IMPROPER HYDROGEN BONDS – A THEORETICAL STUDY ABOUT THE MOLECULAR STRUCTURE OF INTERMOLECULAR SYSTEMS FORMED BY $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{X}$ AND $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ WITH $\text{X} = \text{Cl}^-$ OR F^- AND $\text{Y} = \text{Cl}$ OR F

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ABSTRACT

In this work is presented a theoretical study of the molecular properties of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ intermolecular systems with $\text{X} = \text{Cl}^-$ or F^- and $\text{Y} = \text{Cl}$ or F . In the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ complex, it is formed a traditional hydrogen bond between the Cl^- or F^- anions and the hydrogen atom of the methyl. About the $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ complex, it was observed an improper hydrogen bond because the carbon atom of the methyl cation function as a proton acceptor. In this insight, the capacity of methane to interact with halogen anions (Cl^- or F^-) and molecular acids (HCl or HF) was examined at the B3LYP/6-311++G(3df,3dp) level of calculation. Moreover, the interaction strengths of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ complexes was evaluated by computing their intermolecular distances and binding energies. Finally, QTAIM calculations also were executed with the purpose to examine the intermolecular interactions through the quantification of their electronic densities (ρ) as well as by the interpretation of the Laplacian operators ($\nabla^2\rho$).

Keywords: Methane; anions; acids; hydrogen bonds; improper hydrogen bonds.

INTRODUCTION

It is known by the scientific community the existence of several intermolecular interaction types, which can be represented by hydrophobic, dipole-dipole and hydrogen bonding¹. Characterized by an interaction between a center containing high electronic density concentration and often an electropositive atom², the hydrogen bonding plays a vital role in studies of chemical, physical, and biological systems³. However, few years ago a new class of intermolecular systems known as Dihydrogen-Bonded (DHB)⁴ complexes has been discovered. These systems are formed through the ability of hydrogen atoms to form an intermolecular contact with protonic centers. In other words, not necessarily the hydrogen atoms interact with high electronic sites such as lone electron pairs or π bonds⁵.

Through the X-rays diffraction analysis, the Crabtree's research group⁶ has shown that DHB complexes are formed by proton donors ($\text{H}^{\delta+}$) and hydride compounds ($\text{H}^{\delta-}$)⁷⁻⁸. On the other hand, by considering the formation of the $\text{N}-\text{H}^{\delta+}\cdots\text{H}^{\delta-}-\text{Y}$ DHB complex, where normally N is an electronegative group and Y is a alkali metal (AM) or alkali earth metals (AEM)⁹⁻¹⁴, some theoretical investigations documented by Grabowski¹⁵ has revealed the existence of $\text{H}^{\delta+}\cdots\text{H}^{\delta-}-\text{Y}$ DHB complexes formed by Lithium, Sodium, Magnesium, and a different proton acceptor: the methane. Furthermore, it was also verified that the $\text{F}-\text{H}^{\delta+}\cdots\text{H}^{\delta-}-\text{CH}_3$ DHB complex is formed through the interaction of the methane with hydrofluoric acid. In addition, Grabowski and co-workers¹⁶ demonstrated that the methane also interact with alkali metals and alkali earth metals, where the carbon atom is sufficiently electronegative to form electrostatic interactions with Beryllium or Sodium, for instance. However, the methane also presents an opposite behavior to that observed in DHB complexes, where Cl^- and I^- interact with the hydrogen atoms of the $\text{C}-\text{H}$ bond. Thereby, it is then formed the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{Cl}^-$ and $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{I}^-$ complexes. By all these reasons, definitively the methane can be considered a convergence point by taking into account ionic and neutral intermolecular systems, of which we can mention those formed by F^- and Cl^- entities, or else molecules such as hydrochloric acid.

