Characterization of intermolecular interaction between Cl_2 and HX (X=F, Cl and Br): An ab initio, DFT, NBO and AIM study

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Abstract

The character of the intermolecular interactions in Cl_2-HX (X =F, Cl and Br) complexes has been investigated by means of the second-order Möller–Plesset perturbation theory (MP2) and the density functional theory (DFT) calculations. The results show that there are two types of lowest interaction potential equilibrium structures in the interactions between Cl_2 and HX: X···Cl type geometry and hydrogen-bonded geometry. The calculated interaction energies show that the X···Cl type structures are more stable than the corresponding hydrogen-bonded structures. The nature of the intermolecular interactions has been also investigated by natural bond orbital (NBO) and atoms in molecules (AIM). The AIM analysis reveals that both types of intermolecular interactions are "closed-shell" noncovalent interactions.

Keywords: Intermolecular interaction; halogen bond; DFT; MP2; NBO; AIM.

Introduction

Noncovalent interactions play important role in chemistry, physics, and biology, in particular, as far as intermolecular interactions and supramolecular chemistry are concerned, where the molecular assemblies are usually held together through noncovalent and, quite often, weak interactions [1,2]. Among these weak interactions, hydrogen bonding is the earliest reported and the most extensively investigated [3]. The hydrogen bond is most

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frequently defined as an X–H⋯Y interaction, where X and Y are electronegative elements and Y possess one or more lone electron pairs. However, there are also the so-called unconventional hydrogen bonds such as C–H⋯Y, X–H⋯C, X–H⋯ -electrons or even C–H⋯C [4]. Hydrogen bonds play major roles in chemical and biochemical reactions [5, 6]. Besides the hydrogen bond, a specific intermolecular interaction involving halogen atoms, as acceptors of electron density, has been under active investigation. In the halogen bonds, 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 between a donor D and an acceptor A [7-9]. Halogen bond belongs -hole interaction, which is a non-covalent interaction between a region of positive electrostatic potential on the outer surface of the halogen atoms X (a -hole) and a region of negative potential on another molecule [10]. It is increasingly recognized that halogen-bonding plays a critical role in a wide variety of biochemical phenomena such as protein–ligand complexation, and can be utilized effectively in drug design [11, 12]. The halogen bond has long been the subject of extensive experimental and theoretical investigations [13-19].

In the present study, we use quantum chemical methods to perform a systematic analysis of geometric structure and energetic stability of the intermolecular interactions of Cl_2 with hydrogen halide (HF, HCl and HBr). In addition to the energetic aspects, natural bond orbital, NBO [20], and atoms in molecules, AIM [21], analyses have been used to study the nature of hydrogen bonds and X⋯Cl type interactions.

Computational methods

All calculations in this paper have been carried out at ab initio and DFT levels of theory using the GAUSSIAN 03W program package [22] without any geometrical restrictions. The second-order Möller–Plesset perturbation theory (MP2) and the modern density functional theory (DFT) method using hybrid gradient-corrected (three-parameter nonlocal) exchange functional by Becke [23] with the gradient corrected (non-local) correlation functional of Lee, Yang and Parr [24] have been employed. The basis set applied here was Pople-style 6-311++G(d,p) basis set [25]. The optimized structural parameters are used in the vibrational frequency calculations at the same levels of theory to verify the nature of minima.
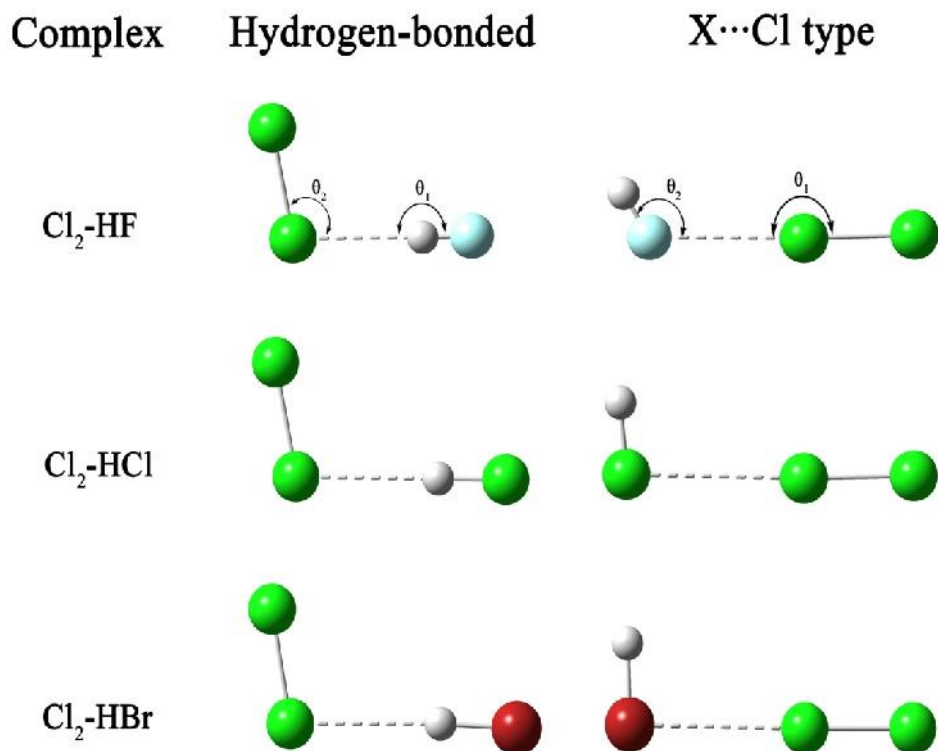
Figure 1. The optimized geometries of X···Cl type and hydrogen-bonded complexes for the studied compounds

