



Original Research article

An Attempt for the Quantitative DFT-based Interpretation of the Conformational Preference of Negative Hyperconjugative Anomeric Effects in *Trans*-2,3- and *Trans*-2,5-dihalo-1,4-dioxanes

Elahe Faramarzia, Reza Ghiasi^{b*}, Masumeh Abdoli-Senejani^a^a Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran^b Department of Chemistry, Faculty of Science, East Tehran Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

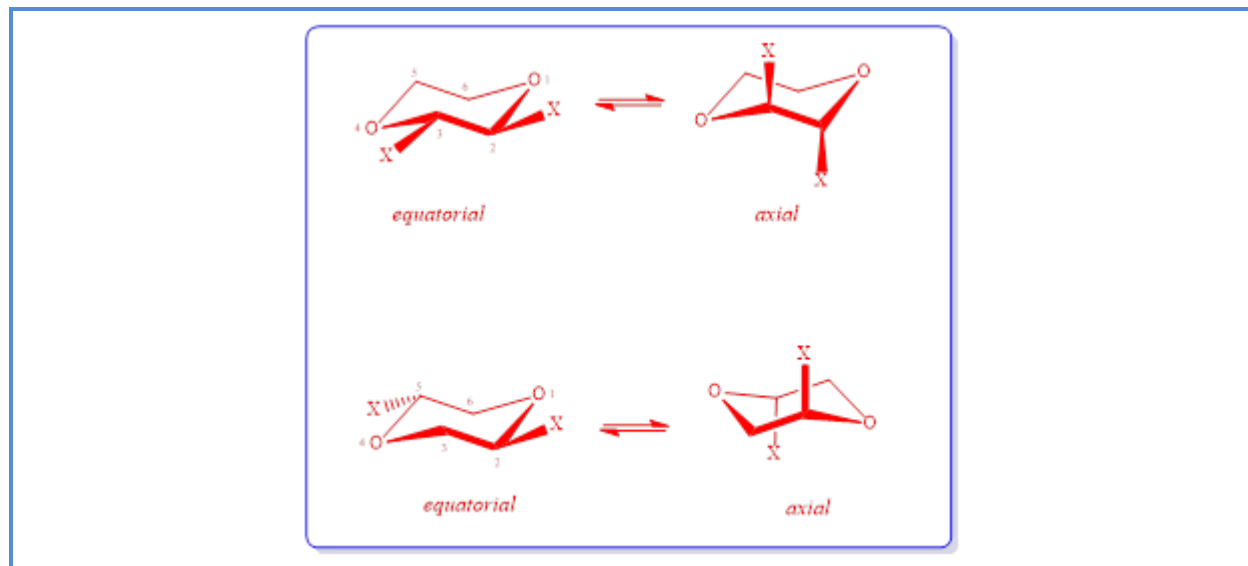
In this study, the stabilities of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes conformers were investigated at the LC-BLYP/6-311+G(d,p) theory level. The total energies and dipole moments of the *axial* and *equatorial* conformations were calculated for the mentioned molecules. The stability of the conformers, bond distances and spin-spin coupling constants of C-H_{ax} and C-H_{eq} bonds were explained with the negative hyperconjugative anomeric effects. The negative hyperconjugative anomeric effects on these conformers were illustrated using the natural bond orbital (NBO) analysis. Deformation maps of electron density for these conformers were provided, as well. In the basis of these calculations, the *axial* conformer was more stable than *equatorial* conformer in the studied molecules. Moreover, the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules were iso-energetic.

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*Corresponding author: E-mail: rezaghiasi1353@yahoo.com; Department of Chemistry, Faculty of Science, East Tehran Branch, Islamic Azad University, Tehran, Iran, Tel: 09125330852

Graphical Abstract



Introduction

1,4-dioxane is a heterocyclic organic compound that is considered as an ether. This colorless liquid has a faintly sweet odor alike to that of diethyl ether. 1,4-dioxane is frequently named simply dioxane since the other dioxane isomers (1,2- and 1,3-) are seldom encountered. Dioxane is used as a solvent in various practical applications, and as a stabilizer for the transport of chlorinated hydrocarbons in aluminum containers [1, 2]. Since 1,4-dioxane is a possible human carcinogen and is very miscible in water [1], distinct attention has been given to its presence in subsurface aquifers where it possesses a health risk. Synthesis and properties of various compounds of the family of 1,4-dioxane molecules have been investigated in several studies [3-11]. The synthesis of 2,3-dichloro- and 2,3-dibromo-1,4-dioxanes [12] and also 2,5-dichloro-1,4-dioxane [13] molecules has been reported, and the geometry and conformations of these compounds have been accurately determined using X-ray diffraction (XRD) techniques [14]. The obtained consequences confirmed the presence of merely the *axial-axial* conformation in this molecule and showed that the endocyclic atomic distances from oxygen atom to a carbon atom bonded to a halogen atom are meaningfully lower than the corresponding lengths to carbon atoms without halogen atoms. Theoretical investigation of stereoelectronic effects on the estimated carbon-hydrogen bond lengths and one bond $^1J_{C-H}$ NMR coupling constants in cyclohexane, cyclohexanone derivatives, and six-membered heterocycles has been studied [15]. Moreover, the structural distances and spectroscopic consequences of stereo-electronic hyperconjugative effects have been

explored. Density functional theory (DFT) methods are very valuable in computational quantum chemistry. These methods have been used to illustrate the structure and properties of the various systems [16-19]. Several theoretical studies have been conducted on the hyperconjugative interactions with natural bond orbital (NBO) analysis in these systems [20-27].

