal/mol, respectively,

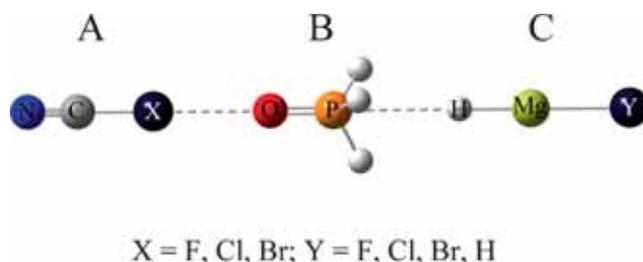


Figure 2. General structure of the $\text{NCX} \cdots \text{OPH}_3 \cdots \text{HMgY}$ complex.

which are more negative than for the OPH_3 monomer ($V_{S,\min} = -56.13$ kcal/mol).

3.2 Geometrics

The geometrical changes can reflect the cooperative effect between the halogen bond and pnictogen–hydride bond. The optimized geometries of $\text{NCX} \cdots \text{OPH}_3 \cdots \text{HMgY}$ ($X = \text{F}, \text{Cl}, \text{Br}; Y = \text{F}, \text{Cl}, \text{Br}, \text{H}$) are graphically shown in Figure 2. The oxygen atom in OPH_3 is attracted to the σ -hole of NCX , at the same time the hydrogen atom in HMgY is attracted to the σ -hole of OPH_3 . The optimized equilibrium C–X \cdots O and P \cdots H–Mg contacts in the complexes are essentially linear.

The intermolecular distances for dyads and the distance difference between triads and dyads are listed in Table 2. The intermolecular distance in the halogen bonded dyads is smaller than that in the pnictogen–hydride bonded dyads. The binding distances in the triads are shorter than those in the dyads, both the halogen bond and pnictogen–hydride distance. For example, the halogen bond distance of $\text{NCF} \cdots \text{OPH}_3$ is 2.807 Å. With the formation of pnictogen–hydride bond in $\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgBr}$, the halogen bond distance becomes shorter to 2.795 Å. The pnictogen–hydride bond distance of $\text{OPH}_3 \cdots \text{HMgBr}$ is 3.054 Å. With the formation of the halogen bond in $\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgBr}$,

Table 1. The most positive electrostatic potential, $V_{S,\max}$ (kcal/mol), on the P and X atoms and the most negative electrostatic potential, $V_{S,\min}$ (kcal/mol), on the O and H atoms in the monomers and dyad complexes.

Monomer	$V_{S,\max}$	$V_{S,\min}$	Complex	$V_{S,\max}$	$V_{S,\min}$
OPH₃	49.00	-56.13	OPH₃ \cdots HMgF	–	-58.32
HMgF	–	-16.71	OPH₃ \cdots HMgCl	–	-58.36
HMgCl	–	-16.54	OPH₃ \cdots HMgBr	–	-58.43
HMgBr	–	-16.59	OPH₃ \cdots HMgH	–	-60.72
HMgH	–	-24.85	NCF \cdots OPH₃	52.56	–
NCF	33.03	–	NCCl \cdots OPH₃	56.46	–
NCCl	41.34	–	NCBr \cdots OPH₃	59.62	–
NCBr	48.93	–			

Table 2. Intermolecular distances R (Å) in the triads and their changes, ΔR (Å), relative to the corresponding dyads.

Complex(A...B...C)	$R_{AB}(T)$	ΔR_{AB}	$R_{BC}(T)$	ΔR_{BC}
NCF...OPH ₃ ...HMgF	2.796	-0.012	3.044	-0.016
NCF...OPH ₃ ...HMgCl	2.795	-0.012	3.039	-0.017
NCF...OPH ₃ ...HMgBr	2.795	-0.012	3.037	-0.017
NCF...OPH ₃ ...HMgH	2.791	-0.016	2.995	-0.021
NCCl...OPH ₃ ...HMgF	2.798	-0.015	3.008	-0.052
NCCl...OPH ₃ ...HMgCl	2.798	-0.014	3.008	-0.048
NCCl...OPH ₃ ...HMgBr	2.798	-0.014	3.005	-0.049
NCCl...OPH ₃ ...HMgH	2.789	-0.024	2.960	-0.056
NCBr...OPH ₃ ...HMgF	2.773	-0.019	2.992	-0.069
NCBr...OPH ₃ ...HMgCl	2.773	-0.019	2.990	-0.067
NCBr...OPH ₃ ...HMgBr	2.773	-0.019	2.988	-0.066
NCBr...OPH ₃ ...HMgH	2.763	-0.029	2.941	-0.076

