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The electronic structure of the $C_2H_4O\cdots2HF$ tri-molecular heterocyclic hydrogen-bonded complex: a theoretical study

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Abstract The geometries of three isomers of the $C_2H_4O\cdots2HF$ tri-molecular heterocyclic hydrogen-bonded complex were examined through B3LYP/aug-cc-pVDZ calculations. Analysis of structural parameters, determination of CHELPG (charge electrostatic potential grid) intermolecular charge transfer, interpretation of infrared stretching modes, and Bader's atoms in molecules (AIM) theory calculations was carried out in order to characterize the hydrogen bonds in each isomer of the $C_2H_4O\cdots2HF$ complex. The most stable structure was determined through the identification of hydrogen bonds between C_2H_4O and HF, (O···H), as well as in the hydrofluoric acid dimer, ($HF^{D-R}\cdots HF^D$). However, the existence of a tertiary interaction ($F^\lambda\cdots H^\alpha$) between the fluoride of the second hydrofluoric acid and the axial hydrogen atoms of C_2H_4O was decisive in the identification of the preferred configuration of the $C_2H_4O\cdots2HF$ system.

Keywords Hydrogen bonds · AIM · CHELPG ·
Infrared spectrum

Introduction

It is well established that synthesis of heterocyclic compounds can take place via distinct routes [1]. One such route is electrophilic addition [2–4], in which a bi-

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molecular hydrogen-bonded complex is formed when a heterocyclic compound interacts with one acid molecule. Experimentally, the geometries of bi-molecular heterocyclic hydrogen-bonded complexes have been characterized satisfactorily in gas phase using Fourier transform microwave spectroscopy (FTMS) [5–7]. On the other hand, quantum chemical calculations have been used extensively to predict not only the geometric parameters of heterocyclic hydrogen-bonded complexes [8], but also molecular stability and interpretation of infrared stretching modes [9, 10].

According to van der Veken et al. [11], the tri-molecular homocyclic hydrogen-bonded complex $C_3H_6\cdots2HCl$ is a typical example of an intermolecular catalytic system due to the presence of two hydrochloride acid molecules [12]. In this case, the second molecule of hydrochloride acid has only a slight influence on the formation of the hydrogen complex. The effect of acid catalysis in hydrogen-bonded complexes has been suggested by Jursic [13] in studies on halogenation of ethylene with hydrofluoric acid. Regarding heterocyclic compounds such as ethylene oxide (C_2H_4O), electrophilic addition reactions also can be executed by two hydrofluoric acid (HF) species. Although the specialized literature informs us that the formation of tri-molecular hydrogen-bonded complexes can lead to several structural configurations, only one configuration can be defined as the most stable [14, 15].

In order to determine the one preferential configuration for the tri-molecular hydrogen-bonded complex $C_2H_4O\cdots2HF$, this work aims to develop a theoretical study of the optimized geometries of possible isomers of this system. In this context, we will explore the optimized geometry of the isomers, analyze their SCF stabilization energies, and identify harmonic infrared stretching modes, but will also apply Bader's atoms in molecules (AIM) [1] theory for identification of seemingly important intermolecular interactions. To obtain a precise overview of the

hydrogen bonds involved, AIM integration quantitatively describes the concentration of electronic densities in separate nuclei, characterizing the intermolecular interactions through low electronic density ($\rho \sim 10^{-3}$) values [16] and positive Laplacian ($\nabla^2 \rho > 0$) fields [17]. These latter properties help evaluate which kind of intermolecular interactions exist in each hydrogen complex. In fact, we are assuming that the stability of the $C_2H_4O \cdots 2HF$ trimolecular hydrogen-bonded complex depend entirely on the formation of hydrogen bonds between C_2H_4O and HF (O$\cdots$HF), and in the HF dimer (HF$\cdots$HF). In this sense, the AIM calculations become essential, but we should note that examination of charge transfer is also a plausible method with which to understand the charge transfer in (O$\cdots$HF) and (HF$\cdots$HF) interactions. Several methods of attributing charge to individual atoms exist. We needed an efficient algorithm that efficiently describes the electrostatic properties of hydrogen-bonded complexes [18, 19], with low computational effort [20, 21]; from this perspective, charge electrostatic potential grid (CHELPG) formalism is an appropriate candidate. In addition, this method provides the possibility to derive meaningful predictions about the charge transfer of the $C_2H_4O \cdots 2HF$ complex.

