

## Exploring the origin of the cis-configurations preferences in 1,2-dihaloethenes. Assessing the roles and contributions of the Pauli exchange type repulsions, hyperconjugative interactions and bonding orbitals deviations

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**Abstract:** The origin of the cis-configurations preferences in 1,2-difluoroethene (1), 1,2-dichloroethene (2) and 1,2-dibromoethene (3) were analyzed by means of G3MP2 composite method and long range corrected hybrid-density functional theory (LC-roPBE) with the 6-311+G\*\* basis set on all atoms and natural bond orbital interpretation. In these methods used in this work showed the cis-configurations preferences (compared to their transconfigurations) decrease from compound 1 to compound 3. Based on the results obtained, the deletions of the hyperconjugative interactions from the Fock matrices of the cis- and transconfigurations of compound 1 lead to the increase of the trans-conformations stability (by 6.11 kcal mol<sup>-1</sup>) compared to its corresponding cis-conformation. Accordingly, the cooperative stabilizations associated with the bent C=C bond paths and total hyperconjugative generalized anomeric effect overcome the destabilizations associated with the exchange component and dipole-dipole interactions, leading to the cis-configuration preference in compound 1.

The cis-conformations of compounds 1-3 with large dipole moments are still more stable than their corresponding trans-conformation, implying that the electrostatic model associated with the dipole-dipole interactions do not play a determining role on the anomeric preferences in these compounds. This is important evidence that reveals the isomer with larger molecular dipole moment is not the less stable one which contradicts the published conclusion in the literature.

**Keywords:** Generalized anomeric effects, Bent C=C bond paths, Exchange component, NBO, 1,2-Dihaloethenes.

### Introduction

The configurational properties of 1,2-dihaloethenes have been the object of a great deal of chemical curiosity [1-13]. The experimental results showed that the cis-configurations of 1,2-difluoroethene (1), 1,2-dichloroethene (2) and 1,2-dibromoethene (3) are more stable than their corresponding trans-configurations. The cis-configurations of compounds 1-3 possess large dipole moments but still they are more stable than their corresponding trans-configurations.

This is an interesting phenomena that contradicts some conclusions published in the literature in which some researchers claims that “the isomer with the larger molecular dipole moments is less stable one [14,15]. In 2008, Yamamoto and co-workers analyzed the origin of the cis-effect in 1,2-dihaloethenes [16]. They pointed out that the halogen atom lone pair delocalizations into the C=C bond antibonding orbitals (LP effect) are the dominant factor of cis-effect.

Also, they pointed out that the cis-configurations of compounds 1-3 possess greater total steric exchange component than their corresponding trans-configurations but the steric forces on the destabilizations of the cis-configurations are less than

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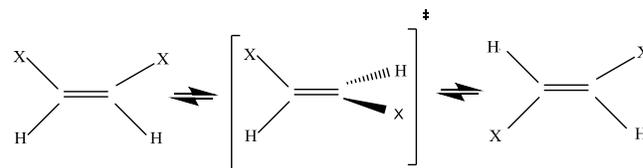
stabilization effects of the hyperconjugative interactions. Their results are not in the line with our findings about the amounts and impacts of the exchange components on the configurational behaviors of compounds **1-3**. To gain further insights into the origin of the cis-effect in 1,2-dihaloethanes, we examined the impacts of the hyperconjugative interactions [17-33], Pauli exchange type repulsion, the electrostatic model associated with the dipole-dipole interactions, the strain effect associated with the deviations of the  $p$  orbital of the carbon atoms from their normal orientations (which forming  $\sigma$ -bond) and the repulsive electrostatic interactions between the natural atomic charges of the carbon atoms on the configurational properties of compounds **1-3** by means of the G3MP2[34] and LC-roPBE/6-311+G\*\*[35,36] based methods with the 6-311+G\*\* basis set [37-40] on all atoms and natural bond orbital interpretation [41]. Further, the potential energy surfaces of the rotations around the C=C bonds in compounds **1-3** were investigated at the G3MP2 and LC-roPBE/6-311+G\*\* based methods with the 6-311+G\*\* basis set levels of theory and the impacts of the exchange components and hyperconjugative interactions on these processes were explored. In order to explore the contributions of the hyperconjugative interactions on the configurational behaviors in compounds **1-3**, we deleted the electronic delocalizations associated with the cis-effect ( $\text{oci}_{\text{H}^{\circ}\text{C}_2\text{-X}}$ ,  $\text{oci}_{\text{X}^{\circ}\text{C}_2\text{-H}}$  trans-effect ( $\text{oci}_{\text{X}^{\circ}\text{C}_1\text{-C}_2}$ ,  $\text{oci}_{\text{H}^{\circ}\text{C}_1\text{-C}_2}$ ), lone pair effect (LP: $\text{X}^{\circ}\text{C}_1\text{-C}_2$ , LP2: $\text{X}^{\circ}\text{C}_1\text{-C}_2$ , LP3: $\text{X}^{\circ}\text{C}_1\text{-C}_2$ ) and through space effect (LP2: $\text{X}(\text{C}_1)^{\circ}\text{C}_2\text{-X}$ ) from the Fock matrices of the cis- and trans-configurations. Then, by rediagonalization and comparison of the current Fock matrices with their original forms, we estimate the contributions of the electronic delocalizations associated with the cis-effect, trans-effect, lone pair effect and through space effect on the configurational preferences in compounds **1-3**. It may be worth to notice that the procedure mentioned above is an efficient approach and can be performed to evaluate the contributions of some specific hyperconjugative interactions on the conformational properties of chemical compounds [42].

## Result and Discussion

### 1. Conformation preference

The enthalpies (H), entropies (S), Gibbs free energies (G), corrected electronic energies ( $E_o = E_{el} + \text{ZPE}$ ) for the cis- and trans-configurations of compounds **1-3** (Scheme 1) and their corresponding differences (AH, AS AG, and AE<sub>o</sub>), as calculated at the G3MP2 and\*\*

and LC-roPBE/6-311+G\*\* levels of theory are given in Tables 1, SI-1 and SI-2.



**Scheme 1:** Schematic representation of the cis- and trans-configurations and their corresponding interconversion transition state structures of compounds **1-3**.

1: X=F, 2: X=Cl, 3: X=Br

The quantities of interest here are the relative values of the thermodynamic functions for different configurations of the same molecule. It is expectable that the errors in such differences will be very small and that even the corresponding errors between the different closely related compounds will be minimal. The smooth variation among the calculated thermodynamic parameters (AH, AS AG, and AE<sub>o</sub>) supports this expectation. The G3MP2 \*\* and LC-roPBE/6-311+G\*\* calculated thermodynamic AH, AS AG, and AE<sub>o</sub> parameters shows the cis-configuration preference in compound **1**. Effectively, the cis-configuration preference decreases going from compound **1** to compound **3** as calculated at the all levels of theory used in this work. Seemingly, compared with the experimental data published about the cis-configuration preferences in compounds **1-3** [4,11], the G3MP2 method gives more reliable results concerning their configurational properties (Table 1).

### 2. Assessing the impacts of the hyperconjugative interactions on the configurational preferences in compounds 1-3

The stabilization energies associated with the hyperconjugative interactions (*cis-effect* and *trans-effect*) and also the negative hyperconjugative interactions (lone pair effect and through space effect) have significant impacts on the configurational behaviors of compounds **1-3**. The NBO-LC-roPBE/6-311+G\*\* interpretations showed that the stabilization energies associated with the *cis-effect* ( $\text{oci}_{\text{C}_1\text{-H}^{\circ}\text{C}_2\text{-X}}$  and  $\text{oci}_{\text{C}_2\text{-X}^{\circ}\text{C}_1\text{-H}}$  hyperconjugative interactions) increase significantly from the cis-configurations of compound **1** to compound **3** but decrease slightly from the trans-configurations of compound **1** to compound **3**, asserting that the cis-effect tends to increase the cis-configuration preference going from compound **1** to compound **3**

(Table 2). On the other hand, based on the results obtained, the stabilization energies associated with the transeffect ( $O_{C1-X}—O^*_{C2-X}$  and  $O_{C1-H}—O^*_{C2-X}$  hyperconjugative interactions) increase drastically from the trans-configurations of compound 1 to compound 3, implying that the *trans-effect* tends to increase of the trans-configuration preference going

from compound 1 to compound 3. Interestingly, the through space effect associated with  $LP_2X_{(C1)}—O^*_{C2-X}$  negative hyperconjugative interaction increases slightly from the *trans*-configurations of compound 1 to compound 2 but it does not change going from the trans-configurations of compound 2 to compound 3.

**Table 1:** G3MP2, CCSD(T)/6-311+G\*\* and LC-roPBE/6-311+G\*\* calculated thermodynamic function differences [ $\Delta H$ ,  $\Delta G$ ,  $\Delta E_o$  (in kcal mol<sup>-1</sup>) and  $\Delta S$  (in cal mol<sup>-1</sup>K<sup>-1</sup>)] for the *cis*- and *trans*-configurations and their corresponding transition state structures of compounds 1-3.

