A DFT AND AIM STUDY OF BLUE-SHIFTING HYDROGEN BONDS AND SECONDARY INTERACTIONS IN SMALL HETEROCYCLIC COMPLEXES

B. G. Oliveira

Departamento de Ciências Farmacêuticas, Universidade Federal de Pernambuco

50740-521, Recife – PE, Brazil

E-mail: boazgaldino@gmail.com

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Abstract

In this work, a computational study of molecular properties of small heterocyclic intermolecular systems is presented. Fundamentally, the B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) theoretical methods were used to determine the optimized geometries of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic complexes and thereby evaluate the existence of blue-shifting hydrogen bonds on these systems. A contraction of the C—H bond length of the fluoroform (HCF_3) was observed by analyzing the main structural parameters. Consequently, results of infrared spectrum analysis showed the blue-shift in the stretch frequency accompanied by a significant decrease in absorption intensity. With the purpose of comprehending this vibrational phenomenon, hybrid functional and split valence basis sets were used and topological parameters derived from Atoms-in-Molecules (AIM) theory were also applied. Moreover, the non-linear deviation in ($O\cdots H$) anti-hydrogen bonds due to the secondary interaction ($H^{\alpha}\cdots F^{\varphi}$) between the fluorine ($F^{\varphi}$) of fluoroform and axial hydrogen atoms (H^{α}) of the heterocyclic structures was verified.

Keywords: DFT, blue-shifting, hydrogen bond, heterocyclic complexes.

Resumen

Se presenta en este trabajo un estudio computacional acerca de las propiedades moleculares de pequeños sistemas heterocíclicos intermoleculares. Fundamentalmente, los métodos teóricos B3LYP/6-31G (d,p) y B3LYP/6-311++G(d,p) fueron usados para determinar las geometrías optimizadas de los complejos heterocíclicos $C_2H_4O\cdots HCF_3$ y $C_4H_6O\cdots HCF_3$ y así evaluar, en estos sistemas, la existencia de un corrimiento al azul en los enlaces de puente de hidrógeno. Analizando los parámetros estructurales principales, se observó una contracción de la longitud de la unión C-H del fluoroform (HCF_3). Como consecuencia, los resultados del análisis de espectroscopía infrarroja mostraron un corrimiento al azul de su frecuencia de estiramiento conjuntamente con una disminución significativa en la intensidad de la absorción. Con el objetivo de entender este fenómeno vibracional, se utilizaron funcionales híbridos y series de bases de valencia desdobladas. También se aplicaron parámetros topológicos derivados de la teoría *Átomos en Moléculas (*AIM). Además, se verificó la no linealidad en los enlaces anti-hidrógeno (O···H) debido la interacción secundaria (Hα···Fφ) entre el átomo de flúor (Fφ) en el fluoroformo y los átomos de hidrógeno axiales (Hα) en estructuras heterocíclicas.

Palabras claves: DFT, desplazamiento al azul, enlace de hidrógeno, complejos hetrocíclicos.

Introduction

Throughout the years, it became well-established that several molecular systems formed by non-covalent interactions have been taken focus of research in chemical, physical and biological areas [1]. Conceptually, in midst of several types of non-covalent interactions, the hydrogen bonding occupies a detached position because there is an immense quantity of phenomena in the contact between a rich charge density site and a proton donor [2], such as those involved in structures of transition state in organic reaction mechanisms [3], activation of bio-molecules [4] and development of AIDS antigen drugs [5], for instance. Only by mentioning these examples, the great importance of hydrogen bonding for the progress of the science is undeniable [6].