Computational procedure

The geometries of the (I), (II), and (III) isomers of the heterocyclic hydrogen-bonded complex $C_2H_4O \cdots 2HF$ were fully optimized through B3LYP/aug-cc-pVDZ calculations executed using GAUSSIAN 98W software [22]. CHELPG atomic charge calculations were also processed using the routine codes implemented within the GAUSSIAN 98 W program. The nature of the electronic density was studied by means of Bader's AIM theory [23] using the AIM 2000 1.0 program [24].

Results and discussion

Optimized geometries

Although the nature of both reactants determines a preferential reaction pathway, three structural possibilities for the $C_2H_4O \cdots 2HF$ tri-molecular hydrogen-bonded complex are suggested in this work. The optimized geometries of the (I), (II), and (III) isomers of the $C_2H_4O \cdots 2HF$ tri-molecular hydrogen-bonded complex derived from B3LYP/aug-cc-pVDZ calculations are illustrated in Fig. 1. However, the purpose of this work was not to explore the potential energy surface of these structures individually, but rather to concentrate on the global minimum energy for each isomer. Thus, the main

structural results for isomers (I), (II), and (III) are listed in Table 1.

Initially, by analyzing the structures of these isomers, it is plausible to admit the formation of a possible tertiary interaction ($F^\lambda \cdots H^\alpha$) between the fluoride (hydrofluoric acid) and the axial hydrogen atoms (methyl groups) of the C_2H_4O three-membered ring. Based on both experimental data and theoretical results reported for the $C_2H_4O \cdots HX$ bimolecular hydrogen-bonded complex (one C_2H_4O molecule and one HX species, where X symbolizes the F and Cl atoms or CN and NC groups), the electronic densities of halides and cyanides interact weakly with the axial hydrogen atoms of the methyl groups of C_2H_4O [8], resulting in a secondary interaction and, consequently, non-linearity of the (O$\cdots$HX) hydrogen bonds. Details of the structures of bi-molecular systems have been suggested recently [9], and these results can be used as a reference for the analysis of the (I), (II), and (III) isomers. According to the results presented in this work, there is a tendency to form a secondary interaction ($F^\lambda \cdots H^\alpha$), which causes deviations from linearity ($\theta 1$ and $\theta 2$ angles) in the (O$\cdots$HF) hydrogen bonds in all isomers. In the (I) isomer, the $\theta 1$ and $\theta 2$ angles are both 14.8°. Whereas $\theta 1$(III) > $\theta 1$ (II) and $\theta 2$(III) > $\theta 2$ (II), $\theta 2$(III) presents the largest opening due to the possibility of the formation of a ($F^\lambda \cdots H^\alpha$) tertiary interaction between the fluoride atom (F^λ) of the hydrofluoric acid molecule and the axial hydrogen atoms (H^α) of the C_2H_4O. This tertiary interaction represents a distance of 2.7264 Å. In the (I) and (II) isomers, the distances of these tertiary interactions are 3.0517 Å and 3.167 Å, respectively. According to [25], the sum of the van der Waals radii values for the fluoride (F= 1.35 Å) and hydrogen (H=1.20 Å) atoms equals 2.55 Å; however, we would like to emphasize that ($F^\lambda \cdots H^\alpha$) tertiary interactions in the (I) and (II) isomers cannot be formed.

At 1.5174 Å and 1.6377 Å, respectively, the $R_{(O \cdots HF)}$ and $R_{(HF^{D-R} \cdots HF^D)}$ distances are the shortest interactions, and thus the (III) isomer is a candidate for the preferred configuration. The lengths of hydrogen bonds diminish as follows: $R_{(O \cdots HF)}$(I) > $R_{(O \cdots HF)}$(II) > $R_{(O \cdots HF)}$ (III). The stronger interactions in (III) induce a pronounced elongation in HF bond lengths, whose $\delta R_{(HF^{D-R})}$ and $\delta R_{(HF^D)}$ values are 0.9795 Å and 0.9473 Å, respectively. Actually, the stronger interaction (O$\cdots$HF) in (III) is determined by the charge transfer between the oxygen n-electron pair of the ethylene oxide and the hydrogen σ* orbital in the HF^{D-R} species, which also transfers charge to the hydrogen σ* orbital of the HF^D molecule.