	G3MP2				LC-roPBE/6-311+G**				Exp.
	$\Delta H$	$\Delta S$	$\Delta G$	$\Delta E_o$	$\Delta H$	$\Delta S$	$\Delta G$	$\Delta E_o$	$\Delta E_o$
1- <i>cis</i>	0.00	0.000	0.00	0.00	0.00	0.000	0.00	0.00	0.00
1- <i>trans</i>	0.78	-0.181	0.84	0.72	0.56	-0.113	0.59	0.48	(1.08 ± 0.12) <sup>a</sup>
2- <i>cis</i>	0.00	0.000	0.00	0.00	0.00	0.000	0.00	0.00	0.0
2- <i>trans</i>	0.91	0.208	0.59	0.49	0.33	0.178	0.28	0.17	(0.72 ± 0.16) <sup>a</sup>
3- <i>cis</i>	0.00	0.000	0.000	0.00	0.00	0.000	0.00	0.00	0.00
3- <i>trans</i>	0.31	0.332	0.21	0.11	-0.20	0.341	-0.30	-0.41	(0.25 ± 0.33) <sup>a</sup>

Note that the through space effect associated with  $LP_2X_{(C1)}—O^*_{C2-X}$  negative hyperconjugative interaction tends to increase the trans-configuration preference. It is worth to note that the differences between the total stabilization energies associated with the hyperconjugative *cis*-, *trans*- and through space-effect ( $HCGAE_{total}$ ) in the *cis*- and *trans*-configurations:

$HCGAE_{total} = L[(cis-effect + trans-effect + through space effect)_{trans} - (cis-effect + trans-effect + through space effect)_{cis}]$  (eq. 2) are in favor of the *cis*-configurations of compounds 1-3.  $HCGAE_{total}$  value increases significantly going from compound 1 to compound 2 but decreases slightly from compound 2 to compound 3.

Since the energy difference between the *trans*- and *cis*-configurations ( $G_{trans} - G_{cis}$ ) decreases from compound 1 to compound 3, the variations of  $HCGAE_{total}$  values do not justify the variations of  $G_{trans} - G_{cis}$  values. Accordingly, the roles and contributions of other factors should be accounted.

Yamamoto and co-workers [16] pointed out previously that the halogen atom lone pair delocalization into the C=C bond antibonding orbitals ( $LP_1X—O^*_{C1-C2}$ ,  $LP_2X—a^*_{C1-C2}$ ,  $LP_3X—rc^*_{C1-C2}$ ) are the dominant electronic factor on the *cis*-configurations

preferences in compounds 1-3 and the results of this work confirm their conclusion. The NBO-LC-mPBE/6-311+G\*\* results showed that the lone pair effects in the *cis*-configurations of compounds 1-3 are greater than those in their corresponding *trans*-configurations. Using the lone pair effects obtained, a “A” parameter can be found as  $A[\$ Lone pair effect (trans) - \$ Lone pair effect (cis)]n(C2h)$ . The calculated  $A[\$ Lone pair effect (trans) - \$ Lone pair effect (cis)]$  parameter increases from compound 1 to compound 2 while decreases from compound 2 to 3. Interestingly, the trend observed for the variations of  $A[\$ Lone pair effect (trans) - \$ Lone pair effect (c/s)]$  and  $HCGAE_{total}$  parameters from compound 1 to compound 3 are the same which is not similar to the trend observed for the energy difference between the *trans*- and *cis*-configurations ( $G_{trans} - G_{cis}$ ). In order to assess the validity of our procedure regarding the estimation of  $HCGAE_{total}$  parameters in compounds 1-3, we deleted all hyperconjugative interactions from the Fock matrices of their corresponding *cis*- and *trans*-configurations.

**Table 2:** NBO-LC-roPBE/6-311+G\*\* calculated stabilization energies ( $E_2$ , in kcal mol<sup>-1</sup>) associated with the *cis-effect*, *trans-effect*, lone pair effect and through space effect, hyperconjugative generalized anomeric effect (HCGAE, in kcal mol<sup>-1</sup>) and off-diagonal elements ( $F_{ij}$ , in a.u.) for the *cis*, *trans* and transition state structures of compounds 1-3. orbital occupancies (e).

	<b>1</b>		<b>2</b>		<b>3</b>	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
<b><math>E_2</math>: APP- and SPP-effects</b>						
$(\sigma_{C1-H} \rightarrow \sigma_{C2-X}^*) \times 2$	15.14	3.68	19.78	1.72	21.7	1.26
$(\sigma_{C1-X} \rightarrow \sigma_{C2-H}^*) \times 2$	2.84	-	5.88	-	7.44	-
$\Sigma$ APP-effect	17.98	3.68	25.66	1.72	29.14	1.26
$\Sigma$ [APP+SPP]effect( <i>trans</i> )- $\Sigma$ [APP+SPP]effect( <i>cis</i> ): <b>a</b>	-14.30		-23.94		-27.88	
<b><math>E_2</math>: APP- and SPP-effects</b>						
$(\sigma_{C1-X} \rightarrow \sigma_{C2-X}^*) \times 2$	-	5.22	-	11.30	-	14.60
$(\sigma_{C1-H} \rightarrow \sigma_{C2-H}^*) \times 2$	-	7.72	2.04	10.38	2.26	11.10
$\Sigma$ APP-effect	-	12.94	2.04	21.68	2.26	25.70
$\Sigma$ [APP+SPP]effect( <i>trans</i> )- $\Sigma$ [APP+SPP]effect( <i>cis</i> ): <b>b</b>	12.94		19.64		23.44	
<b>a+b</b>	1.36		4.30		4.44	
<b><math>E_2</math>: LP-effect</b>						
$(LP_1X \rightarrow \sigma_{C1-C2}^*) \times 2$	-	-	2.06	1.48	2.28	1.54
$(LP_2X \rightarrow \sigma_{C1-C2}^*) \times 2$	15.42	13.98	12.26	10.82	9.52	8.62
$(LP_3X \rightarrow \pi_{C1-C2}^*) \times 2$	59.68	55.92	51.78	46.72	42.90	38.22
$\Sigma$ Lone pair effect	75.10	69.90	66.10	59.02	54.70	48.38
$\Sigma$ LP-effect ( <i>trans</i> )- $\Sigma$ LP-effect ( <i>cis</i> ): <b>c</b>	-5.20		-7.08		-6.32	
<b><math>E_2</math>: TS-effect</b>						
$(LP_2X \rightarrow \sigma_{C2-X}^*)$	-	1.98	-	2.14	-	2.14
$\Sigma$ TS-effect( <i>trans</i> )- $\Sigma$ TS-effect ( <i>cis</i> ): <b>d</b>	1.98		2.14		2.14	
$\Sigma$ effects	93.08	88.50	93.80	84.56	86.10	77.48
$HCGAE_{total} = HCGAE_{total}(trans) - HCGAE_{total}(cis)$ : <b>(a+b+c+d)</b>	-4.58		-9.24		-8.62	
<b><math>F_{ij}</math></b>						
$\sigma_{C1-H} \rightarrow \sigma_{C2-X}^*$	0.081	0.040	0.088	0.026	0.089	0.021
$\sigma_{C1-X} \rightarrow \sigma_{C2-X}^*$	-	0.056	-	0.072	-	0.077
$LP_3X \rightarrow \pi_{C1-C2}^*$	0.125	0.121	0.106	0.101	0.093	0.088

Then, with rediagonalization and comparison of the current Fock matrices with their original forms, we found that with deletion of all hyperconjugative interactions, the trans-configurations of compounds 1-3 became more stable than their corresponding cis-configurations by about 6.11, 9.18 and 7.01 kcal mol<sup>-1</sup>, respectively (Table 3). These findings revealed that the hyperconjugative interactions play a significant role on the configurational preferences in compounds 1-3. The variations of the energy differences between the cis- and trans-configurations of compounds 1-3 (with deletion of all hyperconjugative interactions) and their corresponding HCGAE<sub>total</sub> parameters are the same. This fact justifies the validity of our procedure regarding the estimation of HCGAE<sub>total</sub> parameters [eq. (2)].