The interaction energy (E) is calculated by evaluating the difference between the total energies of complex ($E_{complex}$) and individual monomers according to the following expression:

$$\text{E} = E_{complex} - E_{Cl_2} - E_{HX}$$

In order to take into account the basis set superpostion error (BSSE), the values of interaction energy were corrected with the Boys and Bernardi procedure [26], to give the counterpoise corrected interaction energies (E^{CP}).

The natural bond orbital (NBO) analysis was used to understand the nature of the intermolecular interactions in the studied compounds. NBO analysis has been performed by the NBO 3.1 program [27]. The topological properties of the electron density at the bond critical points (BCPs)

have been characterized using the atoms in molecules methodology (AIM) [21] by means of the AIM2000 software [28] at the B3LYP/6-311++G(d,p) level.

Results and discussion

All possible geometric configurations on the potential surface of monomers and the title system complexes were optimized by the B3LYP and MP2 level with the 6-311++G(d,p) basis set. Two hydrogen-bonded and X···Cl type structures of the Cl_2 with hydrogen halide HX (HF, HCl and HBr) were obtained. Optimized structures of all these complexes are displayed in Figure 1. Table 1 presents the interaction energies (ΔE), basis-set superposition error (BSSE), interaction energies corrected for BSSE (ΔE^{CP}), and dipole moments (μ) obtained at the B3LYP/6-311++G(d,p) and MP2/6-

311++G(d,p) levels. The results of B3LYP calculations show that the interaction energies E^{CP} of hydrogen bonded complex decrease in the order HF>HCl>HBr. This order is correlated to the electronegativity of the X atom of the hydrogen halide HX. In addition, it can be observed from Table 1 that the MP2 calculations show the same trend. The interaction energies E^{CP} of the X···Cl type complex at B3LYP/6-311++G(d,p) level are in the order HF>HBr>HCl. The results of MP2 calculations also show the same trend. It is interesting to compare the hydrogen bonded complex with the corresponding X···Cl type complex. The interaction energies corrected for BSSE (ΔE^{CP}) indicate that all of X···Cl type complex is more stable than the corresponding hydrogen-bonded complexes.

Table 1. Selected interaction energies, basis-set superposition error (BSSE) and dipole moments[a]

Complex	B3LYP/6-311++G(d,p)				MP2/6-311++G(d,p)			
	E	BSSE	E^{CP}		E	BSSE	E^{CP}	
Cl_2···HF	-1.507	0.543	-0.963	2.440	-2.265	1.729	-0.536	2.439
Cl_2···HCl	-0.874	0.537	-0.337	1.700	-1.751	1.407	-0.344	1.645
Cl_2···HBr	-0.683	0.504	-0.178	1.351	-1.659	1.375	-0.284	1.343
HF···Cl_2	-1.272	0.251	-1.020	2.206	-1.557	0.732	-0.826	2.355
HCl···Cl_2	-0.968	0.309	-0.659	1.523	-1.508	1.006	-0.501	1.479
HBr···Cl_2	-1.073	0.119	-0.954	1.386	-1.433	0.821	-0.612	1.182

[a]All energies are in kcal/mol, dipole moments in debye.

