



DFT and NBO Studies of Stability, Electronic, and Structural Features of the 2-fluoroacetaldehyde Conformers

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IN THIS investigation, the stability of the keto-enol forms and conformers of 2-fluoroacetaldehyde was investigated by LC-wPBE, B3LYP and M06-2X functionals and 6-311++G (d,p) basis set. The total energy, the energies of frontier orbitals, HOMO-LUMO gaps and total dipole moment of these molecules were estimated. These calculations show that more stability of the keto form in compared to enol form. Calculations at the LC-wPBE/6-311++G (d,p) level of theory reveal the more stability of I-conformer in compared to other conformers. Natural bond orbital (NBO) analysis was applied for illustrating the negative hyperconjugative effect on the conformers. In the basis of NBO analysis, the LP (O2)→σ*(C-H) and LP (O2)→σ*(C-C) interactions were responsible of the negative hyperconjugation in the examined compounds. The interaction energy, off-diagonal elements, and total steric energy values of these interactions were reported.

Keywords: 2-fluoroacetaldehyde, Negative hyperconjugative effect, Natural bond orbital analysis, DFT calculation.

Introduction

The substitution of fluorine atom reveals effective bene fits in the molecular preparation for applications in biological investigations. Indeed, these molecules have been attracted much attentions in biochemistry, pharmacology, medicinal chemistry and related fields. A main aspect for the usefulness of these molecules attributed to rather minor alteration in the molecular structure in the formation of C-F bonds [1,2]. This can allow interactions of the fluorinated analogue with enzyme active sites, receptors, transport proteins and other macromolecules that are similar to those of a non-fluorinated parent molecule. Nevertheless, the strong electronegativity of fluorine can cause

significant variations to the physico chemical properties of the compound, and these variations can be used for a range of purposes.

Acetaldehyde and its derivatives exemplifies one of the most common but significant instances of molecular systems with keto-enol equilibria with a long past of attention [3-13]. Computational investigations have been reported for illustration the keto-enol equilibrium in various systems [14-20]. In a study, focal-point analysis and ab initio limit were used to investigation of the keto-enol equilibrium in substituted acetaldehydes [14]. In another investigation, conformational analysis of chloroacetaldehyde and bromoacetaldehyde was reported with NMR [21].

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One main occurrence that should be reflected in the investigation of the π - π^* conjugation is the negative hyperconjugation. In the structure bearing = O, negative hyperconjugation appears orbital with π symmetry localized on the oxygen atom interacts with an σ^* orbital localized on the C-C bond. This effect has been studied in the various systems by means of computational methods [22-28].

In this study we report DFT and NBO studies of stability, electronic, and structural features of the 2-fluoroacetaldehyde conformers

Computational Methods

The Gaussian 09 software package was employed in our computations [29]. Geometries of the studied molecules were optimized using the Standard 6-311++G(d,p) basis set [30-32], LC-wPBE functional [33], the hybrid functional of M06-2X, as developed by Truhlar and Zhao [34] and hybrid functional of the B3LYP [35] were used. LC-wPBE is long range corrected (or range separated) hybrid where the amount of exact exchange raises with increasing inter-electronic distance to make them more accurate for transitions to higher lying orbitals [36].

A vibrational analysis was conducted at every stationary point observed, confirming its characteristics as a least energy. Moreover, the population has been analyzed using the NBO process [37] at LC-WPBE/6-311++G(d,p) level of theory with the NBO 6.0 program [38] through the software of Gaussian 09.

Visualization of the NBOs were plotted with Multiwfn 3.5 software package [39].

Results and Discussion

Energetic aspects

Conformers and abbreviations of the 2-fluoroacetaldehyde molecule are depicted in Figure 1. The absolute energy and relative energy values of conformers of the keto and enol forms of the 2-fluoroacetaldehyde are calculated at three levels of theory: LC-wPBE/6-311++G(d,p), M062X/6-311++G(d,p) and B3LYP/6-311++G(d,p) (Table 1). As can be seen, keto form has more stability than enol form. On the other hand, the I-conformer has larger stable conformer at LC-wPBE/6-311++G(d,p) level. Two other levels show that I-conformer and IV-conformer are iso-energetic.