From classic physicochemical concepts the hydrogen bonding can be understood, essentially, according to electronic partition terms, which describe the electrostatic potential, polarizability effect, spin-exchange and repulsion terms, as well as phenomena of charge transfer. In this insight, it is well-known the relative contribution of these parameters for quantification of the total energy, although it also was established that normally the electrostatic potential provides the greater contribution [7]. According to a theoretical study by King and Weinhold [8], dealing with molecular properties of HCN linear chains, there is a remarkable importance of charge transfer for determination of the stabilization energy. In traditional hydrogen-bonded complexes, however, the accumulation of charge density on proton donors (HX, X = Cl, F and CN) provokes drastic changes on its structures. One of these changes is the bond-length enhancement of HX acids [9-10], observed through the downward shift of their stretch frequencies and the noticeable increase on their absorption intensities [11]. In spectroscopic language, the phenomenon above cited is known as red-shift effect, such as it is observed in heterocyclic hydrogen-bonded complexes [12-15], although we must remember that this is not observable in weak van der Waals intermolecular systems [11]. In these heterodimers, the formation of the primary hydrogen bond between the oxygen atom and HX proton donors ($C_2H_4O\cdots HX$) , reveals other interesting structural parameters, such as the non-linearity on the (O···HX) hydrogen bonds. Such distortion occurs because to a secondary interaction between the halogen or cyanide groups of monoprotic acids and the axial hydrogen atoms of the heterocyclic structure [16]. Not only from theoretical point of view, but experimental assays also have demonstrated the existence of secondary interactions in heterocyclic complexes [17-18].

Recently Hobza *et al* [19] reported on a new intermolecular interaction type, the so-called anti-hydrogen bonds, which is due to a blue-shifting observed on the proton donor molecule [20]. In opposition to the traditional viewpoints in hydrogen-bonded systems wherein is observed the red-shift effect, in antihydrogen-bonded complexes is verified a strengthening of the proton donor bond and thereby its stretch frequency is shifted to upward values [21-24]. In the $C_2H_4O\cdots HCF_3$ system, the C—H bond of the fluoroform (HCF_3) was characterized theoretically by highly sophisticated *ab initio* calculations [25]. In such case, the results revealed a blue-shift stretching frequency of the C—H (HCF_3) bond. Thus, the $C_2H_4O\cdots HCF_3$ complex is named as an antihydrogen-bonded system [19] or else heterocyclic blue-shifting hydrogen complex. Intuitively, it will be interesting also evaluate whether there is the possibility to form a non-linear deviation on the (O···H) anti-hydrogen bond, as it was observed in similar systems [12-14]. By considering θ angle values of 110° and 180° between the *n* lone pairs of oxygen and sulphur [26], the non-linear deviation and blue-shift effects are important parameters to be examined not only with the $C_2H_4O\cdots HCF_3$ three-members heteroring complex, but also with other complex species, such as $C_4H_6O\cdots HCF_3$ heterocyclic four-members system. Theoretically, for execution and success of this analysis, it is necessary to use a methodology which efficiently describes molecular properties of intermolecular complexes. Undoubtedly, the specialized literature reports a large number of studies involving hydrogen-bonded complexes where there is proved efficiency of the Density Functional Theory (DFT) [27-28] by means of their exchange-correlation functionals [29-31]. In addition, taking into the account the referential works of Kock and Popelier [32], intermolecular and/or intramolecular hydrogen bonds might be well identified by means of the topological parameters derived from Bader's Atoms in Molecules (AIM) [33] theory. Thus, the AIM calculations also will be applied in this work with the purpose to characterize the (O···H) blue-shift hydrogen bonds and (F···H) secondary interactions through the evaluation of topological operators, such as the electronic density and Laplacian field.

Computational details

The optimized geometries of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic complexes were obtained by using the B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) theoretical levels. All calculations were performed with the GAUSSIAN 98W program [34]. The values of the hydrogen bond energies were determined according to supermolecule approach [2], while the appropriated corrections were performed by means of the Zero Point Energy (ZPE) [35] and Basis Sets Superposition Error (BSSE) [36] calculations. The AIM calculations were processed using the GAUSSIAN 98W program, although some topological integrations were calculated using the AIM 2000 1.0 program [37].