In the present study, the stabilities of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes conformers were studied at the LC-BLYP/6-311+G(d,p) theory level. In addition, the negative hyperconjugative anomeric effects of these conformers were explored using the NBO analysis.

Experimental

Computational methods

All the computations were carried out using the Gaussian 09 software package [28]. The calculations were performed using 6-311+G(d,p) standard basis set [29-31]. The LC-BLYP hybrid functional method was utilized to optimize the geometries [32]. The non-coulomb part of exchange functional typically dies off too quickly and becomes very imprecise at large distances, making them incompatible for modeling processes such as electron excitations to high orbitals. The LC-BLYP method has been devised to handle such cases.

The characteristics of each observed stationary point have been confirmed in terms of having the least energy by conducting a vibrational analysis. In this regard, Gaussian 09 software suite is employed to analyze the population through the NBO process of the NBO 6.0 program [33] at the LC-BLYP/6-311+G(d,p) theory level. Gauge independent atomic orbital (GIAO) method [34] was employed to obtain the chemical shift values for the optimization. The deformation map of electron density provided *via* the Multiwfn 3.5 software package demonstrated the changes of electron density distribution through the molecule formation [35].

Results and discussion

Energetic aspects

Conformers and abbreviations of the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules are depicted in Figure 1. The absolute energy and relative energy values of the conformers are presented in Table 1. As can be seen, the *axial* conformer is more stable than the *equatorial* conformer in both the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxane molecules. Moreover, it was found that the relative energy values of the *equatorial* conformer depend on the characterization of halogen substituent. The highest values were observed when X=F. The more stability of *axial*

conformer compared to *equatorial* conformer is attributed to negative hyperconjugation effects. Figure 2. represents the canonical resonance structure of the mentioned negative hyperconjugation interactions. Furthermore, it shows that *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules are iso-energetic.

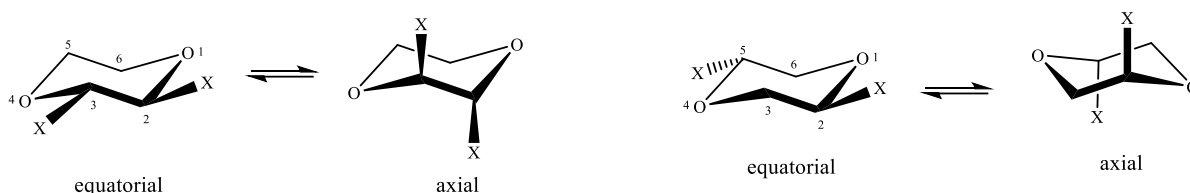


Figure 1. Conformers and abbreviations of the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules (X=F, Cl, Br)

Table 1. Absolute energy (a.u), relative energy (kcal/mol) and dipole moment (μ , debye) values of the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules at LCBLYP/6-311+G(d,p) level of theory

| | E | | ΔE 1 | | ΔE 2 | | μ | |
|------------------|--------------|-------------------|--------------|-------------------|--------------|-------------------|--------------|-------------------|
| Molecule | <i>axial</i> | <i>equatorial</i> | <i>axial</i> | <i>equatorial</i> | <i>axial</i> | <i>equatorial</i> | <i>axial</i> | <i>equatorial</i> |
| <i>2,3-trans</i> | | | | | | | | |
| F | -505.2738 | -505.2635 | 0.00 | 6.44 | 0.71 | 0.85 | 1.61 | 3.78 |
| Cl | -1225.7203 | -1225.7118 | 0.00 | 5.36 | 0.58 | 1.87 | 1.78 | 3.37 |
| Br | -5453.2774 | -5453.2675 | 0.00 | 6.24 | 0.37 | 2.43 | 1.91 | 3.17 |
| <i>2,5-trans</i> | | | | | | | | |
| F | -505.2749 | -505.2648 | 0.00 | 6.31 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cl | -1225.7212 | -1225.7147 | 0.00 | 4.06 | 0.00 | 0.00 | 0.00 | 0.00 |
| Br | -5453.2780 | -5453.2713 | 0.00 | 4.18 | 0.00 | 0.00 | 0.00 | 0.00 |

