Regular Article

PHYSICAL
CHEMISTRY
RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., *Vol. 5, No. 4, 771-781, December 2017*
DOI: 10.22036/pcr.2017.90701.1394

Ab Initio Studies on the Interplay between Unconventional B···X Halogen Bond and Lithium/Hydrogen/Halogen Bond in HB(CO)$_2$···XCN···YF (X = Cl, Br; Y = Li, H, Cl) Complexes

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(Received 27 June 2017, Accepted 16 August 2017)

In this paper, *ab initio* calculations were performed on the ternary complex formed by HB(CO)$_2$, XCN (X = Cl, Br) and YF (Y = Li, H, Cl). In these complexes boron acts as a non-classical electron donor to form an unconventional halogen bond. The cooperative effect between the B···X halogen bond and lithium/hydrogen/halogen bond was investigated. The calculated results show that the B···X and N···Y interactions in the termolecular complexes are stronger compared with those in their corresponding bimolecular complexes. The cooperativity energies of these termolecular complexes span a range from -1.06 to -2.75 kJ mol^{-1} and -1.63 to -4.34 kJ mol^{-1} for X = Cl and Br, respectively, indicating the presence of the cooperativity effect. The nature of interactions is analyzed in terms of parameters derived from molecular electrostatic potential (MEP), natural bond orbital (NBO) and atoms in molecules (AIM) analyses. The amount of charge transfer in the termolecular complexes is stronger compared with those in their corresponding bimolecular complexes. The obtained results from AIM analyses demonstrate that B···X and N···Y bonds in the termolecular complexes are amplified compared to the bimolecular complexes.

Keywords: Cooperativity, Boron, Noncovalent interactions, Molecular electrostatic potential

INTRODUCTION

Noncovalent interactions have been considered as an important area of research because of their unique role in chemistry, physics and molecular biology [1-4]. Although previous studies for noncovalent interactions have mostly focused on the hydrogen bond [5-13], more recently interest in new types of interactions, such as lithium [14,15], halogen [16,17], chalcogen [18,19], pnicogen [20,21] and tetrel [22,23] bonds has greatly increased. The halogen bond refers to an electrostatic-driven R-X···D interaction, where X is a halogen (mostly Cl, Br or I) and D is an electron donor. The formation of halogen bond is generally associated with the σ-hole concept proposed by Politzer and co-workers [24-26]. This term refers to the region of positive electrostatic potential that are present on the outer most portion of the halogen's surface along the R-X bond's direction.

Because of its electron deficiency, boron has long been regarded as an electron-acceptor atom [27]. However, in recent years, a few studies have proposed that boron may act as an electron-pair donor. In 2011, Alkorta *et al.* demonstrated that B-B bond can act as an electron donor to form a hydrogen bond [28]. There are also other studies indicating that boron can act as an electron donor to form a halogen bond [29,30].

Cooperativity is a very important phenomenon in molecular recognition, chemical reactions and regulation of biochemical processes [31-33]. There is two types of

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*Corresponding author. E-mail: M.Vatanparast@tabrizu.ac.ir cooperativity: the first is positive cooperativity which can stabilize a many-body structure, and the second is negative cooperativity which can decrease the stability of complexes [34]. The cooperativity between the different types of noncovalent interactions has been extensively studied [35-46]. For example, recently, we investigated the cooperative effects between tetrel bond and halogen bond in XCN···F_2CO···YCN complexes (X = H, F, Cl, Br; Y = F, Cl, Br) [47].

In the present study, our goal is to investigate systematically into the cooperative effect between the B···X halogen bond and lithium/hydrogen/halogen bonds in $HB(CO)_2$···XCN···YF (X = Cl, Br; Y = Li, H, Cl) complexes (See Fig. 1). In these complexes boron acts as a non-classical electron donor to form an unconventional halogen bond. In order to investigate the nature of the cooperativity, atoms in molecules (AIM) [48], molecular electrostatic potential (MEP) [25], and natural bond orbital (NBO) [49] analyses are performed.