Results and discussion

Geometry

The parameters r(C—H) bond length, υ(C—H) stretch mode and I (C—H) absorption intensity of the HCF_3 monomer, were examined with B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) levels, and the values obtained are listed in Table 1. For the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic complexes, however, their optimized geometries obtained from B3LYP/6-31G(d,p) (**I-II**) and B3LYP/6-311++G(d,p) (**III-IV**) calculations are depicted in Fig. 1, whereas their main structural results, stretch frequency modes and absorption intensities are listed in Table 2.

Table 1. Structural parameters of HCF_3 monomer using the B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameters	**Theoretical levels**	
	B3LYP/6-31G(d,p)	**B3LYP/6-311++G(d,p)**
r(H—F) / Å	1.0939	1.0896
υ(C—H) / cm^{-1}	3125.9	3141.2
I(C—H) / km mol^{-1}	53.4	32.8

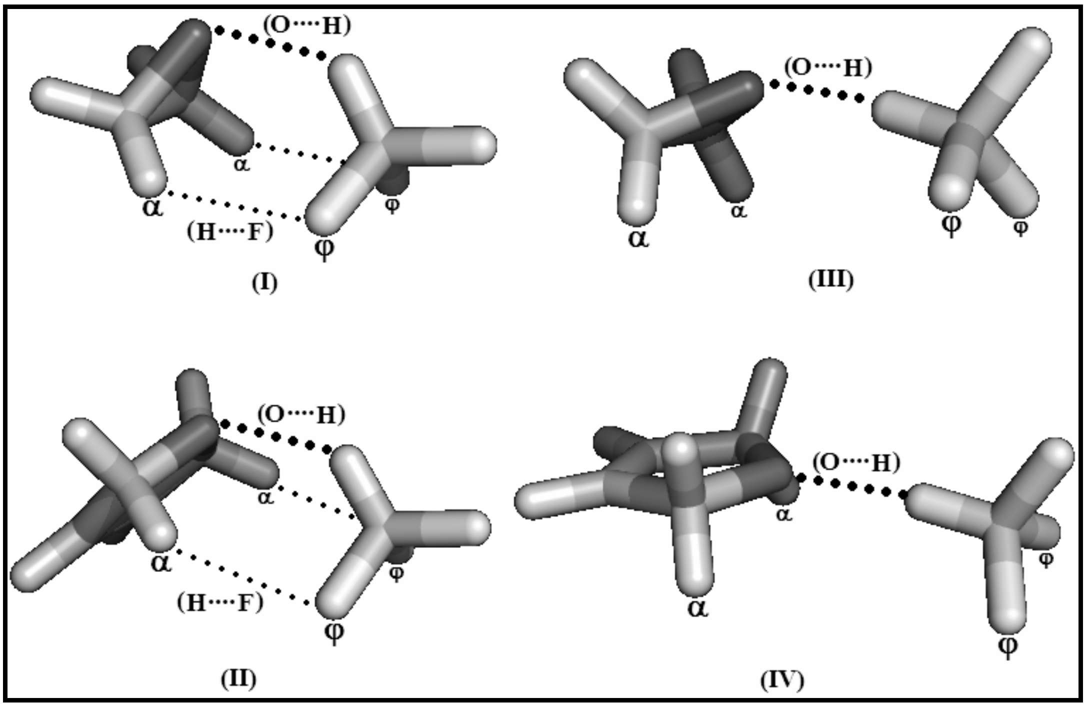

Fig. 1. Optimized geometries of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes. These geometries were obtained by using the B3LYP/6-31G(d,p) (**I-II**) and B3LYP/6-311++G(d,p) (**III-IV**) calculations.

Table 2. Structural parameters of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes using B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameters	Theoretical levels	
	B3LYP/6-31G(d,p)	**B3LYP/6-311++G(d,p)**
R(O···H) / Å	2.340 (2.293)	2.163 (2.144)
$R(H^{\alpha}\cdots F^{\varphi})$ / Å	2.540 (2.60)	4.441 (4.16)
r(H—F) / Å	1.0907 (1.0898)	1.0895 (1.0891)
Δr(H—F) / Å	-0.0033 (-0.0041)	-0.0001 (-0.0005)
Θ (degrees)	54.0 (9.0)	53.0 (7.2)

* Values for $C_4H_6O\cdots HCF_3$ complex are listed in parenthesis.