The more stability of I-conformer compared

to other conformers is attributed to negative hyperconjugation effects. Figure 2 represents the canonical resonance structure of the mentioned negative hyperconjugation interactions.

Total dipole moment

The total dipole moment values of the various conformers of 2-fluoroacetaldehyde molecule are listed in Table 1. Total dipole moment value using the x, y, z components is defined as :

$$\mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

Total dipole moment values of polar I-conformer reveal the smallest total dipole moment values. The obtained results are consistent with smaller total dipole moment values for more stable conformers [40].

Molecular orbital analysis

The frontier orbital energy and HOMO-LUMO gap values of the various conformers of 2-fluoroacetaldehyde molecule are calculated. The calculated values in the Table 2 show that the most stability of HOMO and the lowest stability of LUMO in the I-conformer. Plots of frontier orbital of these conformers are presented in Figure 3.

It is also possible to find out that the largest HOMO-LUMO gap and hardness value in the I-conformer. The hardness value is calculated by the following equation :

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

This increasing is compatible with maximum hardness principle (MHP) and the minimum energy principle (MEP). In the basis of MHP, while a conformer changes from the most stable to the less stable species in most cases, the energy increases, and the hardness decreases [41-45].

The electrophilicity index, ω , for each molecule measured using the expression [46]:

$$\omega = \frac{\mu^2}{2\eta}$$

where μ the chemical potential is:

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2}$$

and η is the hardness.

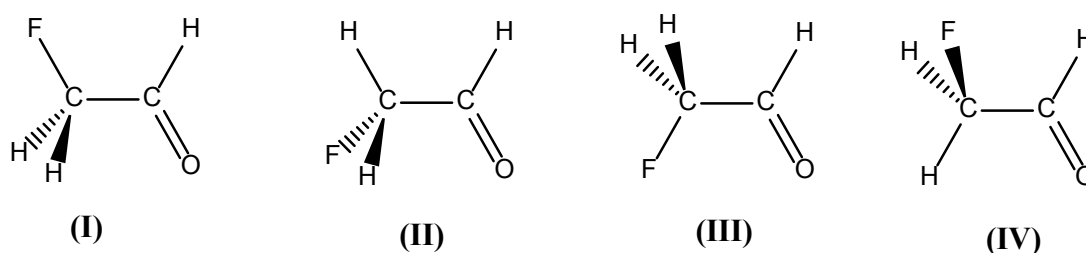


Fig. 1. Possible conformers of 2-fluoroacetaldehyde.

TABLE 1. Energy (E, a.u), relative energy (ΔE , kcal/mol) and dipole moment (μ , Debye) of possible conformers of keto and enol forms of 2-fluoroacetaldehyde at the LC-wPBE/6-311++G(d,p), M062X/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory.

(a) keto form							
	LC-wPBE/6-311++G(d,p)			M062X/6-311++G(d,p)		B3LYP/6-311++G(d,p)	
	E	ΔE	μ	E	ΔE	E	ΔE
I	-252.9834	0.00	1.07	-253.0364	0.00	-253.1406	0.00
II	-252.9754	5.04	3.45	-253.0342	1.38	-253.1384	1.39
III	-252.9808	1.62	3.93	-253.0342	1.38	-253.1384	1.39
IV	-252.9796	2.39	2.19	-253.0364	0.00	-253.1406	0.00