CHELPG charge transfer

Table 2 presents the results of charge transfers (δQ) for the whole set of interactions in the (I), (II), and (III) isomers.

Fig. 1 Optimized geometries of isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O \cdots 2HF$ derived from B3LYP/aug-cc-pVDZ calculations
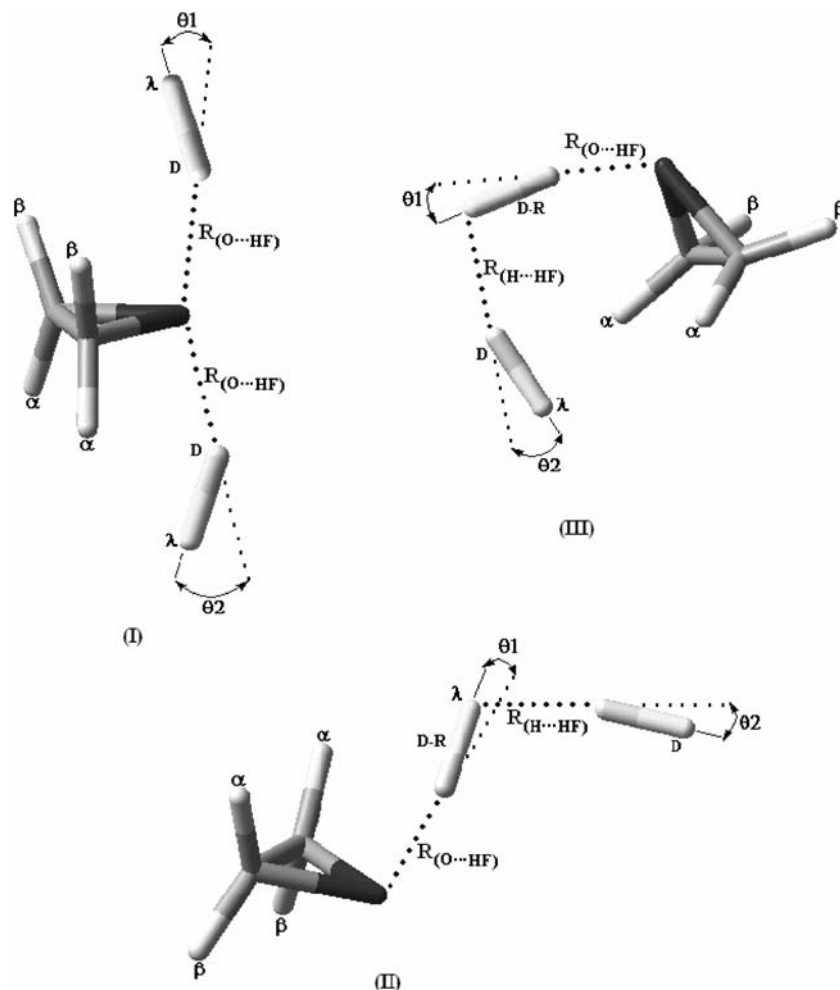
Because HF can function simultaneously as a donor (D) and donor–receptor (D–R) of protons, this double character can reveal new insights about charge transfer mechanisms in the hydrogen bonds of isomers (I), (II) and (III). In practice, the charge transfer indicates the number of

electrons responsible for the intermolecular contact, or, in other words, if a hydrogen bond is formed, the proton donor (HF^{D-R} or HF^D) receives charge density from one acceptor (either the oxygen of C_2H_4O, or HF^{D-R}). Initially, the higher $\delta QH_{(O \cdots HF)}$ result of -0.1564 electronic units (e.u.) indicates that $(O \cdots HF)$ is the strongest interaction in the (I) isomer. However, this is apparently inconsistent with the data because the $R(O \cdots HF)$ interaction distance of 1.7011 Å is longer. In such a case, one important aspect is that $\delta QH_{(O \cdots HF)}$ is partitioned between two HF^D hydro-

Table 1 Structural parameters of isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O \cdots 2HF$ derived from B3LYP/aug-cc-pVDZ calculations. R and θ values are given in Ångströms and degrees, respectively