COMPUTATIONAL METHODS

In this study, the *ab initio* calculations are performed at MP2/aug-cc-pVTZ level of theory using Gaussian 03 program package [50]. The vibrational frequencies were also calculated at the same level of theory and no imaginary values were obtained, indicating that the stationary points correspond to local minima on the potential energy surface. The interaction energy for complexes was obtained at MP2/aug-cc-pVTZ level as the difference between the energy of the complex and the sum of monomer energies. The basis set superposition error (BSSE) values were calculated using counterpoise method and the interaction energies were corrected by these values [51].

MEPs were computed on the 0.001 electrons/Bohr^3 contour of the electronic density using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) [52]. AIM calculation was performed on the optimized structures using Bader's atoms-in-molecule theory implemented in the AIM2000 program [53]. Moreover; NBO analyses of all structures were performed at the MP2/aug-cc-pVTZ level of theory using the NBO program [54] as implemented in the Gaussian program package.

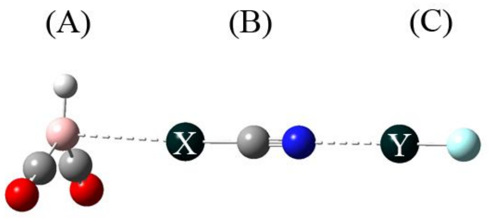
RESULTS AND DISCUSSION

Molecular Electrostatic Potential

MEP is one of the ways that can help to assess the nature of intermolecular interactions and also it can help to predict the behavior of noncovalent interactions. The three dimensional MEP maps on the 0.001 electron/Bohr^3 electron density isosurfaces of the monomers $HB(CO)_2$, ClCN and LiF and their complexes are illustrated in Fig. 2. For XCN (X = Cl and Br), a positive σ-hole was discovered on the X atom. There is also a negative area of MEP beyond the N atom along the extension of C-N bond. The most positive ($V_{S,max}$) and most negative ($V_{S,min}$) electrostatic potentials are given in Table 1. As clearly seen in Table 1, the $V_{S,max}$ values, 39.75 kcal mol^{-1} and 42.58 kcal mol^{-1} are for ClCN and BrCN monomers, respectively. Also, the $V_{S,min}$ values are -32.34 kcal mol^{-1} for ClCN and -33.05 kcal mol^{-1} for BrCN monomers. The minimum value of the MEP for $HB(CO)_2$ is -9.41 kcal mol^{-1} that is located above the B atom. Therefore, $HB(CO)_2$···XCN (X = Cl and Br) complexes could be formed by the B···X halogen bond. From Table 1, it is obvious that with the formation of the B···X halogen bond the $V_{S,min}$ values on the N atom in $HB(CO)_2$···XCN dyads becomes more negative, showing that the complexes are better electron donors than those of the corresponding monomers. On the basis of Table 1, the $V_{S,min}$ values outside the N atom in $HB(CO)_2$···ClCN and $HB(CO)_2$···BrCN are -33.75 kcal mol^{-1} and -34.65 kcal mol^{-1}, respectively. These values are more negative than for the XCN monomer ($V_{S,min}$ = -32.34 kcal mol^{-1} and -33.05 kcal mol^{-1} for ClCN and BrCN, respectively). For YF (Y = Li, H, Cl), there is a positive area of MEP beyond the Y atom along the extension of Y-F bond. The values of $V_{S,max}$, 49.29 kcal mol^{-1}, 75 kcal mol^{-1} and 199.21 kcal mol^{-1}, increase in the order ClF < HF < LiF. Therefore, XCN···YF (X = Cl, Br and Y = Li, H, Cl) dyads could be formed. According to Table 1, when the N···Y noncovalent bond is formed, the $V_{S,max}$ values outside the X atom in XCN···YF dyads become larger than those in XCN monomer.

Geometry

The cooperative effect between noncovalent bonds can be reflected in geometrical changes. Figure 1 illustrates the optimized geometries of $HB(CO)_2$···XCN···YF (X = Cl, Br



X=Cl, Br
Y=Li, H, Cl

Fig. 1. General structure of the $HB(CO)_2\cdots XCN\cdots YF$ complex.