(a) enolform							
	LC-wPBE/6-311++G(d,p)		M062X/6-311++G(d,p)		B3LYP/6-311++G(d,p)		
	E	ΔE^*	E	ΔE	E	ΔE	
I	-252.9640	12.15	-253.0268	6.04	-253.1292	7.17	
II	-252.9707	2.93	-253.0201	8.83	-253.1227	9.87	
III	-252.9707	6.32	-253.0201	8.83	-253.1227	9.87	
IV	-252.9640	9.76	-253.0268	6.04	-253.1292	7.17	

• Respect to keto form

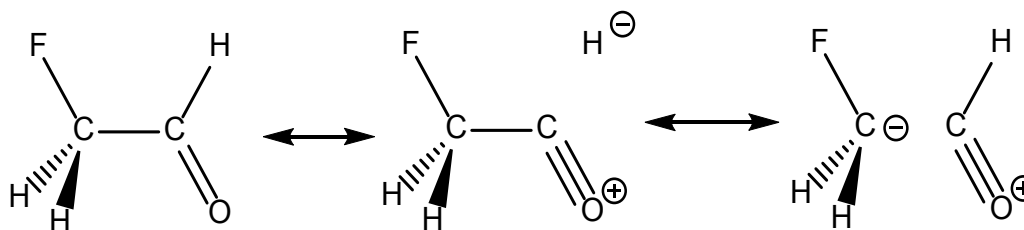


Fig. 2. The predicted resonance structures of 2-fluoroacetaldehyde with NBO analysis.

TABLE 2. Frontier orbital energy (E, eV), HOMO-LUMO gap (ΔE , kcal/mol), hardness (η , eV), electrophilicity (ω , eV) of possible conformers of 2-fluoroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory.

	E(HOMO)	E(LUMO)	ΔE	η	ω
I	-10.85	1.01	11.86	5.93	2.04
II	-10.77	0.59	11.36	5.68	2.28
III	-10.75	0.84	11.59	5.80	2.12
IV	-10.82	0.80	11.63	5.81	2.16