Some structural parameters and the harmonic stretching vibrational frequencies for complexes are summarized in Table 2. As can be seen, there is an elongation of the H–X bond upon hydrogen-bonded complex formation. The corresponding harmonic vibrational frequencies are also shown in Table 2. Also, the frequency analysis shows the red-shifting character of the Cl···H–X interaction. In agreement with the computed H–X bond elongation, the H–X stretching frequencies are lower by 91.9, 44.9 and 2.3 cm^{-1} (at B3LYP/6-311++G(d,p) level) in Cl₂···HF, Cl₂···HCl and Cl₂···HBr, respectively, than the corresponding frequencies in the monomers. The individual red shift can be correlated directly to the magnitude of H–X bond elongations. In agreement with the interaction energies, the extent of the red-shifts is shown to decrease in sequence from Hf to HBr. Also, analyzing of the data from Table 2 shows that, in the case of X···Cl type complexes, there is an elongation of the Cl–Cl bond upon complex formation.

Table 2. Selected geometrical parameters and harmonic stretching vibrational frequencies.[a] The data in parentheses are related to monomers[a]

Complex	B3LYP/6-311++G(d,p)					MP2/6-311++G(d,p)				
	d(Cl···H)	d(H–X)	1	2	(H–X)	d(Cl···H)	d(H–X)	1	2	(H–X)
Cl₂···HF	2.440	0.926(0.922)	178.7	100.5	4003.9(4095.8)	2.443	0.918(0.917)	178.7	100.4	4147.1(4196.1)
Cl₂···HCl	2.725	1.290(1.287)	179.9	101.6	2882.8(2927.7)	2.708	1.275(1.273)	177.2	94.0	3070.6(3087.3)
Cl₂···HBr	2.813	1.429(1.427)	176.9	99.7	2596.3(2598.6)	2.763	1.413(1.412)	178.8	89.7	2732.3(2738.8)
	d(X···Cl)	d(Cl–Cl)	1	2	(Cl–Cl)	d(X···Cl)	d(Cl–Cl)	1	2	(Cl–Cl)
HF···Cl₂	2.870	2.057(2.053)	177.9	121.8	507.9(512.9)	2.916	2.027(2.024)	178.0	136.6	542.6(545.8)
HCl···Cl₂	3.330	2.061(2.053)	177.6	96.9	498.6(512.9)	3.445	2.027(2.024)	176.2	101.3	541.6(545.8)
HBr···Cl₂	3.344	2.067(2.053)	178.9	93.6	485.3(512.9)	3.571	2.028(2.024)	177.1	95.4	539.9(545.8)

[a] bond lengths (d) are in Å, bond angles ( ) are in °, vibrational frequencies ( ) are in cm^{-1}.

The frequency analysis reveals the red-shifting character of the H–X···Cl interactions in the complexes. In agreement with the computed Cl–Cl bond elongation, the Cl–Cl stretching frequencies are lower by 5.0, 14.3 and 27.6 cm^{-1} (at B3LYP/6-311++G(d,p) level) in HF···Cl₂, HCl···Cl₂ and HBr···Cl₂, respectively, than the corresponding frequencies in the monomers.

To better understand the intermolecular interactions, NBO analysis has been carried out at the B3LYP/6-311++G(d,p) level. NBO analysis stresses the role of charge transfer and intermolecular orbital interactions in the complexes. This is actualized by considering all possible interactions between the "filled" Lewis-type NBOs and the "empty" non-Lewis NBOs, and estimating their energetic importance through second order perturbation theory. The orbitals occupancy, orbital energy, the second-order perturbation energy ($E^{(2)}$) (also be termed by the donor-acceptor orbitals interaction stabilization energies that can be taken as an index to judge the strength of the intermolecular interactions) and the difference of energies between acceptor and donor NBOs ( ), are presented in Table 3.

Table 3. The orbitals occupancy, orbital energy, the second-order perturbation energy ($E^{(2)}$) and the difference of energies between acceptor and donor NBOs ( )

Complex	Donor	Orbital occupancy	Orbital energy	Acceptor	Orbital occupancy	Orbital energy	$E^{(2)}$	
$Cl_2 \cdots HF$	LP(Cl)	1.98671(1.99736)	-0.41599	*(H–F)	0.00965(0.00000)	0.00965	3.08	0.42564
$Cl_2 \cdots HCl$	LP(Cl)	1.98917(1.99736)	-0.40023	*(H–Cl)	0.00728(0.00000)	0.00728	1.84	0.40751
$Cl_2 \cdots HBr$	LP(Cl)	1.98934(1.99736)	1.98934	*(H–Br)	0.00749(0.00036)	0.09565	1.64	-1.89369
$HF \cdots Cl_2$	LP(F)	1.99014(1.99816)	-0.53532	*(Cl–Cl)	0.00800(0.00000)	-0.08607	1.64	0.44925
$HCl \cdots Cl_2$	LP(Cl)	1.98027(1.99866)	-0.37042	*(Cl–Cl)	0.01779(0.00000)	-0.09420	2.17	0.27622
$HBr \cdots Cl_2$	LP(Br)	1.96392(1.99904)	-0.34414	*(Cl–Cl)	0.03335(0.00000)	-0.09508	3.42	0.24906