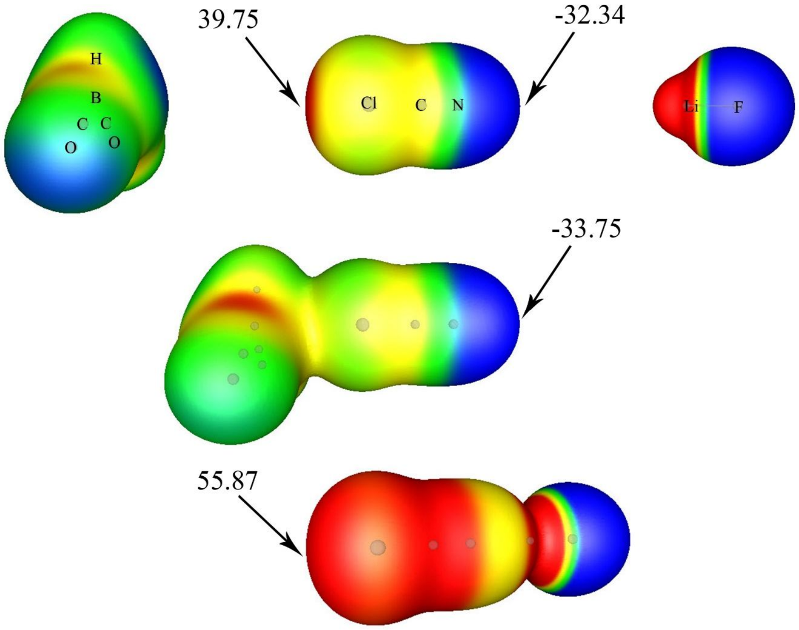


Fig. 2. Electrostatic potential map on the 0.001 (electron/Bohr3) electron density isosurfaces of isolated $HB(CO)_2$, ClCN and LiF and their binary complexes. Color ranges, in kcal mol^{-1}: red > 25 > yellow > 10 > green > -5 > blue.

and Y = Li, H, Cl). The B atom in $HB(CO)_2$ is attracted to the σ-hole of XCN, on the other hand the nitrogen atom in XCN is attracted to the σ-hole of YF. Table 2 presents the intermolecular distances for termolecular complexes and the distance difference between termolecular complexes and bimolecular complexes. The intermolecular distance in the XCN···YF bimolecular complexes is smaller than that in the $HB(CO)_2\cdots XCN$ bimolecular complexes. The binding distances in the termolecular complexes are shorter than those in the bimolecular complexes. For example, the halogen bond distance of $HB(CO)_2\cdots ClCN$ is 3.386 Å. With the formation of a lithium bond in $HB(CO)_2\cdots ClCN\cdots LiF$, the halogen bond distance becomes shorter to 3.289 Å. The lithium bond distance of ClCN···LiF is 2.055 Å. With the formation of the halogen bond in $HB(CO)_2\cdots ClCN\cdots LiF$, lithium bond distance becomes shorter to 2.049 Å. These

Table 1. The most Positive Electrostatic Potential, $V_{S,max}$ (kcal mol^{-1}), on the Cl, Br, Li, H and Cl Atoms and the most Negative Electrostatic Potential, $V_{S,min}$ (kcal mol^{-1}), on the B and N Atoms in the Monomers and Dimers[a]

	$V_{S,max}$	$V_{S,min}$		$V_{S,max}$	$V_{S,min}$
$HB(CO)_2$	-	-9.41	$HB(CO)_2$···ClCN	-	-33.75
ClCN	39.75	-32.34	$HB(CO)_2$···BrCN	-	34.65
BrCN	42.58	-33.05	ClCN···LiF	55.87	-
LiF	199.21	-	ClCN···HF	47.47	-
HF	75.87	-	ClCN···ClF	43.98	-
ClF	49.29	-	BrCN···LiF	62.85	-
			BrCN···HF	51.94	-
			BrCN···ClF	49.49	-

Table 2. Intermolecular Distances R (Å) in the Trimers and their Changes, ΔR (Å), Relative to the Corresponding Dimers