pnictogen-hydride bond distance becomes shorter to 3.037 Å. These results indicate that the halogen and pnictogen-hydride bond interactions become stronger from the dyad to the triad complexes. So, there is positive cooperativity between the halogen and pnictogen-hydride bond interactions in triad complexes. For each triad, the shortening of the intermolecular distance in the pnictogen-hydride bond is more outstanding than that in the halogen bond. For example, it is -0.066 Å in the former and -0.019 Å in the latter for NCBr...OPH₃...HMgBr triad. This demonstrates that the effect of halogen bonds on pnictogen-hydride bonds is more than that of pnictogen-hydride bonds on halogen bonds.

3.3 Interaction energies

The interaction energy has been used generally in the study of the interplay between two types of noncovalent interactions.⁴⁶ The interaction energy has been computed as the difference of the total energy of the complexes and the sum of the isolated monomers in

their most stable formation. For example, the interaction energy in the triads is calculated with the formula of $E_i(ABC) = E_{ABC} - (E_A + E_B + E_C)$. To evaluate the interaction energies, basis set superposition error was corrected by the counterpoise method. Table 3 gives the interaction energy results for the NCX...OPH₃...HMgY (X = F, Cl, Br; Y = F, Cl, Br, H) complexes. The interaction energies of halogen bonds are -6.20, -18.71 and -25.16 kJ/mol in NCF...OPH₃, NCCl...OPH₃ and NCBr...OPH₃ dyads, respectively. As can be seen in Table 3, the range of interaction energies of OPH₃...HMgY (Y = F, Cl, Br, H) dyads is from -7.32 to -10.89 kJ/mol. As is clear from Table 3, in the triads, the interaction energies for NCF...OPH₃...HMgY, NCCl...OPH₃...HMgY and NCBr...OPH₃...HMgY complexes, span a range from -13.93 to -17.93 kJ/mol, from -27.27 to -31.82 kJ/mol and from -34.22 to -39.08 kJ/mol. According to Table 3, the interaction energies of the halogen bond in the triads, $E_i(AB, T)$, are more negative than the respective $E_i(AB, D)$ in the dyads. For example,

Table 3. Interaction energies, E_i (kJ/mol), and cooperative energies, E_{coop} (kJ/mol), in the investigated dyads (D) and triads (T).

Complex(A...B...C)	$E_i(ABC)$	$E_i(AB, D)$	$E_i(AB, T)$	$E_i(BC, D)$	$E_i(BC, T)$	E_{coop}
NCF...OPH ₃ ...HMgF	-13.93	-6.20	-6.61	-7.32	-7.74	-0.41
NCF...OPH ₃ ...HMgCl	-14.02	-6.20	-6.63	-7.39	-7.82	-0.45
NCF...OPH ₃ ...HMgBr	-14.09	-6.20	-6.63	-7.45	-7.89	-0.45
NCF...OPH ₃ ...HMgH	-17.93	-6.20	-7.04	-10.89	-11.74	-0.60
NCCl...OPH ₃ ...HMgF	-27.27	-18.71	-19.95	-7.32	-8.57	-1.02
NCCl...OPH ₃ ...HMgCl	-27.37	-18.71	-19.98	-7.39	-8.67	-1.08
NCCl...OPH ₃ ...HMgBr	-27.46	-18.71	-20.01	-7.45	-8.76	-1.10
NCCl...OPH ₃ ...HMgH	-31.82	-18.71	-20.93	-10.89	-13.11	-1.57
NCBr...OPH ₃ ...HMgF	-34.22	-25.16	-26.90	-7.32	-9.06	-1.50
NCBr...OPH ₃ ...HMgCl	-34.34	-25.16	-26.95	-7.39	-9.18	-1.57
NCBr...OPH ₃ ...HMgBr	-34.43	-25.16	-26.97	-7.45	-9.27	-1.59
NCBr...OPH ₃ ...HMgH	-39.08	-25.16	-28.18	-10.89	-13.92	-2.28