About all aspects cited above, in this work is proposed a theoretical study about the capacity of methane to interact with donors and acceptors of charge density. Such study will be developed through the examination of molecular properties of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ intermolecular systems with $\text{X} = \text{Cl}^-$ or F^- , and $\text{Y} = \text{Cl}$ or F . For this proposal, I will evaluate structural parameters and electronic properties with the purpose to describe the intermolecular strength through the measurement of distance, $R(\text{H}^{\delta+}\cdots\text{X})$, and binding energy, ΔE . Moreover, another electronic evaluation will be effectuated here by means of the Quantum Theory of Atoms in Molecules (QTAIM)¹⁷. From QTAIM calculations, the chemical topology is modeled by a numeric integration of the electronic density, allowing then the description of the molecular interactions through the identification of Bond Critical Points (BCP)¹⁸ between neighboring atoms. The BCP are the basis used by QTAIM algorithm to identify maxima and minima of electronic density. Thus, covalent

bonds containing high electronic density are identified as shared interactions¹⁹ and, centers with low electronic densities, in special those identified as being intermolecular and intramolecular contacts are then known as closed-shell interactions, of which the hydrogen bonding is considered a classic example²⁰⁻²⁵. So, QTAIM analyzes the interaction strength in hydrogen bonded-complexes through the topological parameters, such as the electronic density, ρ , and the Laplacian field, $\nabla^2\rho$. The Laplacian $\nabla^2\rho$ at the BCP provides a measure of the extent to which the charge density is locally compressed or expanded in the chemical bonds. About this, there are two important criteria often used to characterize the chemical bonds according to QTAIM approach: *i*) in the case of locally concentrated charge density, $\nabla^2\rho < 0$, it is indicated a shared interaction, e.g., covalent or unsaturated bonds. *ii*) When the charge density is locally depleted, $\nabla^2\rho > 0$, it is identified a closed-shell interaction, such as hydrogen bonds or else ionic bonds.

Computational procedure

Through the application of the B3LYP/6-311++G(3df,3dp) level of theory implemented in GAUSSIAN 98W software²⁶, the calculations of the optimized geometries of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Y}$ complexes were performed using default convergence criteria. The hybrid B3LYP²⁷ of the Density Functional Theory (DFT)²⁸ was chosen because it has been documented a lot of studies of hydrogen complexes²⁹ in which their molecular parameters were successfully evaluated by means of hybrid density functionals³⁰⁻³¹. The supermolecule approach³² was used to determine the values of the binding energies ΔE , which were corrected by the calculations of the Basis Sets Superposition Error (BSSE)³³ performed through the MESSAGE keyword in the GAUSSIAN 98W program. Finally, the results of the corrected binding energies ΔE^c were computed according to the equation (1), and all QTAIM calculations were executed in the GAUSSIAN 98W program.

$$\Delta E^c = \Delta E - \text{BSSE} \quad (1)$$

RESULTS AND DISCUSSION

Geometry and energy

The Figure 1 illustrates the optimized geometries of the $\text{H}_3\text{C}-\text{H}\cdots\text{Cl}^-$ (**a**), $\text{H}_3\text{C}-\text{H}\cdots\text{F}^-$ (**b**), $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{Cl}$ (**c**) and $\text{H}_3\text{C}^{\delta-}\cdots\text{H}-\text{F}$ (**d**) complexes obtained through the B3LYP/6-311++G(3df,3dp) calculations. In Table 1 are listed the main structural parameters of these complexes, such as their intermolecular distances, $R(\text{H}^{\delta+}\cdots\text{X})$ and $R(\text{C}^{\delta-}\cdots\text{H}-\text{Y})$, and deformations on methane molecule, $\delta r_{\text{C}-\text{H}}$. Moreover, in Table 1 are also presented the values of the corrected binding energies, ΔE^c , as well as the results of the non-corrected binding energies, ΔE , and BSSE amounts.

Fig. 1. Optimized geometries of the $\text{H}_3\text{C}-\text{H}\cdots\text{Cl}^-$ (a), $\text{H}_3\text{C}-\text{H}\cdots\text{F}^-$ (b), $\text{H}_3\text{C}^+\cdots\text{H}-\text{Cl}$ (c) and $\text{H}_3\text{C}^+\cdots\text{H}-\text{F}$ (d) complexes using the B3LYP/6-311++G(3df,3dp) calculations.

Table 1. Structural and electronic parameters of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{Y}$ complexes using the B3LYP/6-311++G(3df,3dp) calculations.