Complex(A···B···C)	R_{AB}(T)	ΔR_{AB}	R_{BC}(T)	ΔR_{BC}
$HB(CO)_2$···ClCN···LiF	3.289	-0.098	2.049	-0.006
$HB(CO)_2$···ClCN···HF	3.340	-0.046	1.850	-0.005
$HB(CO)_2$···ClCN···ClF	3.352	-0.034	2.591	-0.009
$HB(CO)_2$···BrCN···LiF	3.152	-0.115	2.043	-0.009
$HB(CO)_2$···BrCN···HF	3.211	-0.055	1.841	-0.011
$HB(CO)_2$···BrCN···ClF	3.222	-0.045	2.577	-0.013

results suggest that interactions between halogen bond in $HB(CO)_2$···XCN complexes and lithium/hydrogen/halogen bonds in XCN···YF complexes become stronger from the dyad to the triad complexes. Therefore, there is a positive cooperativity between the B···X halogen bond and lithium/hydrogen/halogen bond in termolecular complexes. For each triad, the shortening of the intermolecular distance between B and X in $HB(CO)_2$···XCN is more prominent than that distance between N and Y in XCN···YF. This indicates that the effect of N···Y on B···X bonds is more than that of B···X on N···Y bonds.

Interaction Energies

The interaction energy is one of the most powerful tools for measuring the strength of an intermolecular interaction between two kinds of noncovalent interactions [55]. The interaction energy can be obtained as the discrepancy between the total energy of the complexes and the sum of the isolated monomers in their most stable structure. The interaction energy results for the $HB(CO)_2$···XCN···YF (X

Table 3. Interaction Energies, Ei (kJ mol^{-1}), and Cooperativity Energies, Ecoop (kJ mol^{-1}), in the Investigated Dimers (D) and Trimers (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}
$HB(CO)_2$···ClCN···LiF	-71.60	-7.32	-10.02	-61.59	-64.28	-2.75
$HB(CO)_2$···ClCN···HF	-35.31	-7.32	-8.45	-26.85	-27.98	-1.46
$HB(CO)_2$···ClCN···ClF	-26.19	-7.32	-8.11	-18.08	-18.87	-1.06
$HB(CO)_2$···BrCN···LiF	-77.67	-11.02	-15.01	-62.66	-66.65	-4.34
$HB(CO)_2$···BrCN···HF	-40.00	-11.02	-12.68	-27.32	-28.98	-2.20
$HB(CO)_2$···BrCN···ClF	-30.75	-11.02	-12.18	-18.57	-19.73	-1.63

Table 4. Decomposition of Interaction Energy (kJ mol^{-1}) of the Studied Ternary Complexes

Complex(A···B···C)	ΔE_{A-B}	ΔE_{A-C}	ΔE_{B-C}	ΔE_{A-B-C}	E_R
$HB(CO)_2$···ClCN···LiF	-7.07	-0.41	-61.98	-2.82	0.68
$HB(CO)_2$···ClCN···HF	-7.28	-0.14	-27.22	-1.20	0.53
$HB(CO)_2$···ClCN···ClF	-7.32	-0.10	-18.31	-0.84	0.39
$HB(CO)_2$···BrCN···LiF	-10.63	-0.42	-62.67	-4.87	0.92
$HB(CO)_2$···BrCN···HF	-11.07	-0.14	-27.54	-2.05	0.80
$HB(CO)_2$···BrCN···ClF	-11.14	-0.10	-18.72	-1.46	0.67