In order to better illustrate the cis-effect ( $\sigma_{C_1-H} \rightarrow \sigma_{C_2-X}^*$  and  $\sigma_{C_2-X} \rightarrow \sigma_{C_1-H}^*$  hyperconjugative interactions), trans-effect ( $\sigma_{C_1-X} \rightarrow \sigma_{C_2-X}^*$  and  $\sigma_{C_1-H} \rightarrow \sigma_{C_2-H}^*$  hyperconjugative interactions), through space effect ( $LP_2X_{(C_1)} \rightarrow \sigma_{C_2-X}^*$  negative hyperconjugative interaction) and lone pair effect ( $LP_1X \rightarrow \sigma_{C_1-C_2}^*$ ,  $LP_2X \rightarrow \sigma_{C_1-C_2}^*$ ,  $LP_3X \rightarrow \sigma_{C_1-C_2}^*$ ) on the structural and configurational preferences in compounds 1-3, we analyzed the profiles of the orbital amplitudes (or electron densities) for the mixing of their corresponding donor and acceptor orbitals. Figure 1 shows that the mixing of the  $\sigma_{C_1-H}$  bonding orbitals with the  $\sigma_{C_2-X}^*$  anti-bonding orbitals in the cis-configurations increases significantly from compound 1 to compound 3, tending to increase the cis-configuration preference going from compound 1 to compound 3 but increase the local dipole moments of C-H and C-X bonds leads to increase of the total dipole moments, increasing their corresponding overall energies. On the other hand, the lone pair effect associated with  $LP_2X \rightarrow \sigma_{C_1-C_2}^*$  negative hyperconjugative interactions has an opposite impact and tends to decrease the C-X bond dipole moments. Figure 2 shows that the mixing of  $LP_2X$  nonbonding orbitals with the  $\sigma_{C_1-C_2}^*$  anti-bonding orbitals decrease going from cis-configurations of compound 1 to

compound 3. This trend is also observed for the lone pair effect associated with  $LP_3X \rightarrow \sigma_{C_1-C_2}^*$  negative hyperconjugative interactions (Figure 3). Based on the results obtained, the cis-effect tends to increase the dipole moments of the cis-configurations but the lone pair effect has an opposite impact.

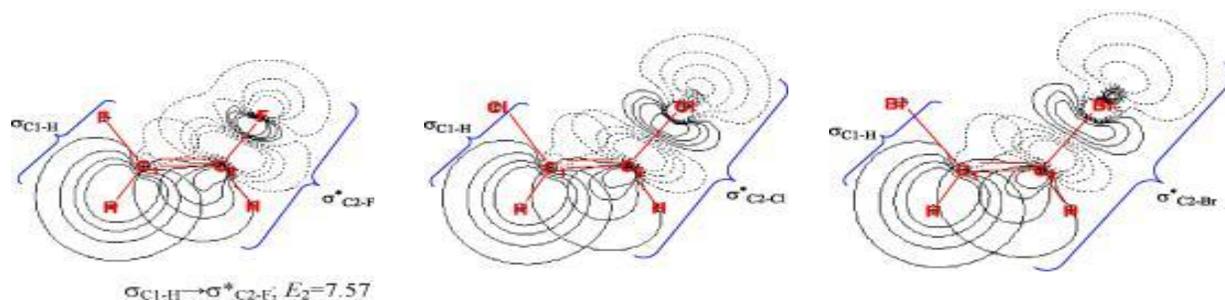
The dipole moments of c-X (X=halogen atoms) bonds can be controlled by two factors [inductive effects (*I-effect*) and resonance effect (*R-effect*)]. As well as the C-X bond lengths increase, the electron-withdrawing inductive effect (*+I-effect*) decreases going from the C-F to C-Br bonds of the cis-configurations of compound 1 to compound 3, causing the decrease of their C-X bond local dipole moments but the *cis*-effect has an opposite impact. The dipole moments of the cis-configurations of compounds 1-3 results from the confrontations between the *I-effect*, *cis-effect* and lone pair effect (*R-effect*).

#### **The electrostatic model (associated with the dipole-dipole interactions) impacts on the configurational preferences in compounds 1-3:**

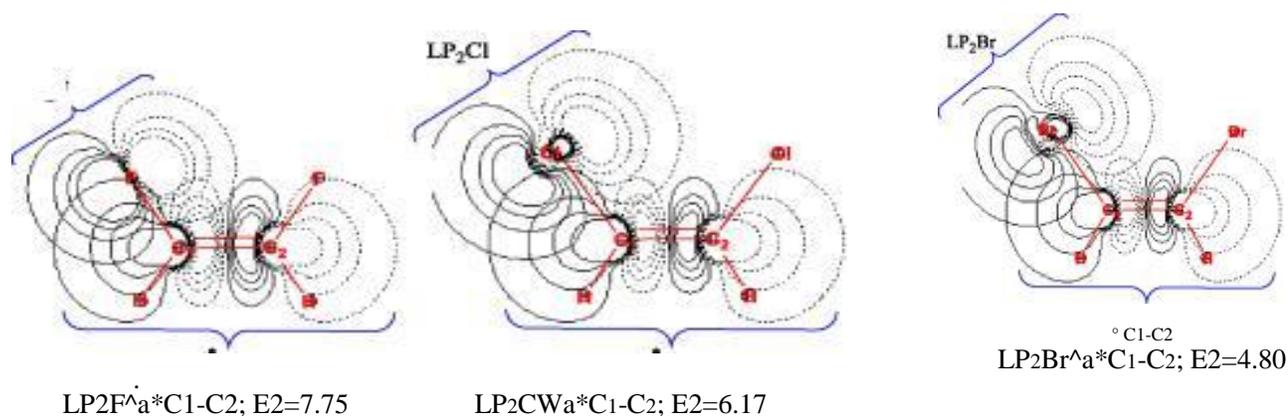
We may expect that there are preferences for the conformations or configurations with the smallest resultant dipole moments in the gas phase or in the nonpolar media and the conformations or configurations with the larger dipole moments (that lead to the larger polarizabilities) are the less stable form [14,15]. The cis-configurations preferences in compounds 1-3 (with large dipole moments) reveals that the expectation mentioned above could not be generalized for all chemical compounds. Due to the central symmetry in the trans-configurations of compounds 1-3, they do not possess any molecular dipole moments but they are less stable than their corresponding cis-configurations (with possessing large total dipole moments) (Table 4).

**Table 3:** NBO-LC-wPBE/6-311+G\*\* calculated total SCF energies (*TSCFE*, in a.u.), energies of deletions (*EOD*, in a.u.), and energy changes (*EC*, in a.u.) associated with the deletion of all donor-acceptor interactions in the *cis*- and *trans*-configurations of compounds 1-3

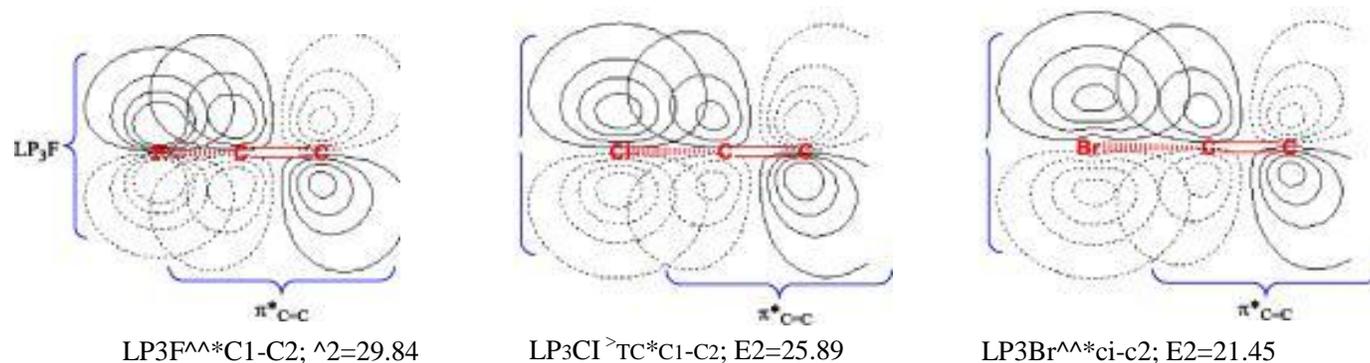
Geometries	1		2		3	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
<i>TSCFE</i>	-276.973009	-276.972462	-997.516095	-997.515452	-5224.872274	-5224.872561
<i>EOD</i>	-276.718826	-276.728009	-997.268336	-997.282329	-5224.643797	-5224.655252
<i>EC</i>	0.254183(159.50) <sup>a</sup>	0.244454(153.40) <sup>a</sup>	0.247759(155.47) <sup>a</sup>	0.233123(146.29) <sup>a</sup>	0.228477(143.37) <sup>a</sup>	0.217309(136.36) <sup>a</sup>
$\Delta[EC_{cis}]$		0.009729(6.11) <sup>a</sup>		0.014636(9.18) <sup>a</sup>		0.011168(7.01) <sup>a</sup>



**Figure 1:** The calculated profiles of the orbital amplitudes (electron densities) for the through-bond *cis-effects* ( $\sigma_{\text{C1-H}} \rightarrow \sigma^*_{\text{C2-X}}$  [X=F (1), Cl (2), Br (3)] negative hyperconjugations) in the *cis*-configurations of compounds 1-3.  $E_2$  values are in kcal mol<sup>-1</sup>



**Figure 2:** The calculated profiles of the orbital amplitudes (electron densities) for the through-bond *lone pair effects* ( $\text{LP}_2\text{X} \rightarrow \pi^*_{\text{C1-C2}}$  [X=F (1), Cl (2), Br (3)] negative hyperconjugations) in the *cis*-configurations of compounds 1-3.  $E_2$  values are in kcal mol<sup>-1</sup>



**Figure 3:** The calculated profiles of the orbital amplitudes (electron densities) for the through-bond *lone pair effects* ( $\text{LP}_3\text{X} \rightarrow \pi^*_{\text{C-C}}$  [X=F (1), Cl (2), Br (3)] negative hyperconjugations) in the *cis*-configurations of compounds 1-3.  $E_2$  values are in kcal mol<sup>-1</sup>.