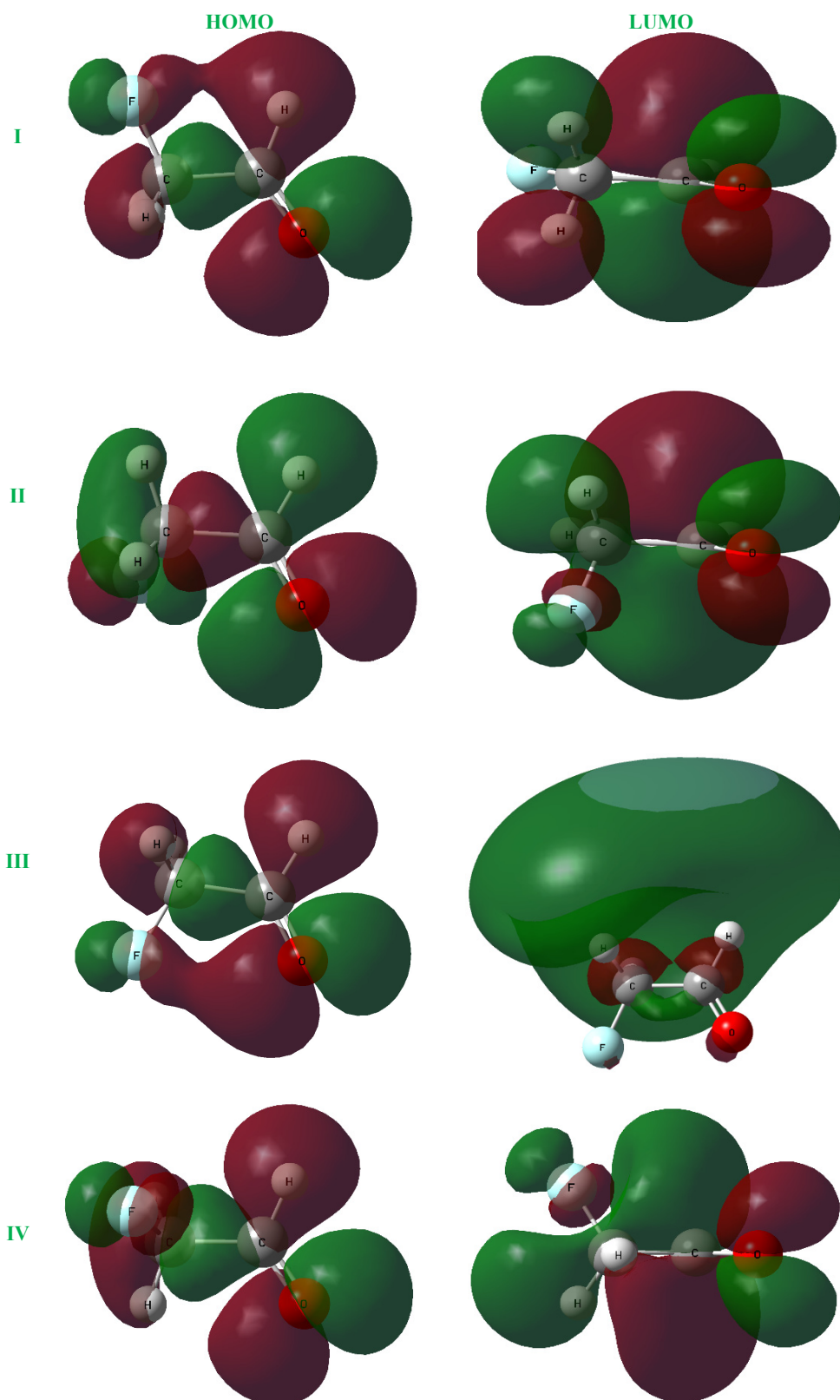


Fig. 3. Plots of frontier orbital of the possible conformers of 2-fluoroacetaldehyde.

The calculated electrophilicity (ω) values are listed in Table 2. It can be observed the smaller ω values in **I**-conformer in compared to other conformers. This trend is compatible with the minimum electrophilicity principle (MEIP) [47, 48] that is, while a conformer changes from the most stable to other less stable species in most cases, the energy rises, and the electrophilicity increases.

Natural bond analysis (NBO)

NBO analysis is useful to find a thorough understanding of the effects that direct the most stable conformations in isolated phase. Also, NBO is a significant tool for illustration of inter- and intramolecular bonding interactions, and as well a suitable origin for exploring conjugative interaction or charge transfer in molecular systems. Some of orbitals are electron donor or acceptors. The difference of energy between such bonding and anti-bonding orbitals, $[E^{(2)}]$, influences the susceptibility of the molecule to interactions [49, 50]. There are more effective interactions with the larger $[E^{(2)}]$ values. This suggests a stronger donating tendency of an electron of one orbital and a higher accepting tendency of other orbitals, which cause a stronger interaction between them.

The second order Fock matrix has been utilized for estimating of interactions corresponding to the donor-acceptor in the NBO analysis [51]. For every donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ corresponding to the delocalizing $i \rightarrow j$ is evaluated as:

$$E^{(2)} = -q_i \frac{(F_{i,j})^2}{E_j - E_i}$$

where q_i represents the i th donor orbital occupancy and E_i and E_j correspond to the donor and acceptor orbitals, respectively. $E_j - E_i$

represents the difference of energy between the donor orbital and acceptor orbital; i.e., the greater donating tendency of the electron donors toward electron acceptors the larger extent corresponding to conjugating the whole system

Second order perturbation theory analysis of Fock matrix in NBO basis

NBO analysis may be utilized for explaining the higher stability of the **I**-conformer comparing to other conformers. The stabilization energies of most important donor-acceptor electron interactions have remarkable influences on the stabilities of the conformations of the studied molecules (Table 3). These LP (O2) \rightarrow σ^* (C-H) and LP (O2) \rightarrow σ^* (C-C) interactions are the negative hyperconjugation associated in the examined compounds (Figure 2). It can be found, LP (O2) \rightarrow σ^* (C-H) interaction is more important than LP (O2) \rightarrow σ^* (C-C) interaction. These NBOs are visualized in Figure 4.