= Cl, Br and Y = Li, H, Cl) are shown in Table 3. The interaction energies of halogen bonds are -7.32 and -11.02 kJ mol^{-1} in $HB(CO)_2$···ClCN and $HB(CO)_2$···BrCN dyads, respectively. From Table 3, it is clear that the range of the interaction energies of XCN···YF (X = Cl, Br and Y = Li, H, Cl) dyads is from -18.08 to -62.66 kJ mol^{-1}. Also, interaction energy of the trimers, E_i(ABC), for $HB(CO)_2$···ClCN···YF and $HB(CO)_2$···BrCN···YF complexes, span a range from -26.19 to -71.60 kJ mol^{-1} and -30.75 to -77.67 kJ mol^{-1}. As shown obviously in Table 3, the interaction energies of the halogen bond in the termolecular complexes, E_i(AB,T), are more negative than the respective E_i(AB, D) in the bimolecular complexes. For example, E_i(AB,T) of the termolecular complexes $HB(CO)_2$···ClCN···LiF is -10.02 kJ mol^{-1}, which is more negative than E_i(AB,D) of the dyad complexes $HB(CO)_2$···ClCN with the value of -7.32 kJ mol^{-1}. The similar trend has been observedfor N···Y bond interactions. The N···Y bond interactions in the triads are stronger than those in the dyads. For example, the lithium bond interaction energies of $HB(CO)_2$···ClCN···LiF and ClCN···LiF are -64.28 and -61.59 kJ mol^{-1}, respectively. So, there is a positive cooperativity between the B···X halogen bond and lithium/hydrogen/halogen bonds in $HB(CO)_2$···XCN···YF (X = Cl, Br and Y = Li, H, Cl) complexes. The cooperative energy E_{coop} is obtained from

Table 5. Electron Densities, ρ (a.u.), at the A···B and B···C Intermolecular Bond Critical Points (BCPs) in the Investigated Triads and its Changes, Δρ (a.u.), Relative to the Corresponding Dyads

Complex(A···B···C)	ρ_{AB}	$\Delta\rho_{AB}$	ρ_{BC}	$\Delta\rho_{BC}$
$HB(CO)_2$···ClCN···LiF	0.00835	0.00121	0.02307	0.00042
$HB(CO)_2$···ClCN···HF	0.00764	0.00050	0.02972	0.00041
$HB(CO)_2$···ClCN···ClF	0.00751	0.00037	0.02197	0.00050
$HB(CO)_2$···BrCN···LiF	0.01339	0.00238	0.02357	0.00069
$HB(CO)_2$···BrCN···HF	0.01202	0.00101	0.03052	0.00086
$HB(CO)_2$···BrCN···ClF	0.01180	0.00079	0.02281	0.00076

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}
$HB(CO)_2$···ClCN···LiF	0.01038	0.00371	0.02986	0.00066
$HB(CO)_2$···ClCN···HF	0.00821	0.00154	0.01609	0.00057
$HB(CO)_2$···ClCN···ClF	0.00776	0.00109	0.01460	0.00076
$HB(CO)_2$···BrCN···LiF	0.02831	0.01076	0.03077	0.00110
$HB(CO)_2$···BrCN···HF	0.02196	0.00441	0.01693	0.00111
$HB(CO)_2$···BrCN···ClF	0.02077	0.00322	0.01582	0.00128

the following formula [56-58]:

$$E_{coop} = E_i(ABC) - E_i(AB) - E_i(BC) - E_i(AC)$$

Table 3 contains the evaluated cooperativity energy E_{coop} of triads. As clearly seen in Table 3, the E_{coop} values are negative in all studied termolecular, indicating that there is positive cooperativity between B···X and N···Y bonds in $HB(CO)_2$···XCN···YF (X = Cl, Br and Y = Li, H, Cl) complexes.

Many-body Interaction Energy Analysis

In this study, we have used many-body interaction energy analysis to calculate the two- and three-body contributions in the total interaction energy. The three-body term ($\Delta E_{A\text{-}B\text{-}C}$) is obtained from the following equation [59]: (1)

$$\Delta E_{A\text{-}B\text{-}C} = E_i\,(ABC)' - \Delta E_{A\text{-}B} - \Delta E_{B\text{-}C} - \Delta E_{A\text{-}C}$$

where $\Delta E_{A\text{-}B}$, $\Delta E_{B\text{-}C}$ and $\Delta E_{A\text{-}C}$ are the two-body terms that can be defined as the discrepancy between the energy of each molecular pair and the energy sum of the monomers, all in the geometry of triad and in similar way $\Delta E_i(ABC)'$ is defined by subtracting the total energy of the optimized termolecular complexes from the energy sum of the monomers frozen in the geometry of the termolecular complexes. Also, the total relaxation energy (E_R) of the termolecular complexes is obtained from the following equation [59]:

$$E_i(ABC) = \Delta E_{A\text{-}B} + \Delta E_{B\text{-}C} + \Delta E_{A\text{-}C} + \Delta E_{A\text{-}B\text{-}C} + E_R \tag{3}$$