Initially, the characterization of these systems as antihydrogen-bonded complexes deals with the contraction on the r(C—H) bond, whose values are -0.0033 Å and -0.0041 Å at B3LYP/6-31G(d,p), as well as -0.0001 Å and -0.0005 Å at B3LYP/6-311++G(d,p) for the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes, respectively. In terms of the R(O···H) intermolecular distances, the B3LYP/6-311++G(d,p) calculations yields shorter lengths, whereas the longer values for $R(H^{\alpha}\cdots F^{\varphi})$ secondary interaction distances were computed through this same theoretical base. Properly, the values of 4.41 Å and 4.16 Å are the longest distances, in fact much longer than van der Waals radii whose data for fluorine and hydrogen atoms sum 2.55 Å [38]. However, a structural aspect related to secondary interactions is the non-linear deviation (θ) on the hydrogen bonds [12-13, 17-18]. It is worth noticing (see results gathered in Table 2) that larger θ values were obtained from B3LYP/6-31G(d,p) calculations, whereas B3LYP/6-311++G(d,p) provides the smaller ones. This result is not surprising, but rather agree with the $R(H^{\alpha}\cdots F^{\varphi})$ secondary interactions, where shorter distances obtained by the B3LYP/6-31G(d,p) method allow a stronger contact between the H^{α} and F^{φ} atoms, what, in turn, leads to greater distortions of linearity (θ) on the (O···H) hydrogen bonds.

Infrared harmonic spectrum

Nevertheless, the (O···H) and $(H^{\alpha}\cdots F^{\varphi})$ intermolecular interactions were also studied through the interpretation of their harmonic vibrational modes, whose values are listed in Table 3.

Table 3. Main vibrational modes of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes using B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameters	Theoretical levels	
	B3LYP/6-31G(d,p)	**B3LYP/6-311++G(d,p)**
$\upsilon(O\cdots H)$) / cm^{-1}	108.0 (106.7)	94.7 (75.3)
$I(O\cdots H)$ / km mol^{-1}	0.70 (0.33)	5.2 (0.80)
$\upsilon(H^{\alpha}\cdots F^{\varphi})$) / cm^{-1}	43.9 (45.5)	— (—)
$I(H^{\alpha}\cdots F^{\varphi})$ / km mol^{-1}	1.70(1.50)	— (—)
$\upsilon(C—H)$) / cm^{-1}	3180.1 (3182.1)	3156.9 (3143.6)
$I(C—H)$ / km mol^{-1}	13.8 (13.0)	9.0 (19.7)
$\Delta\upsilon(C—H)$) / cm^{-1}	54.2 (56.2)	15.7 (2.4)
I(C—H),c/I(C—H),m	0.26 (0.25)	0.17 (0.6)

* Values for $C_4H_6O\cdots HCF_3$ complex are listed in parenthesis.