This fact demonstrates that the *isomer with larger molecular dipole moment is not always the less stable one*. Obviously, some conclusions published in the literature[14,15] (which claim the electrostatic model

associated with the dipole-dipole interactions play a determining role on the conformational or configurational preferences of chemical compounds) should not be generalized for all chemical systems.

### **Assessing the contributions of the off-diagonal elements and the energy differences on the hyperconjugative interactions in compounds 1-3.**

The energies of the C-X bonds bonding orbitals ( $a_{C-X}$ ) increase by the decrease of the electronegativity values of the halogen atoms going from the fluorine to bromine atoms while the energies of the antibonding orbitals of the C-X bonds,  $a^*_{C-X}$ , decrease inversely. Compared to the variations of the energies of the C-X bonds bonding orbitals ( $a_{C-X}$ ), there are no significant differences for the energies of the C-H bonds bonding orbitals ( $o_{C-H}$ ). The results of this work showed that energy difference between donor [ $s(a_{C-H})$ ] and acceptor [ $s(a^*_{C-X})$ ] orbitals (i.e.  $A[s(a^*_{C-X})-s(a_{C-H})]$ ) decreases significantly from the cA-configuration of compound 1 to compound 3 (Table SI-4). This trend is also observed for the variations of  $A[e(t^*_{C=C})-f(LP_3X)]$  parameters going from the cA-configurations of compound 1 to compound 3. We may expect that the second order perturbative energies associated with the lone pair effect ( $LP_3X-t^*_{C=C}$ ) shall increase with the decrease of  $A[e(t^*_{C=C})-f(LP_3X)]$  parameters going from the cA-configurations of compound 1 to compound 3 but the results obtained in this work do not confirm this expectation. Obviously, the variations of the second order perturbative energies associated with the  $LP_3X-tt^*_{C=C}$  negative hyperconjugative interactions in the cA-configurations of compounds 1-3 could be controlled by their corresponding off-diagonal (Fj) elements (Table 2). It is worth noting that there is no confrontation between the  $A[e(t^*_{C=C})-e(LP_3X)]$  parameters and off-diagonal elements values (Fj) for the variations of the second order perturbative energies associated with the cA-effects and *trans-effects* in the *cis*- and *trans*-configurations of compounds 1-3.

### **Orbital occupancies:**

The bonding orbital occupancies of the C-H bonds ( $a_{C-H}$ ) in the *trans*-configurations of compounds 1-3 are greater than those in their corresponding cA-configurations which is attributed to the *cis*-effect associated with the  $o_{C1-H} \wedge o^*_{C2-X}$  hyperconjugative interactions (Table SI-4). The decrease of the bonding orbital occupancies of the C-H bonds ( $a_{C-H}$ ) from the *cis*- configurations of compound 1 to compound 3 results from the increase of their corresponding  $o_{C1-H} \wedge o^*_{C2-X}$  hyperconjugative interactions, decreasing the electron densities of the  $o_{C1-H}$  bonds and increasing the electron densities of the  $o^*_{C2-X}$  antibonding orbitals. It is worth noting that the bonding orbital occupancies of the C-X bonds ( $a_{C-X}$ ) in the cA-configurations of compounds 1-3 are greater than those in their corresponding *trans*-configurations. This fact could be justified by the *trans-effect* associated with the  $o_{C1-X} \wedge o^*_{C2-X}$  hyperconjugative interactions which tends to decrease of the electron densities of the bonding orbitals of the C-X bonds ( $o_{C1-X}$ ) and increase of the electron densities of the  $o^*_{C2-X}$  antibonding orbitals.

The total natural resonance theory (NRT) bond orders (natural bond orders, *nbo*) of the *cis*- and *trans*-configurations of compounds 1-3 were evaluated by means of the NBO-LC-roPBE/6-311+G\*\* method. The examinations of the structural parameters and their corresponding bond orders show that the hyperconjugative interactions have significant impacts on the structural parameters *via* affecting their corresponding bond orders. Based on the results obtained, the calculated total natural resonance theory (NRT) bond orders (natural bond orders, *nbo*) of the C=C bonds of the *trans*-configurations of compound 1-3 are greater than those of their corresponding *cis*-configurations (Table 4). NBO-LC-roPBE/6-311+G\*\* results revealed that the bond orders of the C=C bonds of the *cis*- and *trans*-configurations increase from compound 1 to compound 3. Note that the lone pair effect associated with the  $LP_3X-t^*_{C=C}$  negative hyperconjugative interactions increases the C-X bond orders but decreases the C=C bond orders. The stronger  $LP_3X-t^*_{C=C}$  negative hyperconjugative interactions in the *cis*-configurations of compounds 1-3 compared to those in their *trans*-configurations increase the electronic populations of  $t^*_{C=C}$  antibonding orbitals, decreasing their corresponding  $t_{C=C}$  bond orders. The differences between the natural bond orders (*nbo*) of C=C bonds in the *cis*- and *trans*-configurations,  $A[nbo(C=C)_{trans}-nbo(C=C)_{cis}]$ , increase significantly from compound 1 to compound 3. In addition,  $A[nbo(C-X)_{cis}-nbo(C-X)_{trans}]$  parameters increase drastically going from compound 1 to compound 3, revealing the determining impacts of the  $LP_3X-tt^*_{C=C}$  negative hyperconjugative interactions on the bond orders of the C=C and C-X bonds.

### **Bond orders**

The total natural resonance theory (NRT) bond orders (natural bond orders, *nbo*) of the *cis*- and *trans*-configurations of compounds 1-3 were evaluated by means of the NBO-LC-roPBE/6-311+G\*\* method. The examinations of the structural parameters and their corresponding bond orders show that the hyperconjugative interactions have significant impacts on the structural parameters *via* affecting their corresponding bond orders. Based on the results obtained, the calculated total natural resonance theory (NRT) bond orders (natural bond orders, *nbo*) of the C=C bonds of the *trans*-configurations of compound 1-3 are greater than those of their corresponding *cis*-configurations (Table 4). NBO-LC-roPBE/6-311+G\*\* results revealed that the bond orders of the C=C bonds of the *cis*- and *trans*-configurations increase from compound 1 to compound 3. Note that the lone pair effect associated with the  $LP_3X-t^*_{C=C}$  negative hyperconjugative interactions increases the C-X bond orders but decreases the C=C bond orders. The stronger  $LP_3X-t^*_{C=C}$  negative hyperconjugative interactions in the *cis*-configurations of compounds 1-3 compared to those in their *trans*-configurations increase the electronic populations of  $t^*_{C=C}$  antibonding orbitals, decreasing their corresponding  $t_{C=C}$  bond orders. The differences between the natural bond orders (*nbo*) of C=C bonds in the *cis*- and *trans*-configurations,  $A[nbo(C=C)_{trans}-nbo(C=C)_{cis}]$ , increase significantly from compound 1 to compound 3. In addition,  $A[nbo(C-X)_{cis}-nbo(C-X)_{trans}]$  parameters increase drastically going from compound 1 to compound 3, revealing the determining impacts of the  $LP_3X-tt^*_{C=C}$  negative hyperconjugative interactions on the bond orders of the C=C and C-X bonds.

**Table 4.** NBO-LC-roPBE/6-311+G\*\* calculated natural atomic charges (NAC), natural bond orders (*nbo*), total steric exchange energies (TSEE, in kcal mol<sup>-1</sup>), dipole moments (V, in Debye) and bonding orbitals deviations [from line of nuclear centers for a-bonds and from the perpendicular line to the line of nuclear centers for rc-bonds] for the *cis*, *trans* and transition state structures of compounds 1-3.