In the current study, Natural Bond Orbital (NBO) analysis was employed to partition the total electronic energy E (tot) into Lewis $E(L)$ (orbital population = 2.0) and Non-Lewis $E(NL)$ components (Table 4). The localized Lewis $E(L)$ component gave a good approximation of all the steric and classical electrostatic effects since corresponding to over 99.5% of the full electron density, while all the conjugation types could be described by the Non-Lewis $E(NL)$ component. Table 4 shows that the greater preference of the **I**-conformer when only considering the conjugation effects.

Calculations of the natural coulomb electrostatic energies E (NCE), as well as the total electronic energy and its Lewis components, were conducted [52]. Table 4 reveals the more preferable **I**-conformer based on NCE values.

TABLE 3. Second order perturbation theory analysis of Fock matrix in NBO basis of LP (2) O \rightarrow σ^* (C- H) and LP (2) O \rightarrow σ^* (C- C) negative hyperconjugation interactions of possible conformers of 2-fluoroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory.

Molecule	LP (2) O \rightarrow σ^* (C- H)			LP (2) O \rightarrow σ^* (C- C)		
	E(2)*	E(NL)-E(L)**	F(L,NL)**	E(2)*	E(NL)-E(L)**	F(L,NL)**
I	29.69	0.85	0.142	27.84	0.97	0.139
II	29.79	0.85	0.142	28.23	0.85	0.139
III	31.68	0.83	0.145	29.64	0.86	0.143
IV	29.44	0.85	0.141	27.38	0.87	0.138