Firstly, both B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations allowed the identification of all $\upsilon(O\cdots H)$ frequency signals and $I(O\cdots H)$ intensities, which are in the ranges of 75.3-108 cm^{-1} and 0.33-5.2 km mol^{-1}, respectively. However, only 3LYP/6-31G(d,p) theoretical level allowed characterizing the frequency of the secondary interaction for the $C_2H_4O\cdots HCF_3$ complex, whose values obtained for $\upsilon(H^{\alpha}\cdots F^{\varphi})$ are 43.9 cm^{-1} (45.5 cm^{-1} for $C_4H_6O\cdots HCF_3$), as well as $I(H^{\alpha}\cdots F^{\varphi})$ results of 1.70 km mol^{-1} (1.50 km mol^{-1} for $C_4H_6O\cdots HCF_3$). It is to be expected that B3LYP/6-311++G(d,p) can not predict a frequency signal, when this tool is used to compute longer distances for the secondary interactions. Regarding the main goal of this work, the characterization of the changes of $\upsilon(C—H)$ frequencies is essential to prove the existence of blue-shift effects on the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes. According to the results presented in Table 1, we can affirm that $\Delta\upsilon(C—H)$ values of 54.2 cm^{-1} and 56.2 cm^{-1} obtained from B3LYP/6-31G(d,p) calculations for the (**I**) and (**II**) systems indicate blue-shift hydrogen bonds. For B3LYP/6-311++G(d,p) level, so, the shorter shifts of 15.7 cm^{-1} and 2.4 cm^{-1} also indicate the presence of blue-shifting, although less significant and slightly intenser than those obtained by the B3LYP/6-31G(d,p) calculation. Henceforth, we can entitle the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ systems as antihydrogen-bonded or more properly blue-shift hydrogen complexes [20].

Intermolecular energies

From B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations, the Table 4 list the uncorrected (ΔE) and corrected (ΔE^C) intermolecular energies, as well as the (ΔZPE) and BSSE correction amounts for the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ systems. The results of intermolecular energy are very contradictory because B3LYP/6-311++G(d,p) provides higher and lower stability for ΔEC and ΔE, respectively. Such stability paradigm is merit of smaller BSSE amounts of 1.74 kJ mol^{-1} and 1.60 kJ mol^{-1} for (**III**) and (**IV**) systems, undoubtedly due the application of diffuse and valence basis sets [39-40]. Of course, by omitting these wave functions, the incomplete 6-31G(d,p) basis sets yielded larger BSSE results, which values are more than 50 % larger than the ΔE values. In contrast, the ΔZPE results were not affected intensively neither by B3LYP/6-31G(d,p) nor by B3LYP/6-311++G(d,p) calculations, although the difference between these levels in the ΔZPE calculations varies in the 0.9-1.22 kJ mol^{-1} range.

Table 4. Electronic parameters of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes using B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameters	**Theoretical levels**	
	B3LYP/6-31G(d,p)	**B3LYP/6-311++G(d,p)**
ΔE / km mol^{-1}	22.10 (21.70)	16.24 (17.87)
ΔZPE / km mol^{-1}	3.33 (3.03)	2.11 (2.13)
BSSE / km mol^{-1}	13.80 (13.90)	1.74 (1.60)
ΔE^{C} / km mol^{-1}	5.00 (4.77)	12.40 (14.14)

* Values for $C_4H_6O\cdots HCF_3$ complex are listed in parenthesis.

AIM calculations

Developed by Bader and co-workers [41], the AIM algorithm was built through the implementation of purely physical arguments, e.g., the Schwinger's stationary action [42]. In this insight, Bader projected AIM as an alternative quantum-chemical method, by which many studies of electronic structure have been developed successfully [43]. In essence, the AIM describes the molecular topology through the determination of *Bond Critical Points* (BCP) between two neighboring atoms [44]. The BCP is a source to develop a numeric integration of the electronic density. Thereby, some observable topologic parameters are obtained, such as the electronic density (ρ) and Laplacian field ($\nabla^2\rho$). These parameters describe the molecular stability through the identification of charge density centers within the chemical bond and, so, the internuclear pathways are classified as shared (covalent) or closed-shell (hydrogen bonds) when the electronic density is concentrated or depleted, respectively. Based on this abbreviated explanation, the results of the topological analysis for the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes are presented in Table 5, where values of ρ and ($\nabla^2\rho$) were obtained by B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations. To explain better our results, the discussion will be performed separately, firstly the AIM data obtained from B3LYP/6-31G(d,p) and later the B3LYP/6-311++G(d,p) level.