Parameter	Isomer		
	I[a]	II	III
$R_{(O \cdots HF)}$	1.7011	1.5378	1.5174
$R_{(HF^{D-R} \cdots HF^D)}$	–	1.6817	1.6377
$R_F^{\lambda \cdots H^\alpha}$	3.0517	3.1670	2.7264
$\delta R_{(HF^{D-R})}$	–	0.9724	0.9795
$\delta R_{(HF^D)}$	0.9459	0.9411	0.9473
$\theta 1$	14.8	6.0	7.5
$\theta 2$	14.8	1.7	16.8

[a] In the case of the (I) isomer, the hydrofluoric acid acts solely as proton donor (HF^D)

Table 2 Charge electrostatic potential grid (CHELPG) charge transfers (δQ) in isomers (I), (II), and (III) of the $C_2H_4O \cdots 2HF$ heterocyclic hydrogen-bonded complex derived from B3LYP/aug-cc-pVDZ calculations. Q values are given in electronic units (e.u.)

Charge transfer	Isomer		
	I	II	III
$\delta QH_{(O \cdots HF)}$	-0.1564	-0.0402	-0.0733
$\delta QH_{(HF^{D-R} \cdots HF^D)}$	–	-0.0968	-0.0541
δQH^α	0.0124	0.0125	0.0053
δQH^β	0.0124	0.0197	0.0055

fluoric acid proton donors. On the other hand, the $\delta QH_{(O\cdots HF)}$ charge transfer in isomers (II) and (III) is smaller because, due to formation of the $(HF^{D-R}\cdots HF^D)$ hydrogen bonds in the HF dimer, a distribution of electronic density of −0.0968 e.u. and −0.0541 e.u. is observed. Nevertheless, for the three isomers studied here, all axial hydrogen atoms have an intense positive charge. In comparison with the H^β atoms in (III), the positive δQH^α value of 0.0053 e.u. suggests a slight acceptance of charge from the fluoride (F^λ) of the second hydrofluoric acid molecule. Thus, it becomes plausible to admit the existence of the $(F^\lambda\cdots H^\alpha)$ tertiary interaction, despite the apparent improbability of forming this interaction, as discussed in the section on structural analysis. In fact, relative to isomer (III), the positive δQH^α values of 0.0124 e.u. and 0.0125 e. u. indicate that $(F^\lambda\cdots H^\alpha)$ tertiary interactions do not exist in isomers (I) and (II).

AIM topological parameters

Koch and Popelier [26] have developed a successful theoretical study of hydrogen-bonded systems through the analysis of topological parameters of the AIM theory. In essence, this methodology localizes bond critical points (BCP) and paths of maximum and minimum electronic density over the whole molecular surface. Consequently, the chemical bond can be characterized when BCP are localized between two neighboring atoms. Our main objective in this work was to evaluate the preferred structure from among isomers (I), (II) and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O\cdots 2HF$ through the theoretical study of $(O\cdots HF)$ and $(HF^{D-R}\cdots HF^D)$ hydrogen bonds, as well as the possible $(F^\lambda\cdots H^\alpha)$ tertiary interaction. Thus, Table 3 presents the electronic density and Laplacian values of the relevant bonds in isomers (I), (II), and (III).

In comparison with the hydrofluoric acid monomer, the electronic densities in isomers (I), (II) and (III) decrease by $-0.0367^{e/a_0^3}$, $-0.0327^{e/a_0^3}$ and $-0.0407^{e/a_0^3}$ relative to HF^D, as well as $-0.0717^{e/a_0^3}$ and $-0.0787^{e/a_0^3}$ for HF^{D-R}, respectively. This leads us to consider that HF^{D-R} exhibits a tendency to rupture or, in terms of AIM concepts, forms a closed-shell interaction, mainly in isomer (III). In other words, due to the decrease in electronic density to a minimum BCP in HF^{D-R}, its Laplacian of $-1.844^{e/a_0^5}$ automatically becomes more positive when compared with the $-2.754^{e/a_0^5}$ for the hydrofluoric acid monomer. Regarding the formation of hydrogen bonds, these interactions present low concentrations of ρ, i.e., the electronic density of $(O\cdots H)$ hydrogen bonds are in the range of $0.042^{e/a_0^3} - 0.068^{e/a_0^3}$. Moreover, the $(HF^{D-R}\cdots HF^D)$ hydrogen bonds have the lowest electronic densities, with values of $0.036^{e/a_0^3}$ and $0.042^{e/a_0^3}$ for isomers (II) and (III), respectively. To sum up, all these hydrogen bonds have positive Laplacian values and hence are termed closed-shell interactions. Specifically, this is an essential condition for the further characterization of the formation of hydrogen-bonded complexes once the electronic density has accumulated in separated nuclei.