* in kcal/mol. ** in a.u

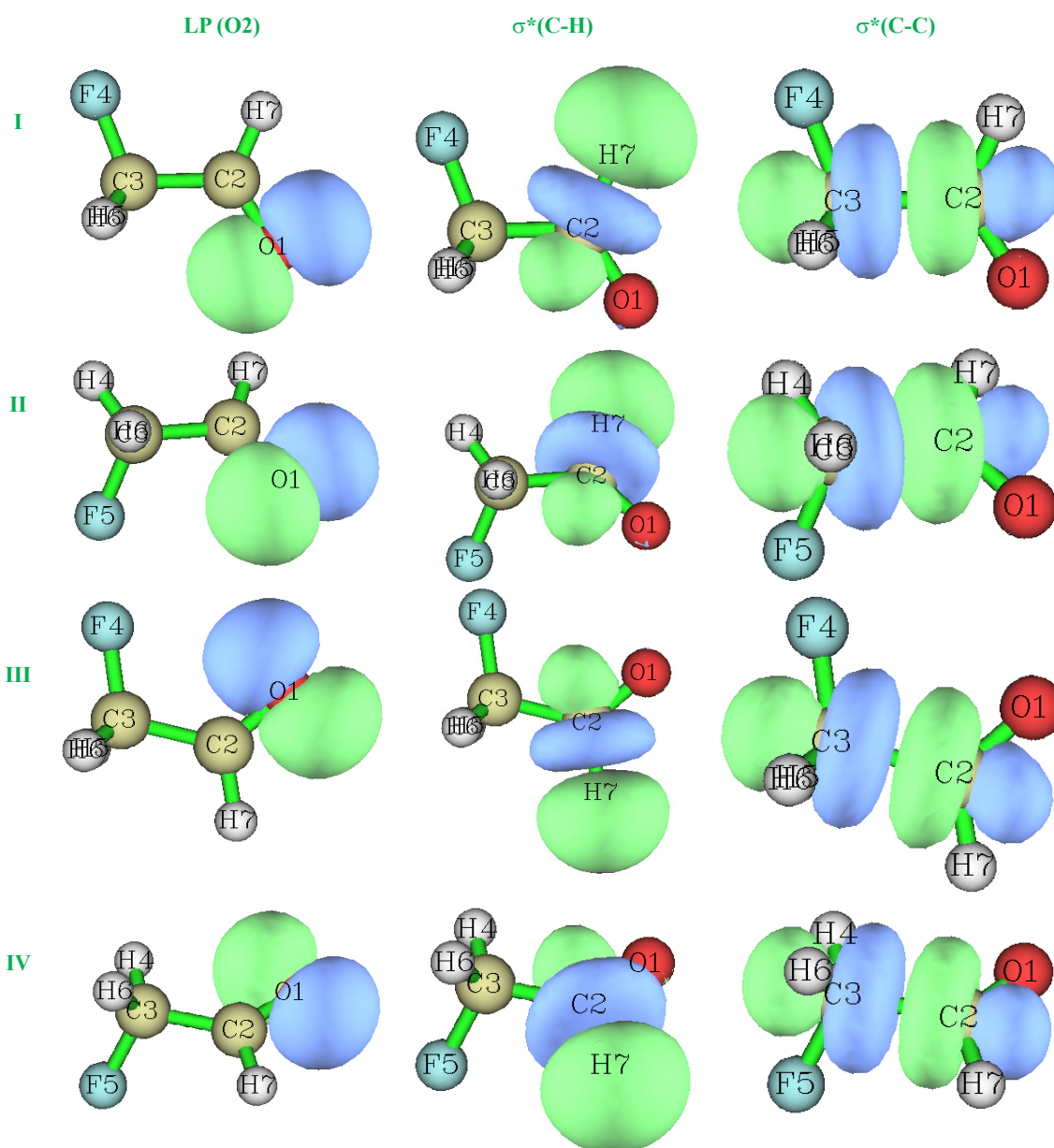


Fig. 4. Visualizations of the LP (O2), $\sigma^*(\text{C-H})$ and $\sigma^*(\text{C-C})$ NBOs of the possible conformers of 2-fluoroacetaldehyde.

TABLE 4. Results of the NBO analysis and energy decomposition of total electronic energy E(total) into Lewis E(L), non-Lewis E(NL), total steric E(steric) and electrostatic E(NCE) energies (in kcal/mol) of possible conformers of 2-fluoroacetaldehyde at the LC-wPBE/6-311++G(d,p) level of theory.

Molecule	E(steric)	$\Delta E(\text{steric})$	E(NCE)	$\Delta E(\text{NCE})$	E(NL)	$\Delta E(\text{NL})$
I	55.15	0	-0.11940	0.00	0.04903	0.00
II	61.42	6.27	-0.09834	13.22	0.04223	-4.27
III	63.22	8.07	-0.09515	15.22	0.04445	-2.87
IV	60.66	5.51	-0.10922	6.39	0.04506	-2.49

*ina.u.

Calculation of the total steric energy E(ST) was done through the NBO analysis. Table 4 further displays the more pronounced steric interactions occurring in the **III**- conformer. It can be seen, the lowest steric interactions occurring in the **I**- conformer.

Conclusion

In current study, we investigated the stability corresponding to the various conformers of 2-fluoroacetaldehyde. The main computation of current work can be outlined as follows:

1. **I**- conformation has a greater stability than other conformations in all studied molecules at the LC-WPBE/6-311++G** level of theory. The greater stability of this conformation was attributed to negative hyperconjugative effect.
2. The negative hyperconjugative anomeric effect of these molecules was investigated by the LP(O2)→σ*(C-H) interaction.
3. The largest HOMO-LUMO gap value, the smallest electrophilicity (ω) value for the **I**-conformer are is compatible with the principles of minimum energy (MEP), and maximum hardness (MHP), the minimum electrophilicity principle (MEIP).
4. The total steric energy E (ST) revealed that the more pronounced steric interactions occurring in the **III**- conformer. The lowest steric interactions found in the **I**- conformer.

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