[a]The calculations are carried out at B3LYP/6-311++G(d,p) level. $E^{(2)}$ is in kcal/mol, all other values in a.u.

For the hydrogen-bonded complexes, the interaction between the lone pair (LP) orbital of Cl atom, as donor, and the anti-bonding sigma orbital of the H–X bond, as acceptor, is directly related to the hydrogen-bond. The second-order perturbation energies (E(2)) are computed to be 3.08, 1.84 and 1.64 kcal/mol for LP(Cl) *(H–F), LP(Cl) *(H–Cl) and LP(Cl) *(H–Br) interactions, respectively, which are comparable in magnitude to their interaction energies ECP. For the X···Cl type complexes, the charge transfer from the lone pair (LP) orbital of X atom in the hydrogen halide (HX) is mainly directed to the anti-bonding sigma orbital of the Cl–Cl bond of the Cl2 molecule and the second-order perturbation energies (E(2)) are computed to be 1.64, 2.17 and 3.42 kcal/mol for LP(F) *(Cl–Cl), LP(Cl) *(Cl–Cl) and LP(Br) *(Cl–Cl) interactions, respectively. The topological analysis of Bader's theory is applied in this

study. The topological analysis of the electron density shows the presence of a single intermolecular bond critical point (BCP) in all the studied complexes. Figure 2 displays the molecular graphs and contour maps of the Laplacian of the electron density for all complexes. Dashed contours denote negative and solid contours show positive values of $\nabla^2 \rho_b$. The Laplacian of the electron density $\nabla^2 \rho_b$, provides information about either the charge concentration ($\nabla^2 \rho_b < 0$) or the charge depletion ($\nabla^2 \rho_b > 0$) of the electron distribution.
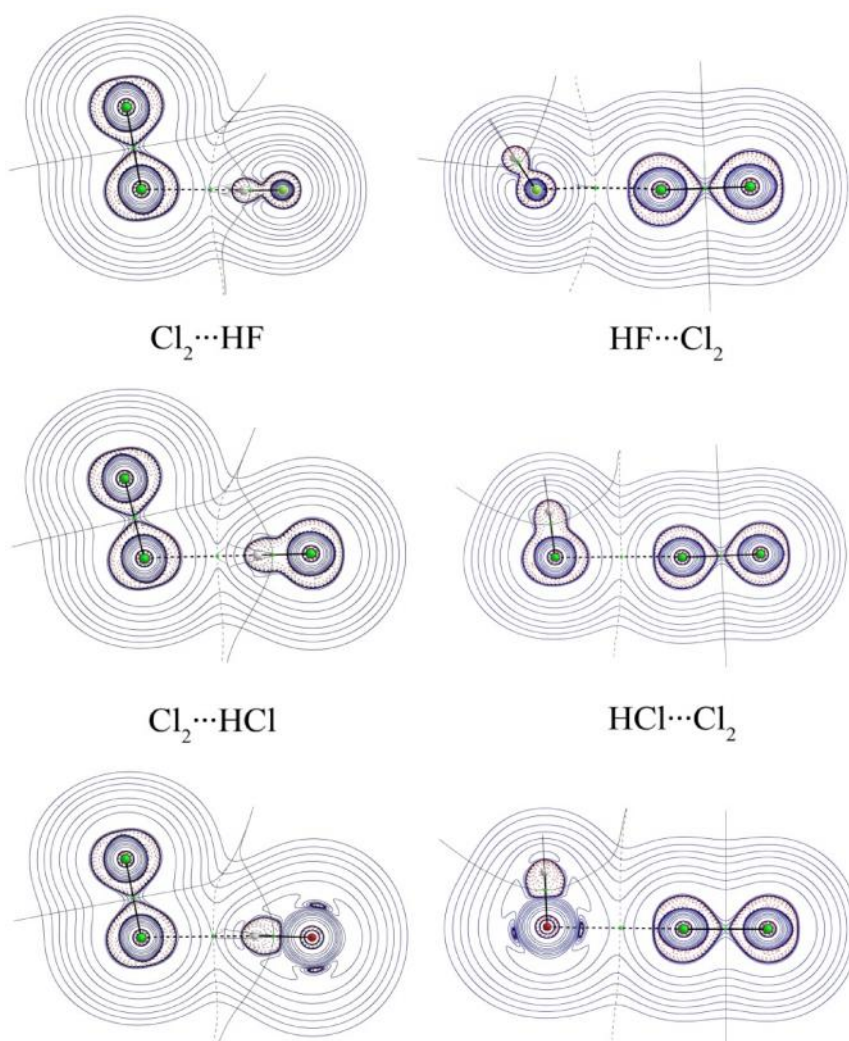