Table 5. AIM topological parameters of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes using B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameters	**Theoretical levels**	
	B3LYP/6-31G(d,p)	**B3LYP/6-311++G(d,p)**
$\rho(O\cdots H)$ / e.u.	0.014 (0.015)	0.016 (0.0173)
$\rho\nabla^2(O\cdots H)$ / e.u.	0.043 (0.047)	0.056 (0.0610)
$\rho(H^{\alpha}\cdots F^{\varphi})$ / e.u.	0.007 (0.006)	— (—)
$\rho\nabla^2(H^{\alpha}\cdots F^{\varphi})$ / e.u.	0.030 (0.206)	— (—)
$\rho(H—F)$ / e.u.	0.310 (0.311)	0.304 (0.304)
$\rho\nabla^2(H—F)$ / e.u.	-1.314 (-1.318)	-1.162 (-1.163)

* Values for $C_4H_6O\cdots HCF_3$ complex are listed in parenthesis;

* Values of ρ and $\rho\nabla^2$ for HCF_3 monomer are 0.304 e.u. and -1.238 e.u. at B3LYP/6-31G(d,p), whereas 0.302 e.u. and -1.124 e.u. at B3LYP/6-311++G(d,p) level, respectively.

Initially by taking into account the B3LYP/6-31G(d,p) calculations, the characterization of the $(O\cdots H)$ blue-shift hydrogen bond on $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes can be described by means of the $\rho(O\cdots H)$ and $\rho\nabla^2(O\cdots H)$ values of 0.014 e.u. and 0.015 e.u., as well as 0.043 e.u. and 0.047 e.u., respectively. By analyzing the Fig. 2 in which the sets of BCP on the $C_2H_4O\cdots HCF_3$ (**I**) and $C_4H_6O\cdots HCF_3$ (**II**) complexes are illustrated, we can perceive that the secondary interactions between the fluorine and the axial hydrogen atoms were entirely identified through the $\rho(H\alpha\cdots F\varphi)$ and $\rho\nabla 2(H\alpha\cdots F^{\varphi})$ topological parameters, whose results are 0.007 e.u. and 0.030 e.u. Moreover, the contraction of the (C—H) is corroborated by means of an enhancement on its electronic density, as well as substantial reduction of $\rho\nabla^2$ (H—F) from -1.238 e.u. (HCF_3 mononer) to -1.314 e.u. and -1.3187 e.u.