The results are shown in Table 4 in which all the energies are corrected for BSSE. As clearly seen for all the complexes, the two-body interaction energies are attractive. Thus, it can be concluded that they have a positive contribution to the total interaction energy. For the two-body interaction energy in each termolecular complexes $\Delta E_{B\text{-}C}$ is larger than $\Delta E_{A\text{-}B}$. For all termolecular complexes $\Delta E_{A\text{-}C}$ is smallest because the distance between the interacting molecules A and C of the corresponding triad is the largest. The three-body interaction energy for all complexes is attractive and makes a positive contribution to the total interaction energy. As can be seen from Table 4, the relaxation energy is positive for all complexes indicating that it makes a negative contribution to the total interaction energy of the triads.

AIM Analysis

The atoms in molecules (AIM) methodology has been used for understanding the nature of various types of noncovalent interactions, extensively [48]. The electron density at the A···B and B···C bond critical points (BCPs) is applied to evaluate the cooperativity in the target complexes. Table 5 presents the values of the electron density (ρ) at bond critical points (BCPs) located between A, B and C molecules in the trimers and its change (Δρ) relative to the corresponding dimers. The electron density at the A···B BCP is in the range of 0.00751-0.01339 au and at the B···C BCP is in the range of 0.02197-0.03052 au. Based on the results, the electron density values at the BCPs in all termolecular complexes are greater than those in the corresponding bimolecular complexes, which indicates the strengthening of the interactions and may indicate the presence of the cooperative effect.

NBO Analysis

The natural bond orbital (NBO) analysis has been applied to study the nature of $HB(CO)_2$···XCN··YF (X = Cl, Br and Y = Li, H, Cl) complexes. The value of charge transfer (CT) from A to B (CT_{AB}) and from B to C (CT_{BC}) in the termolecular complexes and its change (ΔCT) relative to the corresponding bimolecular complexes are given in Table 6. In the $HB(CO)_2$···ClCN···YF triads, the values of charge transfer for the B···X bonds are in the range of 0.00776-0.01038 and for the N-Y bonds are in the range of 0.01460-0.02986, and the corresponding values in the ternary $HB(CO)_2$···BrCN···YF complexes are between 0.02077-0.02831 and 0.01582-0.03077 for B-Br and N-Y bonds, respectively. In all complexes except for $HB(CO)_2$···XCN···ClF, the charge transfer values in the N···Y bonds are larger than those in the B···X bonds. On the basis of the obtained results the charge transfer values in the triads are greater than those in the corresponding dyads, which demonstrates the strengthening of the interactions.

CONCLUSIONS

The $HB(CO)_2$···XCN···YF (X = Cl, Br and Y = Li, H, Cl) complexes have been studied with quantum chemical calculations. It was found out that the $V_{S,min}$ values outside the N atom in XCN is more negative in the presence of halogen bond in $HB(CO)_2$···XCN bimolecular complexes, that the complexes are better electron donors. Also, with the formation of the N···Y noncovalent bond, the $V_{S,max}$ values outside the X atom in XCN···YF dyads become larger than those in XCN monomer. It is clear that the binding distances in the triads are shorter than those in the dyads. For each triad, the shortening of the intermolecular distance between B and X in $HB(CO)_2$···XCN is more prominent than that between N and Y in XCN···YF. By comparing the results obtained from intermolecular distances, interaction energies and two- and three-body interaction we can claim that there is a positive cooperativity between B···X and N···Y bonds. The obtained results from AIM analyses indicate that B···X and N···Y bonds in the triads are amplified with respect to the dyads. Based on the results of NBO analysis, the amount of charge transfer in the termolecular complexes is greater than that in the corresponding bimolecular complexes.

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