$E_i(\text{AB}, \text{T})$ of the termolecular complexes $\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgH}$ is -28.18 kJ/mol, which is more negative than $E_i(\text{AB}, \text{D})$ of the dyad complexes $\text{NCBr} \cdots \text{OPH}_3$ with the value of -25.16 kJ/mol. The same trend has been observed, for pnictogen-hydride bond interactions. The pnictogen-hydride bond interactions in the triads are stronger than those in the dyads. For example, the pnictogen-hydride bond interaction energies of $\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgH}$ and $\text{OPH}_3 \cdots \text{HMgH}$ are -13.92 and -10.89 kJ/mol, respectively. Hence, there is positive cooperativity between halogen and pnictogen-hydride bonds in $\text{NCX} \cdots \text{OPH}_3 \cdots \text{HMgY}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$; $\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{H}$) complexes. The cooperative energy (E_{coop}) is used to estimate the cooperativity, frequently. It is computed to be the difference between the total interaction energy in the termolecular complexes and the sum of interaction energy in the corresponding bimolecular complexes.^{14,47} The cooperative energy is calculated with the formula of $E_{\text{coop}} = E_i(\text{ABC}) - E_i(\text{AB}) - E_i(\text{BC}) - E_i(\text{AC})$. The evaluated cooperativity energy E_{coop} of the ternary complexes is shown in Table 3. As is shown from Table 3, the E_{coop} values are negative in all cases, indicating that there is positive cooperativity between halogen and pnictogen-hydride bonds. This cooperative energy is greater than that between the halogen and halogen-hydride bonds.²⁵

3.4 Vibrational analysis

The amount of calculated frequency shifts of the C–X and O=P stretching vibrations in the investigated dyads (D) and triads (T) relative to those in the isolated NCX and OPH_3 monomers are shown in Table 4. As can be seen, the formation of the complexes leads to a red-shift of the C–X and O=P stretching vibrations in the infrared spectra. The red-shift of the C–X and O=P stretching vibrations in the triads are larger than those in

the dyads. From Table 3 and Table 4, it is seen that the amount of red-shift depends on the strength of the interaction energies. The amount of red-shift increases with an increase in the strength of interactions energies. This red shift is smaller than that observed in OH stretching frequency of the water chain,⁴⁸ which indicates a lower cooperativity between halogen and pnictogen-hydride bonds.

3.5 Many-body interaction energy analysis

The two- and three-body contributions to the total interaction energy are calculated by many-body analyses.^{25,49} The non-additive term of the interaction energy or cooperativity has been appraised using the many-body interaction analysis. For this purpose, the two and three-body contributions to total binding energy have been computed. The two-body terms ($\Delta E_{\text{A-B}}$, $\Delta E_{\text{A-C}}$, and $\Delta E_{\text{B-C}}$) can be calculated as the difference between the energy of each molecular pair and the energy sum of the monomers, all in the geometry of triad.⁵⁰ The three-body term ($\Delta E_{\text{A-B-C}}$) was calculated with the formula of $\Delta E_{\text{A-B-C}} = E_i(\text{ABC})' - \Delta E_{\text{A-B}} - \Delta E_{\text{B-C}} - \Delta E_{\text{A-C}}$, where $E_i(\text{ABC})'$ was calculated as the difference between the total energy of the optimized triad and the energy sum of the monomers, all in the geometry of triad. Also, the total relaxation energy (E_{R}) was calculated with the formula of $E_{\text{R}} = E_i(\text{ABC}) - \Delta E_{\text{A-B}} - \Delta E_{\text{B-C}} - \Delta E_{\text{A-C}} - \Delta E_{\text{A-B-C}}$.^{51,52} The results are listed in Table 5, in which all the energies are corrected for BSSE. The obtained results indicate that for all the complexes, the two- and three-body interaction energies are attractive and they make a positive contribution to the total interaction energy. For the two-body interaction energy in each triad, except the $\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgY}$ ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{H}$) complexes, $\Delta E_{\text{A-B}}$ is larger than $\Delta E_{\text{B-C}}$. Because the distance

Table 4. Frequency shift, $\Delta\nu$ (cm^{-1}), of C–X and O=P stretching vibrations in the investigated dyads (D) and triads (T) relative to corresponding monomers.