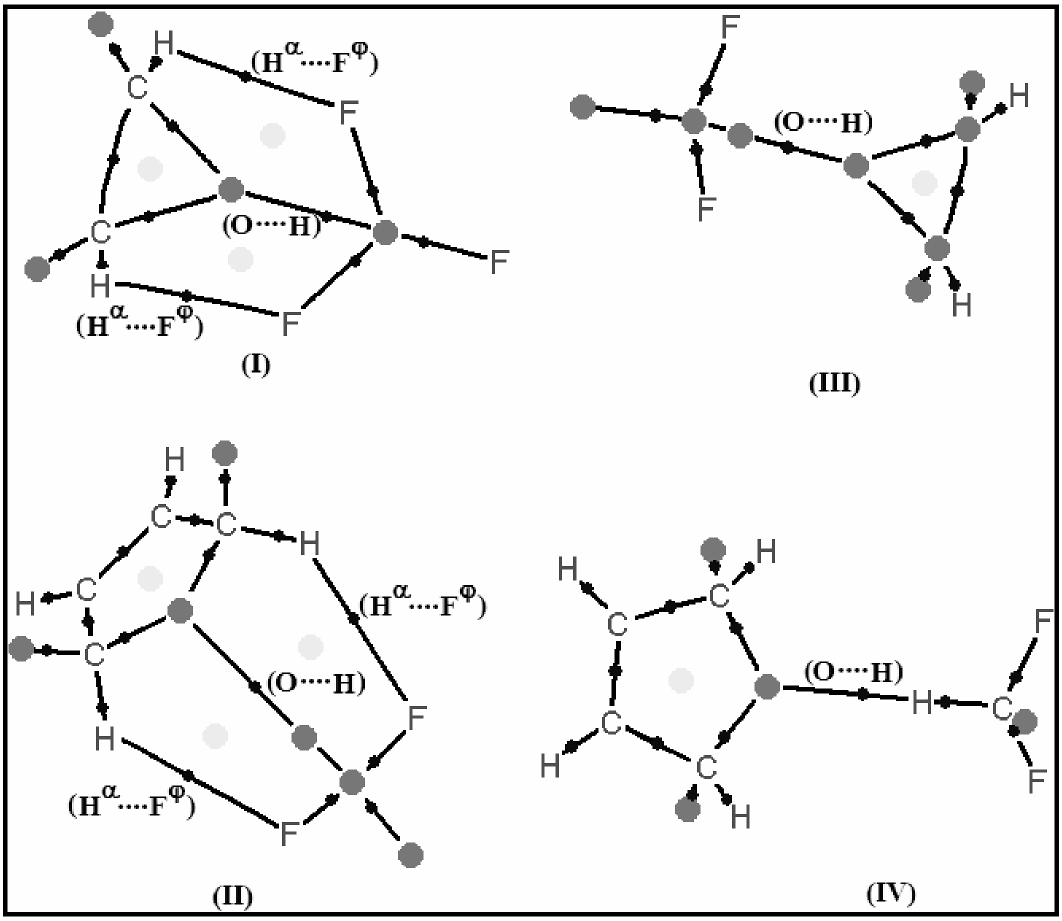

Fig. 2. BCP for whole chemical bonds, hydrogen bonds and secondary interactions in the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ heterocyclic blue-shifting hydrogen complexes by using the B3LYP/6-31G(d,p) (**I-II**) and B3LYP/6-311++G(d,p) (**III-IV**) calculations.

For B3LYP/6-311++G(d,p), however, the concentration of charge density ρ on the (O···H) blue-shift hydrogen bonds exhibits low values of 0.016 e.u. (**III**) and 0.056 e.u. (**IV**), while the intense electronic accumulation on HF bond exhibits high values of 0.304 e.u. (**III**) and 0.305 e.u. (**IV**). However, the secondary interaction was not characterized by the AIM theory when the optimized geometry of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes were obtained by the B3LYP/6-311++G(d,p) calculations. In other words, no BCP was localized between H^{α} and F^{φ} atoms. In addition, contrary to B3LYP/6-31G(d,p) calculations where secondary interactions were identified in terms of vibrational modes and topological parameters, the results determined by the B3LYP/6-311++G(d,p) level indicate that only one intermolecular interaction must exist on the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$, i.e., the O···H blue-shift hydrogen bonds. As direct consequence, the intermolecular energies of 12.40 kJ mol^{-1} and 14.14 kJ mol^{-1} would be only related to the O···H bond, something that is not possible when we consider the B3LYP/6-31G(d,p) results because the 5.00 kJ mol^{-1} and 4.77 kJ mol^{-1} are distributed between both (O···H) and ($H^{\alpha}\cdots F^{\varphi}$) interactions.

Conclusions

In this work, a theoretical study about vibrational blue-shift effect and formation of non-linearity in antihydrogen bonds of the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$

complexes was presented through the analysis of B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations. Besides, to formulate an explanation about the blue-shift effect in the (C—H) of the fluoroform, the set of quantum structural, vibrational and electronic parameters used here allowed to characterize the formation of the anti-hydrogen bond in the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes. The essential functions of AIM theory allowed to decipher, the topology of the (C—H) bond since, the higher charge density values computed for (C—H) indicated that this bond became stronger. Through the B3LYP/6-31G(d,p) calculations, however, the AIM topology revealed the existence of the secondary interaction formed between the fluorine (F^{φ}) of HCF_3 and axial hydrogen (H^{α}) of the C_2H_4O and C_4H_6O rings. By performing the B3LYP/6-311++G(d,p) calculations, no BCP was characterized between H^{α} and F^{φ}, indicating that (O···H) blue-shifting hydrogen bonds were verified on the $C_2H_4O\cdots HCF_3$ and $C_4H_6O\cdots HCF_3$ complexes.

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