	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
NAC						
C	0.15298	0.15352	-0.21961	-0.24382	-0.32870	-0.31953
X	-0.33607	-0.33913	0.01142	0.01408	0.09454	0.08426
<hr/>						
C-C	1.9259	1.30	1.9267	1.9366	1.9352	1.9578
C-X	1.0400	1.54	1.0395	1.0289	1.0301	1.0178
A [ <i>nbo(c-c)trans-nbo(C-c)Cis</i> ]		0.0071		0.0099		0.0226
A [ <i>nbo(c-X)Cis-nbo(C-X)trans</i> ]		0.0046		0.0106		0.0123
TSEE	58.08	51.3	104.50	104.46	109.06	117.21
A[TSEE( <i>cis</i> ) - TSEE( <i>trans</i> )]		6.25		0.04		-8.15
V	2.6511	0.00	2.0631	0.000	1.8045	0.0000
<hr/>						
<i>bond deviatuions</i>						
^C=C	0.1	5.7	0.1	5.4	0.1	5.5
a c-c	3.7	1.8	5.0	2.5	5.3	2.7
OC-X	1.3	1.3	3.0	2.8	2.9	2.4
Edev(ftc=c+a c-c)	3.8	7.3	5.1	7.9	5.4	8.2
'Ldev('KC=C+aC-C)( <i>trans-cis</i> )		3.5		2.8		2.8

### Structural parameters

Representative structural parameters (bond lengths, bond angles and torsion angles) for the *cis*- and *trans*-configurations of compounds 1-3 as calculated at the LC-roPBE/6-311+G\*\* are summarized in Table 5. Although we perform theoretical calculations to obtain structural parameters and many properties with an accuracy that is competitive with experiments, we do not expect to reproduce exactly the experimental values by means of the theoretical techniques. It is worth

noting that we perform calculations for single molecules (gas phase), nonetheless there is reasonable agreement between the calculated and reported experimental structural parameters of the *cis*- and *trans*-configurations of compounds 1-3 (see Table 5). LC-roPBE/6-311+G\*\* levels of theory used in this work revealed that the C=C bond lengths in the *cis*-configurations of compounds 1-3 are significantly longer compared to those in their corresponding *trans*-conformations while the C-X bonds are shorter. The

longer C=C and the shorter C-X bond lengths in the cis-configurations of compounds 1-3, compared to those in their corresponding trans-configurations result from their stronger lone pair effect associated with the  $LP_2X^{\wedge}a^*_{C-C}$  and  $LP_3X^{\wedge}a^*_{C-C}$  negative hyperconjugative interactions which decrease the bond orders of the C=C bonds *via* increasing their corresponding anti-bonding orbitals occupancies.

***The Role of the Pauli exchange-type repulsions on the potential surface energies of the hydrogen molecule dissociation reactions of compounds 1-4.***

The well-established physical picture of steric repulsions could be expressed by the natural steric analysis. Weinhold has pointed out that the steric exchange energy is expressed as the energy differences between the filled orthonormal NBOs (er.) and their preorthogonal PNBO counterparts ( $\sigma^{\wedge}$ ):<sup>[54-58]</sup>  $\langle \sigma^{\wedge} | \hat{H} | \sigma^{\wedge} \rangle - \langle \sigma^{\wedge} | \hat{H} | \sigma^{\wedge} \rangle$  ( $\ll 13$ ) where  $F/V^{50} = \langle \sigma^{\wedge} | \hat{H} | \sigma^{\wedge} \rangle$  and  $\langle \sigma^{\wedge} | \hat{H} | \sigma^{\wedge} \rangle = \langle \sigma^{\wedge} | \hat{H} | \sigma^{\wedge} \rangle$  (cTy |.:F |cr.)\_ Accordingly, the steric exchange energy (or the Pauli exchange type repulsion) includes effects from all occupied orbitals and therefore typically contains contributions from covalent (intrabond) groups.

The NBO-LC-roPBE/6-311+G\*\* analysis showed that the total steric exchange energy of the cis-conformation of compound 1 is greater than that in its trans-configurations, favoring the trans-configuration of compound 1. Contrary to compound 1, there is no significant difference between the Pauli exchange type repulsions of the *cis*- and *trans*-configurations of compound 2 (Table 4). Interestingly, the exchange component of the *trans*-configuration of compound 3 is greater than that in its *cis*-configuration, favoring the *cis*-configuration of compound 3. The differences between the exchange components of the *cis*- and *trans*-configurations of compounds 2 and 3 are not in the line with the results obtained by Yamamoto and co-workers [16]. The results of this work revealed that the Pauli exchange type repulsion differences between the *cis*- and *trans*-configurations ( $A[TSEE(cis)-TSEE(trans)]$ ) decrease going from compound 1 to compound 3. Most interestingly, the steric effect destabilizes the *cis*-configuration of compound 1 about 6.25 kcal mol<sup>-1</sup> compared to its *trans*-configuration. On the other hand, the deletion of the hyperconjugative interactions from the Fock matrices of the *cis*- and *trans*-configurations of compound 1 revealed that the hyperconjugative interactions are in favor of the *cis*-configuration of compound 1 by about 6.11 kcal mol<sup>-1</sup>. Accordingly, by considering the destabilization energies associated with

the steric repulsions and the electrostatic model (dipole-dipole interactions) and also the stabilization energies associated with the hyperconjugative interactions, we found that the hyperconjugative interactions are not solely responsible for the *cis*- configuration preference in compound 1 and other factors should be accounted.

***The impacts of the bonding orbitals deviations [dev(Gc-c), dev(nc=c)] from their normal values on the configurational preferences in compounds 1-3***

Wiberg has pointed out that the C=C bond paths in the *cis*-configuration of compound 1 are bent in essentially the same direction (toward the C-F bonds), leading to increased overlap and a stronger C-C bond whereas the C-C bond paths in the *trans*-configuration are bent in opposite directions, leading to a reduced overlap and a weaker C-C bond.<sup>[59]</sup> In this regard, we examined the deviations of the C=C bonds from the line of nuclear centers in the *cis*- and *trans* configurations of compounds 1-3 (Table 4).

The NBO-LC-roPBE/6-311+G\*\* results revealed that the  $a_{C-C}$  bonding orbitals of the *cis*- configuration of compound 1 are bent in the same direction from the line of nuclear centers by 3.7°. Importantly, the bending of the  $a_{C-C}$  bonding orbitals increase going from the *cis*-configurations of compound 1 to compound 3, causing the increase of their corresponding C-C bond strengths, leading to the increase of the *cis*-configurations stabilities going from compound 1 to compound 3. On the other hand, the bending of the  $a_{C-C}$  bonding orbitals of the *cis*- configurations in the opposite direction from the line of their nuclear centers increase from compound 1 to compound 3, causing to the weakness of their corresponding C-C bonds, leading to the decrease of the *trans*-configurations stabilities going from compound 1 to compound 3. Accordingly, the bending of the  $a_{C-C}$  bond paths tends to increase of the *cis*-configuration preferences going from compound 1 to compound 3.

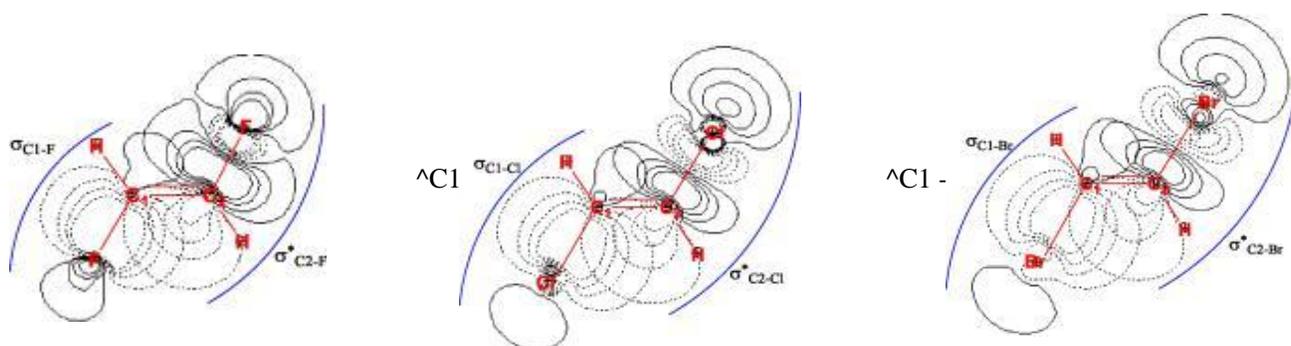
It is worth noting that the deviations of the *p* orbitals of the carbon atoms from their normal orientations (which forming  $\pi$ -bond) in the *trans*-configurations of compounds 1-3 are about 5.7°, 5.4° and 5.5°, respectively, as calculated by means of the NBO-LC-roPBE/6-311+G\*\* interpretation. It is worth noting that the deviations of the *p* orbitals of the carbon atoms from their normal orientations may decrease the C-C bond strengths in the *trans* configurations of compounds 1-3.

This fact reasonably explains the greater stability of the *cis*- configurations of compounds 1-3 compared to their *trans*-configurations.