Complex(A \cdots B \cdots C)	$\Delta\nu_{\text{C-X}}$ (T)	$\Delta\nu_{\text{C-X}}$ (D)	$\Delta\nu_{\text{O=P}}$ (T)	$\Delta\nu_{\text{O=P}}$ (D)
$\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgF}$	-2.24	-1.40	-9.69	-8.31
$\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgCl}$	-2.01	-1.40	-9.65	-8.33
$\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgBr}$	-2.41	-1.40	-9.61	-8.30
$\text{NCF} \cdots \text{OPH}_3 \cdots \text{HMgH}$	-3.65	-1.40	-11.17	-10.45
$\text{NCCl} \cdots \text{OPH}_3 \cdots \text{HMgF}$	-9.08	-8.56	-11.33	-8.31
$\text{NCCl} \cdots \text{OPH}_3 \cdots \text{HMgCl}$	-9.20	-8.56	-11.41	-8.33
$\text{NCCl} \cdots \text{OPH}_3 \cdots \text{HMgBr}$	-9.10	-8.56	-11.67	-8.30
$\text{NCCl} \cdots \text{OPH}_3 \cdots \text{HMgH}$	-10.23	-8.56	-14.36	-10.45
$\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgF}$	-16.56	-15.68	-13.86	-8.31
$\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgCl}$	-16.76	-15.68	-14.11	-8.33
$\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgBr}$	-16.98	-15.68	-14.32	-8.30
$\text{NCBr} \cdots \text{OPH}_3 \cdots \text{HMgH}$	-19.88	-15.68	-16.56	-10.45

Table 5. Decomposition of interaction energy (kJ/mol) of the studied ternary complexes.

Complex(A···B···C)	ΔE_{A-B}	ΔE_{A-C}	ΔE_{B-C}	ΔE_{A-B-C}	E_R
NCF···OPH ₃ ···HMgF	-6.26	-0.09	-7.36	-0.36	0.14
NCF···OPH ₃ ···HMgCl	-6.26	-0.10	-7.45	-0.38	0.17
NCF···OPH ₃ ···HMgBr	-6.26	-0.10	-7.51	-0.38	0.17
NCF···OPH ₃ ···HMgH	-6.27	-0.35	-10.97	-0.54	0.19
NCCl···OPH ₃ ···HMgF	-18.82	-0.26	-7.34	-1.09	0.24
NCCl···OPH ₃ ···HMgCl	-18.83	-0.27	-7.42	-1.12	0.26
NCCl···OPH ₃ ···HMgBr	-18.82	-0.27	-7.50	-1.12	0.25
NCCl···OPH ₃ ···HMgH	-18.81	-0.70	-10.97	-1.63	0.29
NCBr···OPH ₃ ···HMgF	-25.40	-0.34	-7.32	-1.56	0.41
NCBr···OPH ₃ ···HMgCl	-25.40	-0.35	-7.42	-1.60	0.44
NCBr···OPH ₃ ···HMgBr	-25.39	-0.36	-7.49	-1.62	0.43
NCBr···OPH ₃ ···HMgH	-25.40	-0.86	-10.97	-2.36	0.51

between the interacting molecules A and C in all the ternary complexes is the largest, ΔE_{A-C} of the corresponding triad is the smallest. As is evident, the monomer relaxation energy, E_R , is slightly small at no more than 0.41 kcal/mol. The relaxation energy is largest in NCBr···OPH₃···HMgF and smallest in NCF···OPH₃···HMgF.

3.6 NBO analysis

The natural bond orbital (NBO) method has been used to investigate the nature of NCX···OPH₃···HMgY (X = F, Cl, Br; Y = F, Cl, Br, H) complexes with coexisting halogen and pnictogen-hydride bonds, which were performed at the MP2/6-311++g(d,p) level of theory based on their geometry optimizations at this level. Table 6 shows the value of charge transfer (CT) from B to A (CT_{AB}) and from C to B (CT_{BC}) in the triads and its change (ΔCT) relative to the corresponding dyads. In the NCF···OPH₃···HMgY triads, the charge transfer values for the halogen bond are in range of 0.00126–0.00133, the values for the pnictogen-hydride bond are

in range of 0.00463–0.00672, and the corresponding values in the ternary NCCl···OPH₃···HMgY complexes are between 0.00487–0.00508 and 0.00514–0.00732 for the halogen and pnictogen-hydride bonds, respectively. Also, in the ternary NCBr···OPH₃···HMgY complexes, the amount of charge transfer for the halogen bond is in the range of 0.00798–0.00840 and for the pnictogen-hydride bond the value is in the range of 0.00145–0.00182. The charge transfer is largest in ternary complexes associated with bromine halogen bonds. As can be seen from the results, the charge transfer values in the ternary complexes are more than that in the corresponding binary complexes, which indicates amplification of the interactions.

3.7 AIM analysis

The atoms in molecules (AIM) methodology has been extensively applied to study the various types of noncovalent interactions. We used the AIM method to analyze the cooperative effects of halogen and pnictogen-hydride bonds. The values of the electron den-

Table 6. Charge transfer, CT (e), in the investigated triads and its changes, ΔCT (e), relative to the corresponding dyads.