As can be observed in the BCP and bond paths illustrated in Fig. 2, AIM calculations confirm the main goal of this work, which is the identification of a tertiary interaction formed between the fluoride (F^λ) and axial hydrogen atoms (H^α) in isomer (III), even though the sum of the van der Waals radii of these atoms is shorter than that of the $(F^\lambda\cdots H^\alpha)$ hydrogen bond distance. By taking into the account the geometry results discussed here, formation of $(F^\lambda\cdots H^\alpha)$ hydrogen bonds in isomer (III) is implausible, although the electronic density of $0.005^{e/a_0^3}$ and the Laplacian function of $0.022^{e/a_0^5}$ indicate the existence of a $(F^\lambda\cdots H^\alpha)$ tertiary interaction in isomer (III). Confirmation of the $(F^\lambda\cdots H^\alpha)$ tertiary interaction as closed-shell or hydrogen bond is an indication that isomer (III) is the most stable configuration.

Table 3 Atoms in molecules (AIM) charge densities and Laplacian fields of the hydrogen bonds in isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O\cdots 2HF$. $\rho(\vec{r}, x)$ and $\nabla^2\rho(\vec{r}, X)$ values are given in e/a_0^3 and e/a_0^3 respectively.

The $\rho(\vec{r}, X)$ and $\nabla^2\rho(\vec{r}, X)$ values for the hydrofluoric acid monomer are $0.3657^{e/a_0^3}$ and $-2.754^{e/a_0^3}$ respectively. Variations in the electronic densities for the hydrofluoric acid molecules due the formation of isomers (I), (II), and (III) are shown in parenthesis

Bonds	Isomers and AIM parameters					
	I		II		III	
	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
$(O\cdots HF)$	0.042	0.153	0.064	0.176	0.068	0.171
$(HF^{D-R}\cdots HF^D)$	–	–	0.036	0.155	0.042	0.168
$F^\lambda\cdots H^\alpha$	–	–	–	–	0.005	0.022
HF^{D-R}	–	–	0.294 (−0.0717)	−1.984	0.287 (−0.0787)	−1.844
HF^D	0.329 (−0.0367)	−2.554	0.333 (−0.0327)	−2.767	0.325 (−0.0407)	−2.623

Fig. 2 Atoms in molecules (AIM) bond critical points (BCP) and atomic pathways for isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O\cdots2HF$. BCP are denoted by interatomic *dotted lines*

(I)

(III)