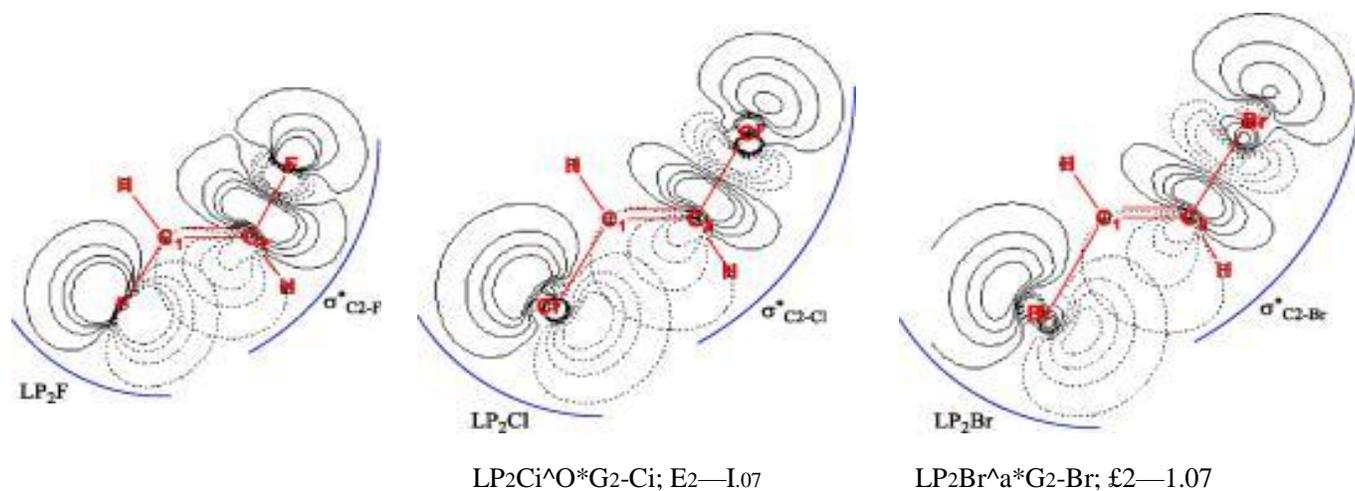
**Table 5:** CCSD(T)/6-311+G\*\* and LC-roPBE/6-311+G\*\*(a) calculated structural parameters for the *cis*- and *trans*-configurations and their corresponding transition state structures of compounds 1-3.

<sup>b</sup> From gas electron diffraction and microwave data, Ref. [6]. <sup>c</sup> From real-time gas electron diffraction, Ref. [7]. <sup>d</sup> From gas-phase electron diffraction, Ref. [1]. <sup>e</sup> From gas-phase electron diffraction, Ref. [5]. <sup>f</sup> From gas phase electron diffraction, Ref. [12]. <sup>g</sup> From microwave spectra, Ref. [13].

Bond lengths (Å)	1		2		3	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
rc=c	1.337 (1.316) <sup>a</sup> (1.330±0.011) <sup>b</sup> (1.331±0.004) <sup>d</sup> (1.311±0.008) <sup>e</sup> (1.324) <sup>f</sup>	1.336 (1.315) <sup>a</sup> (1.329±0.004) <sup>d</sup> (1.320±0.009) <sup>e</sup>	1.343 (1.320) <sup>a</sup> (1.337±0.004) <sup>c</sup>	1.341 (1.317) <sup>a</sup> (1.332±0.008) <sup>c</sup>	1.343 (1.319) <sup>a</sup> (1.360±0.010) <sup>d</sup>	1.340 (1.317) <sup>a</sup>
rc-x	1.342 (1.336) <sup>b</sup> (1.342±0.005) <sup>b</sup> (1.335±0.002) <sup>d</sup> (1.332±0.003) <sup>e</sup> (1.335) <sup>f</sup>	1.349 (1.342) <sup>a</sup> (1.344±0.002) <sup>d</sup> (1.338±0.003) <sup>e</sup>	1.726 (1.710) <sup>a</sup> (1.717±0.002) <sup>c</sup>	1.734 (1.718) <sup>a</sup> (1.725±0.002) <sup>c</sup>	1.885 (1.861) <sup>a</sup> (1.871±0.005) <sup>d</sup>	1.896 (1.870) <sup>a</sup>
A[rc=c( <i>cis</i> )-rc=c( <i>trans</i> )]	0.001		0.002		0.003	
A[rc-x( <i>trans</i> )-rc-x( <i>cis</i> )]	0.007		0.008		0.011	
<b>Bond angles (°)</b>						
\$X-C=C	122.2 (122.3) <sup>a</sup> (122.0±0.2) <sup>b</sup> (123.7±0.8) <sup>d</sup> (122.5±0.2) <sup>e</sup> (122.1) <sup>f</sup>	119.6 (120.1) <sup>a</sup> (119.33±0.24) <sup>d</sup> (119.8±0.2) <sup>e</sup>	124.8 (125.0) <sup>a</sup> (124.0±0.2) <sup>c</sup>	121.3 (121.6) <sup>a</sup> (120.8±0.6) <sup>c</sup>	125.8 (125.8) <sup>a</sup> (124.1±0.5) <sup>d</sup>	121.2 (121.7) <sup>a</sup>
#X-C-H	114.9 (114.6) <sup>a</sup>	114.8 (114.4) <sup>a</sup>	114.8 (114.5) <sup>a</sup>	115.1 (114.7) <sup>a</sup>	114.1 (114.0) <sup>a</sup>	114.8 (114.5) <sup>a</sup>
<b>Torsion angles (°)</b>						
\$ X-C=C-X	0.0	180.0	0.0	180.0	0.0	180.0
\$ H-C=C-H <sup>b</sup>	0.0	180.0	0.0	180.0	0.0	180.0

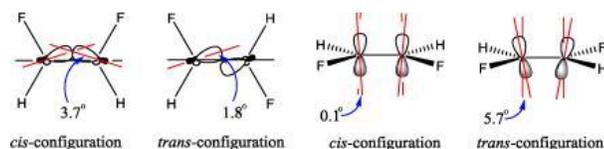


**Figure 4:** The calculated profiles of the orbital amplitudes (electron densities) for the through-bond *trans-effects* ( $a_{C1-X} \wedge a_{C2-X}^*$  [X=F (1), Cl(2), Br (3)] negative hyperconjugations) in the *cis*-configurations of compounds 1-3.  $E_2$  values are in kcal mol<sup>-1</sup>.



LP2F<sup>a</sup>\*G2-F;  $E_2=0.99$

**Figure 5:** The calculated profiles of the orbital amplitudes (electron densities) for the through-space  $LP_2X^a \wedge a_{C2,X}^*$  [X=F (1), Cl (2), Br (3)] negative hyperconjugations in the *cis*-configurations of compounds 1-3.  $E_2$  values are in kcal mol<sup>-1</sup>.



### 10-Global hardness and electronegativity

The energies of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbitals) of the *cis*- and *trans*-configurations of compounds 1-3, as calculated at the LC-roPBE/6-311+G\*\* levels of theory, are given in Table SI-5, respectively. The separations of the frontier molecular orbitals (i.e. the HOMO-LUMO gap) can be used to

interpret the molecular hardness [60-63]. The relationships between the global *hardness* ( $n$ ) [60-62], global *electronegativity* ( $\chi$ ) [66], ionization potential and electron affinity of a molecule are defined as the following expressions:

$$n = 0.5 (I - A) \quad (\text{eq. 4})$$

$\chi = \frac{I + A}{2}$  (eq. 5) where  $A$  and  $I$  are electron affinity and ionization potential of the molecules, respectively [63-66]. Because of the general validity of Koopmans' theorem for closed-shell, the hardness ( $n$ ) and electronegativity ( $\chi$ ) can be written as:

$$n = \frac{1}{2} (s_{\text{lumo}} - s_{\text{homo}}) \quad (\text{eq. 6})$$

$$\chi = -0.5 (s_{\text{lumo}} + s_{\text{homo}}) \quad (\text{eq. 7})$$

Using the electronegativity values obtained, a “A” parameter can be found as  $A[x(\text{trans}) - x(\text{cis})]$ .  $A[x(\text{trans}) - x(\text{cis})]$  parameter (without considering its negative sign) decreases from compound 1 to compound 3, revealing that the variations of the global electronegativity ( $x$ ) differences between the *trans*- and *cis*-configurations succeed in accounting for the decrease of the *cis*-configuration preferences going from compound 1 to compound 3.

LC-roPBE/6-311+G\*\* results showed that the *trans*-configuration of compound 1 is harder than their corresponding *cis*-configuration while an opposite trend is observed for compounds 2 and 3. The great dipole moments of the *cis*-configurations of compounds 1-3 lead to their great polarizabilities, decreasing their global hardness compared to their corresponding *trans*-configurations. This fact reveals that the configurational properties of compounds 1-3 do not obey the *maximum hardness principle*.

## Conclusions

The origin of the *cis*-configurations preferences in 1,2-difluoroethene (1), 1,2-dichloroethene (2) and 1,2-dibromoethene (3) were analyzed by means of G3MP2 composite method, long range corrected hybrid-density

functional theory (LC-roPBE) with the 6-311+G\*\* basis set on all atoms and natural bond orbital interpretation. In these methods used in this work showed the *cis*-configurations preferences (compared to their *trans*-configurations) decrease from compound 1 to compound 3. G3MP2 calculated corrected electronic energies between the *cis*- and *trans*-configurations are in good agreement with the reported experimental data. Most importantly, the deletions of the all donor-acceptor electronic interactions from the Fock matrices of the *cis*- and *trans*-configurations of compound 1 lead to the increase of the *trans*-conformations stability (by 6.11 kcal mol<sup>-1</sup>) compared to its corresponding *cis*-conformation. On the other hand, the Pauli exchange type repulsion difference between the *cis*- and *trans*-configurations of compound 1 is in favor of its *trans*-configuration (by 6.25 kcal mol<sup>-1</sup>). It is worth noting that the strain effect associated with the deviations of the *p* orbital of the carbon atoms from their normal orientations (which forming  $\pi$ -bond) in the *trans*-configuration of compound 1 is significantly greater than that in its *cis*-configuration, justifying the *trans*-configuration instability and the *cis*-configuration preference of compound 1.