Parameters	$\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{Y}$ complexes			
	X = Cl^-	X = F^-	Y = Cl	Y = F
$R(\text{H}^{\delta+}\cdots\text{X})$	1.9823	0.9340	—	—
$R(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$	—	—	2.072	2.1098
$\delta r\text{C}-\text{H}^{\alpha\delta+}$	0.0305	0.9955	—	—
$\delta r\text{C}-\text{H}^{\alpha}$	-0.0018	-0.0090	-0.0119	-0.0116
$\delta r\text{C}-\text{H}^{\beta}$	-0.0018	-0.0090	-0.0119	-0.0116
$\delta r\text{H}-\text{Y}$	—	—	0.020	0.0121
ΔE	-4.9	-135.6	-9.30	-14.11
BSSE	-0.80	-19.3	-0.46	-1.50
ΔE^c	-4.1	-116.3	-8.84	-12.61

* Values of R are given in angstroms, Å;

* Values of ΔE^c , BSSE, and ΔE are given in kJ mol^{-1} .

Firstly, analyzing the $R(\text{H}^{\delta+}\cdots\text{X})$ intermolecular distances of the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{Cl}^-$ and $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ complexes, the values of 1.9823 Å and 0.9340 Å indicates that the fluorine ion provides a stronger bound system, once $\text{H}_3\text{C}^+\cdots\text{H}-\text{Cl}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{F}$ complexes present longer intermolecular distances, whose values of $R(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$ are 2.072 Å and 2.1098 Å, respectively. As it is well established that hydrogen bonds often presents typical distance value in range of 2.5 Å⁵, the results of 0.9340 Å of the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ is considered a very short interaction. However, an interesting aspect related to the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ must be emphasized. Note that the methane structure assumes a planar configuration, or in other words, there is a tendency to form the CH_3^+ methyl cation and hydrofluoric acid molecular. Indeed, by means of the binding energy of -116.3 kJ mol^{-1} , the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ complex is more stable than $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{Cl}^-$, which presented a value for ΔE^c of -4.1 kJ mol^{-1} . As the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ complex presented the stronger interaction, it was verified drastic alterations on its structure, e.g., the variation of 0.9955 Å of the $\text{C}-\text{H}^{\delta+}$ bond in comparison with results of 1.0881 Å and 2.0837 Å of the methane isolated and when the $\text{H}_3\text{C}-\text{H}^{\delta+}\cdots\text{F}^-$ complex is formed, respectively.

QTAIM topology

By giving continuity the discussion of the molecular properties of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{Y}$ complexes, the Table 2 present the results of the QTAIM calculations. According to the low values of ρ and positive results of $\nabla^2\rho$, the $(\text{H}^{\delta+}\cdots\text{X})$ and $(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$ contacts were identified as closed-shell interactions¹⁷, in other words, concentration of charge density in separate nuclei. Moreover, I should assume that $(\text{H}^{\delta+}\cdots\text{X})$ and $(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$ are

considered ionic hydrogen bonds, which are improper types because the carbon of methane is a proton acceptor (c and d complexes), as will be discussed later. However, the interaction of the fluorine ion with the methane still provides special aspects, once the electronic density of 0.365 e.u. for $\text{H}^{\delta+}\cdots\text{F}^-$ is higher in comparison with the $\text{H}^{\delta+}\cdots\text{Cl}^-$, $\text{C}^{\delta+}\cdots\text{H}-\text{Cl}$ and $\text{C}^{\delta+}\cdots\text{H}-\text{F}$ interactions, whose values are in range of 0.021-0.041 e.u. In this sense, the stronger interaction of fluorine ion with the methane suggests another kind of closed-shell interaction, which is formed between the carbon and the $\text{H}^{\delta+}$ hydrogen atom of HF, as can be seen in the BCP depicted in Figure 2 (b).

Table 2. QTAIM topological parameters of the $\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{Y}$ complexes.