(II)
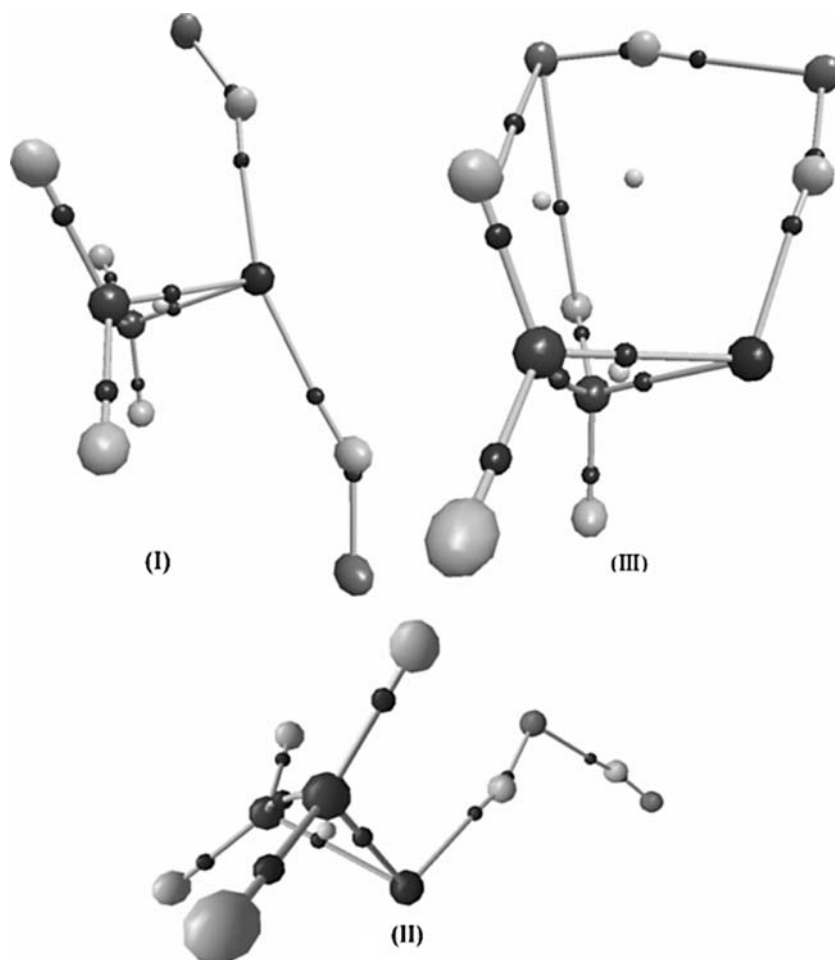
Interaction energies

By analyzing the energies of the C_2H_4O monomer and 2HF dimer, the stabilization energies (E) of isomers (I), (II), and (III) were computed by application of the supermolecule approach [27]. The corrected stabilization energies (E^{CORR}) were then determined as follows:

$$E = E_{Complex} - E_{Monomers} \qquad (1)$$

$$E^{CORR} = E - (\Delta ZPE + BSSE) \qquad (2)$$

Although physical arguments provide support for the supermolecule approach [28], its application to the

Table 4 Electronic parameters of isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O\cdots2HF$ derived from B3LYP/aug-cc-pVDZ calculations. E values are in Hartree; ΔZPE, BSSE and E^{CORR} values are in kJ mol^{-1}

Parameter	Isomer		
	I	II	III
E	−354.7579735	−354.7596049	−354.7625547
ΔZPE	17.98	16.93	18.08
BSSE	3.57	2.90	3.91
E^{CORR}	−49.25	−55.24	−60.82

Table 5 Harmonic stretching modes and absorption intensities of isomers (I), (II), and (III) of the heterocyclic hydrogen-bonded complex $C_2H_4O\cdots2HF$ derived from B3LYP/aug-cc-pVDZ calculations. υ^{Str} and I^{Str} values are given in cm^{-1} and km mol^{-1} respectively. The υ^{Str} and I^{Str} values for the hydrofluoric acid monomer are 4,059.9 cm^{-1} and 111.3 km mol^{-1}, respectively

Infrared mode	Isomer		
	I	II	III
$\upsilon^{Str}_{(O\cdots HF)}$	179.0	334.3	334.7
$I^{Str}_{(O\cdots HF)}$	0.8	31.0	45.6
$\upsilon^{Str}_{(F^{D-R}\cdots HF^D)}$	–	215.6	254.1
$I^{Str}_{(F^{D-R}\cdots HF^D)}$	–	33.3	20.1
$\upsilon^{Str}_{(F\gamma\cdots H\alpha)}$	–	–	70.3
$I^{Str}_{(F\gamma\cdots H\alpha)}$	–	–	8.24
$\Delta\upsilon^{Str}_{HF^{D-R}}$	−444.0	−993.2	−1,115.5
$I^{Str}_{HF^{D-R,C}}/I^{Str}_{HF^{D-R,i}}$	3.6	20.0	16.6
$\Delta\upsilon^{Str}_{HF^D}$	–	−355.4	−455.5
$I^{Str}_{HF^{D,C}}/I^{Str}_{HF^{D,i}}$	–	6.3	6.4

$C_2H_4O\cdots2HF$ heterocyclic hydrogen-bonded complex has some limitations because the interaction energies (49.25 kJ mol^{-1}, −55.24 kJ mol^{-1} and 60.82 kJ mol^{-1}) are not distributed uniformly among the (O⋯HF), (HF^{D-R}⋯HF^D), and (F$^\lambda$⋯H$^\alpha$) hydrogen bonds [29]. However, comparing the E^{CCOR} results, isomer (III) is −5.58 kJ mol^{-1} and −11.57 kJ mol^{-1} more stable than isomers (II) and (I), respectively (Table 4). This finding implies that isomer (III) is the energetically preferred configuration of the $C_2H_4O\cdots2HF$ heterocyclic hydrogen-bonded complex.