**Table 6:** CCSD(T)/6-311+G\*\* calculated energies (in hartree) of HOMO ( $S_{\text{HOMO}}$ ), LUMO ( $S_{\text{LUMO}}$ ),  $S_{\text{LUMO}} - S_{\text{HOMO}}$ , global hardness ( $n$ ), global electronegativity ( $x$ ) for the *cis*- and *trans*-ground state structures of compounds 1-3.

**Table SI-1:** G3MP2 calculated zero point energies, corrected electronic energies [ $E_o = E_{\text{el}} + \text{ZPE}$ ], thermodynamic functions [ $H$ ,  $S$ ,  $G$ ] and their corresponding differences [ $\Delta ZPE$ ,  $\Delta H$ ,  $\Delta G$  (in kcal mol<sup>-1</sup>) and  $\Delta S$  (in cal mol<sup>-1</sup> K<sup>-1</sup>)] at 300 K for the *cis*- and *trans*-configurations and their corresponding transition state structures of

	SHOMO	SLUMO	SLUMO-S HOMO	$I$	$A$	$n$	$X$	$An$	$^A X$
1 - <i>cis</i>	-0.39258	0.06580	0.45838	0.39258	-0.06580	0.22919	0.16339	0.00000	0.00000
1 - <i>trans</i>	-0.39219	0.07635	0.46854	0.39219	-0.07635	0.23427	0.15792	0.00508(3.19) <sup>a</sup>	-0.00547(-3.43) <sup>a</sup>
2 - <i>cis</i>	-0.36913	0.06557	0.43470	0.36913	-0.06557	0.21735	0.15178	0.00000	0.00000
2 - <i>trans</i>	-0.36910	0.06930	0.43840	0.36910	-0.06930	0.21920	0.14990	0.00185(1.16) <sup>a</sup>	-0.00188(-1.18) <sup>a</sup>
3 - <i>cis</i>	-0.35990	0.05722	0.41712	0.35990	-0.05722	0.20856	0.15134	0.00000	0.00000
3 - <i>trans</i>	-0.35976	0.05724	0.41700	0.35976	-0.05724	0.20850	0.15126	-0.00006(-0.04) <sup>a</sup>	-0.00008(-0.05) <sup>a</sup>

compounds 1-3.

	<i>H</i>	<i>S</i>	<i>G</i>	<i>ZPE</i>	<i>E<sub>o</sub></i>	<i>AH</i>	<i>AS</i>	<i>AG</i>	<i>AZPE</i>	<i>AE<sub>o</sub></i>	<i>AE<sub>o</sub></i>
1 - <i>cis</i>	-276.740885	64.128	-276.771379	0.036108	-276.745722	0.00	0.000	0.00	0.00	0.00	0.00
1 - <i>trans</i>	-276.739635	63.947	-276.770043	0.035757	-276.744577	0.78	-0.181	0.84	-0.22	0.72	(1.08 ± 0.12)
2 - <i>cis</i>	-996.748379	69.184	-996.781277	0.033277	-996.753622	0.00	0.000	0.00	0.00	0.00	0.0
2 - <i>trans</i>	-996.747338	69.392	-996.780335	0.032957	-996.752839	0.91	0.208	0.59	-0.20	0.49	(0.72 ± 0.16)
3 - <i>cis</i>	-5222.897277	74.742	-5222.932818	0.031971	-	5222.902856	0.00	0.000	0.000	0.00	0.00
3 - <i>trans</i>	-5222.896787	75.074	-5222.932486	0.031696	-	5222.902684	0.31	0.332	0.21	-0.17	(0.25 ± 0.33)

<sup>a</sup> From gas chromatography, Ref. [4].

**Table SI-2:** CCSD(T)/6-311+G\*\* calculated zero point energies, corrected electronic energies [ $E_o = E_{el} + ZPE$ ], thermodynamic functions [ $H$ ,  $S$ ,  $G$ ] and their corresponding differences [ $AZPE$ ,  $AH$ ,  $AG$  (in kcal mol<sup>-1</sup>) and  $AS$  (in cal mol<sup>-1</sup>K<sup>-1</sup>)] for the *cis*- and *trans*-configurations and their corresponding transition state structures of compounds 1-3.

	<i>H</i>	<i>S</i>	<i>G</i>	<i>ZPE</i>	<i>E<sub>o</sub></i>	<i>AS</i>	<i>AG</i>	<i>AZPE</i>	<i>AE<sub>o</sub></i>	<i>AE<sub>o</sub></i>
1 - <i>cis</i>	-276.491846	64.252	-276.522374	0.036782	-276.496690	0.000	0.00	0.005276	0.00	0.00
1 - <i>trans</i>	-276.491076	64.141	-276.521552	0.036431	-276.496033	-0.111	0.52	0.004925	0.41	(1.08 ± 0.12)
2 - <i>cis</i>	-996.479827	69.263	-996.512736	0.034036	-996.485077	0.000	0.00	0.004174	0.00	0.0
2 - <i>trans</i>	-996.479470	69.483	-996.512483	0.033770	-996.484963	0.220	0.16	0.003908	0.07	(0.72 ± 0.16)
3 - <i>cis</i>	-5222.171049	74.807	-5222.206592	0.032601	-5222.176635	0.000	0.00	0.004151	0.00	0.00
3 - <i>trans</i>	-5222.171898	75.100	-5222.207580	0.032381	-5222.177780	0.293	-0.62	0.003931	-0.72	(0.25 ± 0.33)

**Table SI-3:** LC- $\omega$ PBE/6-311+G\*\* calculated zero point energies, corrected electronic energies [ $E_0 = E_{el} + ZPE$ ], thermodynamic functions [H, S, G] and their corresponding differences [ $\Delta ZPE$ ,  $\Delta H$ ,  $\Delta G$  (in kcal mol<sup>-1</sup>) and  $\Delta S$  (in cal mol<sup>-1</sup>K<sup>-1</sup>)] at 300 K for the *cis*- and *trans*-configurations of compounds 1-3.

	LC- $\omega$ PBE/6-311+G**										Exp.	
	ZPE	$E_0$	H	S	G	$\Delta ZPE$	$\Delta E_0$	$\Delta H$	$\Delta S$	$\Delta G$	$\Delta E_0$	
<b>1-cis</b>	0.037673	-276.935966	-276.931192	63.999	-276.961600	0.00	0.00	0.00	0.000	0.00	0.00	
<b>1-trans</b>	0.037268	-276.935195	-276.930302	63.886	-276.960656	-0.25	0.48	0.56	-0.113	0.59		(1.08 $\pm$ 0.12) <sup>a</sup>
<b>2-cis</b>	0.035165	-997.480930	-997.475803	68.791	-997.508488	0.00	0.00	0.00	0.000	0.00	0.00	0.0
<b>2-trans</b>	0.034794	-997.480659	-997.475279	68.969	-997.508048	-0.23	0.17	0.33	0.178	0.28		(0.72 $\pm$ 0.16) <sup>a</sup>
<b>3-cis</b>	0.033892	-5224.838383	-5224.832951	74.193	-5224.868203	0.00	0.00	0.00	0.000	0.00	0.00	0.00
<b>3-trans</b>	0.033528	-5224.839033	-5224.833275	74.534	-5224.868688	-0.23	-0.41	-0.20	0.341	-0.30		(0.25 $\pm$ 0.33) <sup>a</sup>

**Table SI-4:** NBO-LC-roPBE/6-311+G\*\* calculated orbital occupancies ( $e$ ) and orbital energies ( $s$ , in a.u.) for the *cis*, *trans* and transition state structures of compounds 1-3.

	1		2		3	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
$e$						
Oc-H	1.98285	1.98655	1.97488	1.98278	1.97217	1.98203
<sup>0</sup> C-X	1.99652	1.99489	1.99158	1.98638	1.98872	1.98032
LP <sub>3</sub> X	1.92942	1.93537	1.92259	1.93194	1.92961	1.93929
O*C-X	0.01407	0.01156	0.01922	0.01807	0.02339	0.02329
O*C-H	0.01966	0.02073	0.02334	0.02359	0.02205	0.02206
	0.13383	0.12329	0.14841	0.13088	0.13523	0.11713
ri*C=C						
$f$						
Oc-H	-0.70496	-0.70646	-0.69573	-0.70128	-0.69328	-0.70008
Oc-X	-1.16131	-1.15108	-0.88813	-0.88037	-0.81937	-0.81086
LP3X	-0.54573	-0.54849	-0.44486	-0.44927	-0.41582	-0.42043
O*C-X	0.38302	0.37549	0.27491	0.26798	0.21290	0.20532
O*C-H	0.48360	0.48338	0.50191	0.50268	0.51111	0.51216
ri*C=C	0.09133	0.09277	0.07644	0.07787	0.07821	0.07787
A [ $f$ (ri*C=C)- $f$ (LP 3X)]	0.63706	0.64126	0.52130	0.52714	0.49403	0.4983
A [ $f$ (O*C-X)- $f$ (Oc-H)]	1.08798	1.08195	0.97064	0.96926	0.90618	0.9054
A [ $f$ (O*C-X)- $f$ (Oc-X)]	1.54433	1.52657	1.16304	1.14835	1.03227	1.01618

**Table SI-5:** LC-wPBE/6-311+G\*\* calculated energies (in hartree) of HOMO ( $s$  HOMO), LUMO ( $s$  LUMO),  $s$ LUMO- $s$  HOMO, global hardness ( $n$ ), global electronegativity ( $x$ ) for the *cis*- and *trans*-configurations of compounds 1-3.