Complex (A···B···C)	CT_{AB}	ΔCT_{AB}	CT_{BC}	ΔCT_{BC}
NCF···OPH ₃ ···HMgF	0.00126	0.00019	0.00672	0.00031
NCF···OPH ₃ ···HMgCl	0.00126	0.00019	0.00475	0.00026
NCF···OPH ₃ ···HMgBr	0.00127	0.00020	0.00463	0.00027
NCF···OPH ₃ ···HMgH	0.00133	0.00026	0.00637	0.00040
NCCl···OPH ₃ ···HMgF	0.00488	0.00017	0.00732	0.00091
NCCl···OPH ₃ ···HMgCl	0.00487	0.00016	0.00536	0.00087
NCCl···OPH ₃ ···HMgBr	0.00487	0.00016	0.00514	0.00078
NCCl···OPH ₃ ···HMgH	0.00508	0.00037	0.00703	0.00106
NCBr···OPH ₃ ···HMgF	0.00799	0.00064	0.00792	0.00151
NCBr···OPH ₃ ···HMgCl	0.00799	0.00064	0.00597	0.00148
NCBr···OPH ₃ ···HMgBr	0.00798	0.00063	0.00581	0.00145
NCBr···OPH ₃ ···HMgH	0.00840	0.00105	0.00779	0.00182

Table 7. Electron densities, ρ (au), at the A...B and B...C intermolecular bond critical points (BCPs) in the investigated triads and its changes, $\Delta\rho$ (au), relative to the corresponding dyads.

Complex(A...B...C)	ρ_{AB}	$\Delta\rho_{AB}$	ρ_{BC}	$\Delta\rho_{BC}$
NCF...OPH ₃ ...HMgF	0.00689	0.00022	0.00557	0.00016
NCF...OPH ₃ ...HMgCl	0.00690	0.00023	0.00561	0.00017
NCF...OPH ₃ ...HMgBr	0.00691	0.00023	0.00564	0.00017
NCF...OPH ₃ ...HMgH	0.00699	0.00031	0.00624	0.00023
NCCl...OPH ₃ ...HMgF	0.01252	0.00049	0.00592	0.00052
NCCl...OPH ₃ ...HMgCl	0.01249	0.00046	0.00600	0.00056
NCCl...OPH ₃ ...HMgBr	0.01251	0.00047	0.00595	0.00048
NCCl...OPH ₃ ...HMgH	0.01279	0.00076	0.00662	0.00061
NCBr...OPH ₃ ...HMgF	0.01511	0.00066	0.00608	0.00068
NCBr...OPH ₃ ...HMgCl	0.01511	0.00066	0.00611	0.00067
NCBr...OPH ₃ ...HMgBr	0.01511	0.00066	0.00613	0.00067
NCBr...OPH ₃ ...HMgH	0.01546	0.00101	0.00684	0.00084

sity (ρ) at bond critical points (BCPs) located between A, B and C molecules in the triads and its change ($\Delta\rho$) relative to the corresponding dyads are shown in Table 7. In the ternary complexes, the electron density at the A...B BCP is in the range of 0.00689–0.01546 au and at the B...C BCP is in the range of 0.00557–0.00684 au. The results show that the electron density values at the BCPs in all the triads are greater than that in the corresponding dyads, which indicates the strengthening of the interactions. So, comparing the results of the triads and the corresponding dyads may indicate the presence of the cooperative effect.

4. Conclusions

MP2/6-311++G(d,p) level calculations were performed to study the interplay between halogen and pnictogen-hydride bonds which coexist in the NCX...OPH₃...HMgY (X = F, Cl, Br; Y = F, Cl, Br, H) complexes. The σ -hole was detected on the outer surface of OPH₃ molecule. The σ -hole potential in the OPH₃ increases with the presence of halogen bond in NCX...OPH₃ dyads, which means that the complexes are better electron donors than those of the corresponding monomers. Also, the $V_{S,\min}$ values outside the oxygen atom become more negative due to the presence of HMgY in OPH₃...HMgY complexes. The R_{AB} and R_{BC} distances in the triads are shorter than those in the dyads. Halogen and pnictogen-hydride bonds in ternary complexes are stronger than in binary complexes. In all cases, halogen bond and pnictogen-hydride bond in triad complexes are stronger than in dyad complexes. There is positive cooperativity between the halogen bond and pnictogen-hydride bond, based on the obtained results. The amount of charge transfer in the triads is greater

than those in the corresponding dyads, according to the NBO analysis results. AIM analyses indicate that the halogen bond and pnictogen-hydride bond in the triads are reinforced with respect to the dyads.

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