Figure 2. The contour maps of Laplacian of the electron density for the studied compounds. Dashed contours denote negative and solid contours positive values of $\nabla^2 \rho_b$.

Table 4. The topological and energetic properties at the Cl···H and X···Cl BCPs of the complexes[a]

Complex	ρ_b	$\nabla^2\rho_b$	ε	G_b	V_b	H_b	$-G_b/V_b$
Cl_2···HF	0.0122	0.0429	0.0722	0.0081	-0.0054	0.0027	1.4927
Cl_2···HCl	0.0080	0.0230	0.0824	0.0045	-0.0033	0.0012	1.3618
Cl_2···HBr	0.0071	0.0194	0.0860	0.0039	-0.0030	0.0009	1.3164
HF···Cl_2	0.0107	0.0468	0.0953	0.0103	-0.0089	0.0014	1.1572
HCl···Cl_2	0.0082	0.0317	0.0961	0.0062	-0.0044	0.0018	1.3994
HBr···Cl_2	0.0102	0.0353	0.0871	0.0071	-0.0054	0.0017	1.3172

[a]The calculations are carried out at B3LYP/6-311++G(d,p) level. All values in a.u.

The topological and energetic properties at the BCPs of the interactions between Cl_2 and HX were analyzed in terms of the following parameters: the electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$), the bond ellipticity (ε), the kinetic electron energy density (G_b), the potential electron energy density (V_b), the total electron energy density ($H_b=G_b+V_b$), and $-G_b/V_b$. The results are collected in Table 4. The character of the A···B interaction could be classified as a function of the Laplacian of the electron density and the total electron energy density at the associated critical points. A negative value of $\nabla^2\rho_b$ indicates that there is a shared interaction as in a covalent bond, and a positive value of $\nabla^2\rho_b$ that concerns the interaction of closed-shell complexes: ionic interactions, van der Waals forces, or hydrogen bonding. $\nabla^2\rho_b$ and H_b may be useful in characterization of the strength of the interactions. It means that for strong A···B interactions ($\nabla^2\rho_b < 0$ and $H_b < 0$), the

covalent character is established; for medium strength ($\nabla^2\rho_b > 0$ and $H_b < 0$), their partially covalent character is defined, and weak strength ($\nabla^2\rho_b > 0$ and $H_b > 0$) are mainly electrostatic.

According to Ziolkowski et al. [29], the $-G_b/V_b$ ratio has been used as a measure of the covalency in noncovalent interactions. Values greater than 1, generally, indicate a noncovalent interaction, whereas ratios smaller than unity are indicative of the covalent nature of the interaction. In Table 4, for all hydrogen-bonded and X···Cl type complexes, $\nabla^2\rho_b > 0$, $H_b > 0$, and $-G_b/V_b > 1$. Hence, the studied interactions display the characters of "closed-shell" noncovalent interactions.

From Table 4, comparing the values of the electron density (ρ_b) in hydrogen bonded complex, it can be seen that the electron density decreases in the order HF>HCl>HBr. Also, the electron densities of the X···Cl type complex are in the order HF>HBr>HCl.

These results are in the line with the interaction energy.

Conclusion

Ab initio and DFT calculations have been employed to optimize the geometries between Cl$_2$ and HX (HF, HCl and HBr) at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. Atoms in molecules (AIM) and Natural bond orbital (NBO) analyses were performed to investigate the nature of the intermolecular interactions in studied target molecules. There are two types of the lowest interaction potential equilibrium structures in the interactions between Cl$_2$ and HX: X···Cl type geometry and hydrogen-bonded geometry. The interaction energies corrected for BSSE (E^{CP}) of the X···Cl type complexes are greater than the corresponding hydrogen-bonded complexes. The atoms in molecule analyses show that the studied interactions can be classified as "closed-shell" noncovalent interactions.

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