Vibrational harmonic spectrum

The formation of hydrogen-bonded complexes occurs due to the origin of new vibrational modes—more commonly known as hydrogen bond stretching frequencies [30]. Normally, these modes can be observed at low frequency as weak bands in the infrared spectrum. For the isomers of the $C_2H_4O\cdots2HF$ hydrogen-bonded complex studied here, the values presented in Table 5 show that $\upsilon^{Str}_{(O\cdots HF)}$ new vibrational modes are 179 cm^{-1}, 334.3 cm^{-1} and 334.7 cm^{-1} for isomers (I), (II), and (III), respectively. Moreover, $\upsilon^{Str}_{(F^{D-R}\cdots HF^D)}$ stretching presents lower frequencies, with values of 215.6 cm^{-1} and 254.1 cm^{-1} for isomers (II) and (III), respectively. However, the new vibrational mode for the tertiary interaction in isomer (III) was identified at 70.3 cm^{-1}. In addition, all these weak interactions have low absorption intensities, with values in the range of 0.8–45.6 km mol^{-1}.

However, the most prominent effect due to formation of hydrogen bonding is the bathochromic effect in proton donors, where their stretching modes are shifted to downward values following a pronounced increase in absorption intensity [31]. In the $C_2H_4O\cdots2HF$ hydrogen-bonded complex, the $\Delta\upsilon^{Str}_{HFD-R}$ donor–receptor bathochromic shifts for isomers (I), (II), and (III) are −444.0 cm^{-1}, −993.2 cm^{-1}, and −1,115.5 cm^{-1}, respectively. Indeed, the variation in absorption intensities is also in agreement with the bathochromic phenomenon. For instance, the $I^{Str}_{HF^{D-R},C}/I^{Str}_{HF^{D-R},i}$ absorption intensity proportion for hydrofluoric donor is 3.6 in isomer (I), and 20.0 and 16.6 for donor–receptor in isomers (II) and (III). Moreover, $I^{Str}_{HF^D,C}/I^{Str}_{HF^D,i}$ proportions of 6.3 and 6.4 for the hydrofluoric acid proton donors were observed in isomers (II) and (III), respectively.

Conclusions and perspectives

A theoretical study on the formation of hydrogen bonds in the tri-molecular heterocyclic hydrogen-bonded complex $C_2H_4O\cdots2HF$ is presented. According to the structural parameters, AIM charge density, and analysis of the infrared spectrum, the isomer of the $C_2H_4O\cdots2HF$ complex formed by the (O⋯H), (HF^{D-R}⋯HF^D), and (F$^\lambda$⋯H$^\alpha$) hydrogen bonds exhibited better stability. Following CHELPG calculations, the distribution of charge density in isomer (III) was evaluated through examination of the (O⋯H) and (HF^{D-R}⋯HF^D) hydrogen bonds. Analyzing the AIM calculations, however, the identification of the tertiary interaction between the fluoride and hydrogen atoms of the methyl groups is very interesting because the R(F$^\lambda$⋯H$^\alpha$) intermolecular distance is longer than sum of the van der Waals radii. Thus, formation of the (F$^\lambda$⋯H$^\alpha$) tertiary interaction provides better stabilization for isomer (III) by −5.58 kJ mol^{-1} and −11.57 kJ mol^{-1} as compared to the corresponding values for the (I) and (II) isomers, respectively.

In this work, a preferred configuration for the $C_2H_4O\cdots2HF$ complex was determined. The results of this work point to future studies addressing the characterizatino of solvent effects in isomer (III) through the application of discrete methodologies [32, 33]. It is widely known that monoprotic acids are efficient protonation species in open ring reactions involving small compounds, and our group recently reported a theoretical study on solvent effects in the bi-molecular heterocyclic hydrogen-bonded complex $C_2H_4O\cdots2HF$ [34]. The results indicated that one hydrofluoric acid molecule does not perturb the aqueous solvated structure of the $C_2H_4O\cdots2HF$ bi-molecular complex. In this context, the excess of two hydrofluoric acid molecules would indicate a higher solvation in the case of the $C_2H_4O\cdots2HF$ tri-molecular heterocyclic hydrogen-bonded complex, specifically isomer (III), and hence we expect that a suitable explanation of solvent effects in reactions involving three-membered rings can be obtained.

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