Parameters	$\text{H}_3\text{C}-\text{H}\cdots\text{X}$ and $\text{H}_3\text{C}^+\cdots\text{H}-\text{Y}$ complexes			
	X = Cl^-	X = F^-	Y = Cl	Y = F
$\rho(\text{H}^{\delta+}\cdots\text{X})$	0.041	0.365	—	—
$\rho(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$	—	—	0.021	0.022
$\rho\text{C}-\text{H}^{\delta+}$	0.253	—	—	—
$\rho\text{C}\cdots\text{H}^{\delta+}-\text{F}$	—	0.021	—	—
$\rho\text{C}-\text{H}^{\alpha}$	—	—	0.290	0.291
$\rho\text{C}-\text{H}^{\beta}$	0.284	0.290	0.290	0.291
$\rho\text{H}-\text{Y}$	—	—	0.239	0.364
$\nabla^2\rho(\text{H}^{\delta+}\cdots\text{X})$	$2.7 \cdot 10^{-5}$	-3.20	—	—
$\nabla^2\rho(\text{C}^{\delta+}\cdots\text{H}-\text{Y})$	—	—	0.0422	0.0425
$\nabla^2\rho\text{C}-\text{H}^{\delta+}$	-0.825	—	—	—
$\nabla^2\rho\text{C}\cdots\text{H}^{\delta+}-\text{F}$	—	0.042	—	—
$\nabla^2\rho\text{C}-\text{H}^{\alpha}$	—	—	-0.010	-0.0106
$\nabla^2\rho\text{C}-\text{H}^{\beta}$	-1.017	-1.067	-0.010	-0.0106
$\nabla^2\rho\text{H}-\text{Y}$	—	—	-0.714	-3.18

* All values are given in electronic units (e.u.);

* $\rho_{\text{CH}} = 0.287$ e.u. and $\nabla^2\rho_{\text{CH}} = -1.107$ e.u. for the methane monomer;

* $\rho_{\text{HF}} = 0.369$ e.u. and $\nabla^2\rho_{\text{HF}} = -2.80$ e.u. for the hydrofluoric acid monomer.

Fig. 2. BCP of the $\text{H}_3\text{C}-\text{H}\cdots\text{Cl}^-$ (a), $\text{H}_3\text{C}-\text{H}\cdots\text{F}^-$ (b), $\text{H}_3\text{C}^+\cdots\text{H}-\text{Cl}$ (c) and $\text{H}_3\text{C}^+\cdots\text{H}-\text{F}$ (d) complexes

Thus, the values of ρ and $\nabla^2\rho$ of 0.021 e.u. and 0.042 e.u. indicates the co-existence of a improper hydrogen bond $\text{C}\cdots\text{H}^{\delta+}-\text{F}$, although the $\nabla^2\rho$ value of -3.2 e.u. shows that $\text{H}^{\delta+}$ and F^- interact as a shared contact. In this situation, the electronic density of 0.365 e.u. of the $\text{H}^{\delta+}-\text{F}$ bond is very similar to 0.369 e.u. of the hydrofluoric acid monomer. At last, corroborating with the results presented above, the formation of $\text{H}^{\delta+}\cdots\text{F}^-$ provokes substantial changes in the electronic structure of the intermolecular system. For instance, the weakness of the $\text{C}-\text{H}^{\delta+}$ bond has caused the formation of the improper hydrogen bond $\text{C}\cdots\text{H}^{\delta+}-\text{F}$, whose electronic density of 0.021 e.u. is lower in comparison with 0.029 e.u. of the $\text{C}-\text{H}^{\beta}$ bond.

CONCLUDING REMARKS

The capacity of methane to interact with anions Cl^- and F^- as well as molecular acids HF and HCl was demonstrated in this work. Due to the accentuated electronegative character of the fluorine, we observe that besides $\text{H}^{\delta+}\cdots\text{F}^-$ contact, a $\text{C}\cdots\text{H}^{\delta+}\cdots\text{F}$ improper hydrogen bond was formed. Such aspect was demonstrated by the QTAIM calculations, where positive and negative Laplacian results were quantified between C and $\text{H}^{\delta+}$, as well as between $\text{H}^{\delta+}$ and F. In this last case, the calculated electronic density value of 0.365 e.u. is very close to 0.369 e.u. of the hydrofluoric acid monomer.

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