	$s$ HOMO	$s$ LUMO	$s$ LUMO- $s$ HOMO	$I$	$A$	$n$	$X$	$An$	$^A X$
1- <i>cis</i>	-0.38700	0.06048	0.44748	0.38700	-0.06048	0.22374	0.16326	0.00000	0.00000
1- <i>trans</i>	-0.38652	0.07354	0.46006	0.38652	-0.07354	0.23003	0.15649	0.00629 (3.95) <sup>a</sup>	-0.00677 (-4.25) <sup>a</sup>
2- <i>cis</i>	-0.37318	0.06032	0.43350	0.37318	-0.06032	0.21675	0.15643	0.00000	0.00000
2- <i>trans</i>	-0.37258	0.05111	0.42609	0.37258	-0.05111	0.21350	0.15909	0.00325	0.00266
3- <i>cis</i>	-0.36463	0.05276	0.41739	0.36463	-0.05276	0.20870	0.15594	0.00000	0.00000
3- <i>trans</i>	-0.36364	0.04875	0.41239	0.36364	-0.04875	0.20620	0.15745	-0.00250 (-1.57)	0.00151 (0.95) <sup>a</sup>

<sup>a</sup> Values are in kcal mol<sup>-1</sup>.

Contrary to the information published in the literature, there is no significant difference between the Pauli exchange type components of the *cis*- and *trans*-configurations of compound 2 but it is in favor of the *cis*-configuration of compound 3. The deletions of the all donor-acceptor electronic interactions from the Fock matrices of the *cis*- and *trans*-configurations of compounds 2 and 3 lead to the increase of the *trans*-conformations stability compared to their corresponding *cis*-conformations, revealing the determining impacts of the donor-acceptor electronic interactions on the configurational preferences in compounds 2 and 3.

The *cis*-conformations of compounds 1-3 with large dipole moments are still more stable than their corresponding *trans*-conformation, implying that the electrostatic model associated with the dipole-dipole interactions do not play a determining role on the anomeric preferences in these compounds. This is important evidence that reveals the *isomer with larger molecular dipole moment is not the less stable one* which contradicts the published conclusion in the literature.

Based on the results obtained, the *cis*-effect (associated with  $o_{C1-H}^{\wedge}o_{C2-X}^*$  and  $o_{C2-X}^{\wedge}o_{C1-H}^*$  hyperconjugative interactions) tends to increase the *cis*-conformation preferences going from compound 1 to compound 3 while the *trans*-effect (associated with  $o_{C1-X}^{\wedge}o_{C2-X}^*$  and  $o_{C1-H}^{\wedge}o_{C2-H}^*$  hyperconjugative interactions) has an opposite impact and tends to increase the *trans*-conformation preferences. As the *cis*-effect increases from the *cis*-configurations of compound 1 to compound 3, the *trans*-effect increases

going from the *trans*-configurations of compound 1 to compound 3 as well. The differences between the *cis*-effects in the *cis*-configurations and the *trans*-effects in the *trans*-configurations [*Zcis-effects(cis)*-*Y,trans-effects(trans)*] increase going from compound 1 to compound 3. Also, the differences between the lone pair effect (associated with  $LP_1X_{(C1)}^{\wedge}a_{C-C2}^*$ ,  $LP_2X_{(C1)}^{\wedge}a_{C-C2}^*$  and  $LP_3X_{(C1)}^{\wedge}TC_{C-C2}^*$  negative hyperconjugative interactions) in the *cis*- and *trans*-configurations are in favor of the *cis*-configurations preferences in compounds 1-3. Effectively, the outcomes of the electronic effects mentioned above are in favor of the *cis*-configurations, tending to increase of the *cis*-configurations preferences going from compound 1 to compound 3 but the Pauli exchange type components have opposite impacts. Based on the results obtained, the Pauli exchange type component difference between the *cis*- and *trans*-configurations of compound 1 is positive but there is no significant difference for compound 2. The exchange component of the *trans*-configuration of compound 3 is greater than that in its *cis*-configuration. The large dipole moments of the *cis*-configurations of compounds 1-3 lead to their great polarizability, decreasing their hardness compared with their corresponding *trans*-configurations. The global hardness ( $n$ ) differences between the *cis*- and *trans*-configurations ( $A[n(cis) - n(trans)]$ ) decrease going from compound 1 to compound 3, revealing that the configurational properties of compounds 1-3 do not obey the *maximum hardness principle*.

### Computational details

G3MP2 and LC-roPBE (long-range corrected wPBE) methods with the 6-311+G\*\* basis set on all atoms were performed to optimize the structural parameters and also to calculate the electronic energies and thermodynamic functions of the *cis*- and *trans*-configurations of compounds 1-3 with the GAMESS US package of programs [43,44]. It is worth noting that due to the smallest many-electron self-interaction errors in the LC-wPBE functional among widely exchange-correlation functionals, this functional predicts correctly the degree of electrons localizations and delocalizations [45-47]. The natural bond orbital interpretation with the LC-roPBE/6-311+G\*\* method (NBO-LC-roPBE/6-311+G\*\*) was performed to estimate the contributions of the plausible hyperconjugative interactions and Pauli exchange type repulsions on the configurational and structural properties of compounds 1-3. Also, the NBO-LC-roPBE/6-311+G\*\* interpretation was performed to investigate the bonding and antibonding orbital occupancies and energies of the *cis*- and *trans*-configurations of compounds 1-3 by use of the NBO 5.G program [41].

The stabilization energies (second order perturbational energies) associated with the hyperconjugative interactions (donor ( $i$ )<sup>th</sup>-acceptor ( $j$ )<sup>th</sup> electron delocalizations) are proportional directly to the magnitudes of the orbital overlap integrals [41,48-50] and inversely to the energy differences between the donor and acceptor orbitals:

### Stabilization or resonance energy

Accordingly, the stabilization or second order perturbative energy ( $E_2$ ) associated with  $i^{\text{th}}$  electron delocalization, is explicitly estimated by the following equation:

Eq. (1) where  $q_i$  is the  $i^{\text{th}}$  donor orbital occupancy,  $s_i$ ,  $s_j$  are diagonal elements (orbital energies) and  $F(ij)$  is the off-diagonal natural bond orbital Fock matrix element. The desirable orbital overlapping is reachable with the substantial adjustments of off-diagonal when going from one compound to the next [51,52]. The impacts of the hyperconjugative interactions associated with the *cis*-effect ( $g_{C1-h}^{>g^*C2-x}$ ,  $OC1-X \wedge o^*C2-h$ ) (Figure 1), *trans*-effect ( $g_{C1-x}^{\wedge g^*C2-x}$ ,  $g_{C1-h}^{\wedge g^*C2-h}$ ) (Figure 2), lone pair effect ( $LP_1X^{\wedge g^*C1-C2}$ ,  $LP_2X^{\wedge g^*C1-C2}$ ,  $LP_3X^{\wedge t^*C1-C2}$ ) (Figures 3 and 4) and through space effect ( $LP_2X(C1)^{\wedge g^*C2-x}$ ) (Figure 5), the attractive electrostatic interactions between two adjacent atoms, Pauli exchange type repulsion (total steric exchange energy,

*TSEE*), the electrostatic model associated with the dipole-dipole interactions and the strain effect associated with the deviations of the  $p$  orbital of the carbon atoms from their normal orientations (which forming  $\pi$ -bond) on the structural and conformational properties of compounds 1-3 quantitatively investigated by means of the natural bond orbital interpretations.

In order to assess the impacts of the hyperconjugative interactions associated with the *cis*- effect, *trans*-effect, lone pair effect and through space effect on configurational properties of compounds 1-3, we deleted their corresponding orbital overlappings from the Fock matrices of their *cis*- and *trans*-configurations. Then, by rediagonalization and comparing the current Fockmatrices with their original forms, we estimated the contributions and impacts of the hyperconjugative interactions mentioned above on the configurational properties of compounds 1-3. Effectively, the natural bond orbital interpretation is a sufficient and competent theoretical approach to investigate quantitatively the influences of the hyperconjugative interactions and steric effects on the reactivity and dynamic behaviors of chemical compounds [53].

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