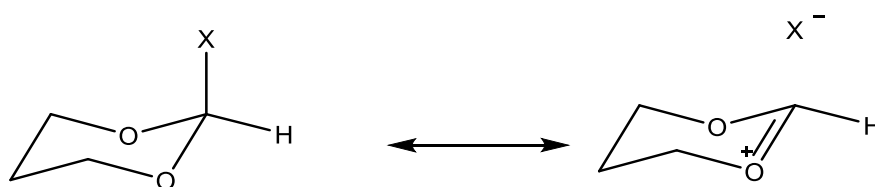


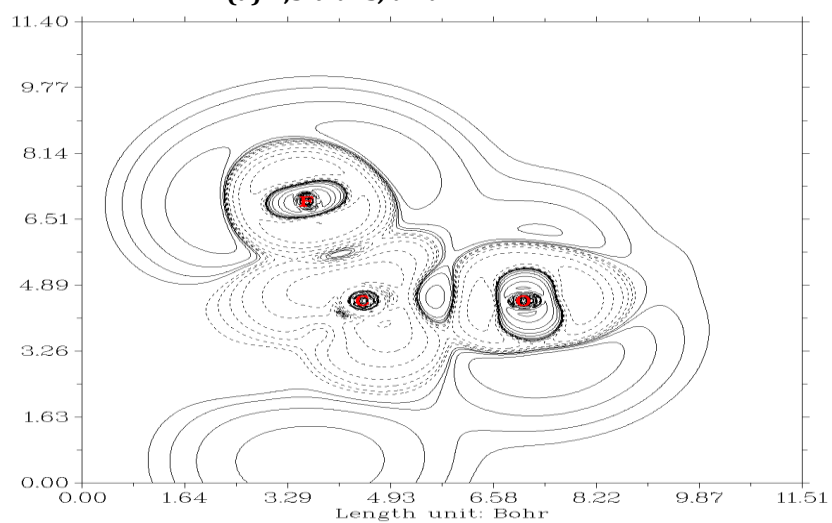
Figure 2. The canonical resonance structures representing the mentioned negative hyperconjugation interactions in the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules (X=F, Cl, Br)

Deformation map of electron density

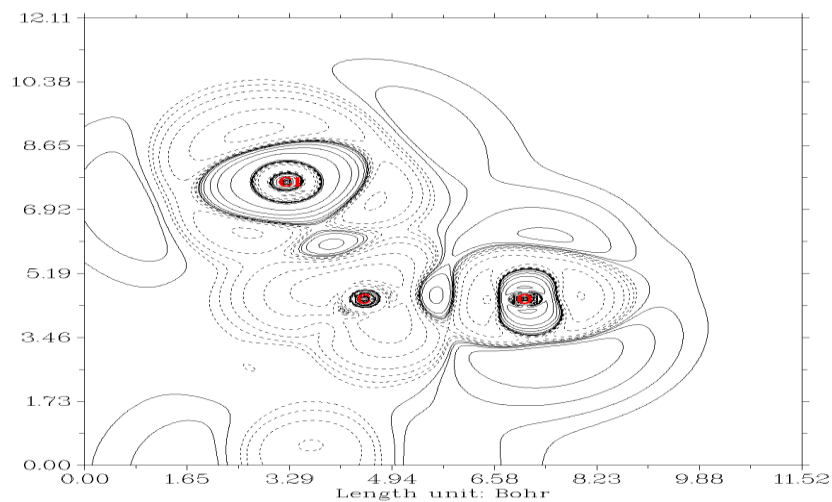
Deformation map of electron density obviously presents the changes of electron density distribution through formation of a molecule. This map is expressed as subtracting actual molecular electron density by electron density of all of its constituent atoms in their free states. Figure 3. presents the electron deformation density for the *axial* and *equatorial* conformers of the *trans*-2,3-dihalo-1,4-dioxanes molecules (section through O-C-X).

(a) 2,3-trans; axial

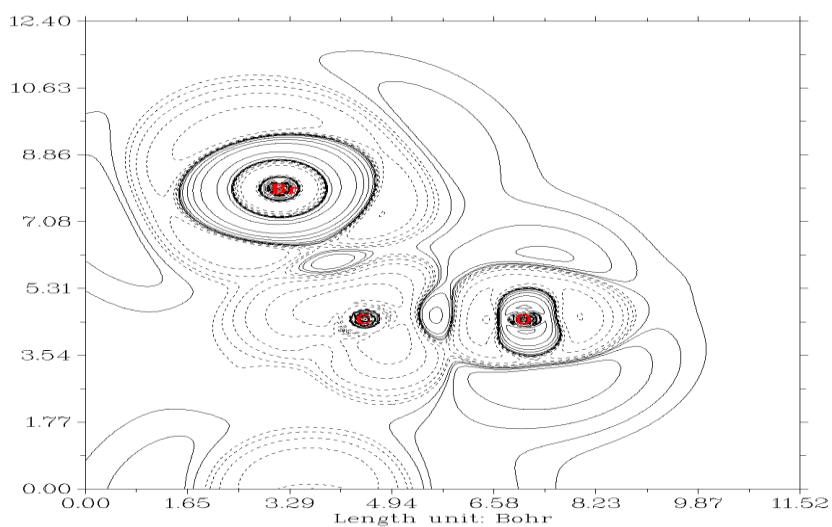
X=F



X=Cl



X=Br



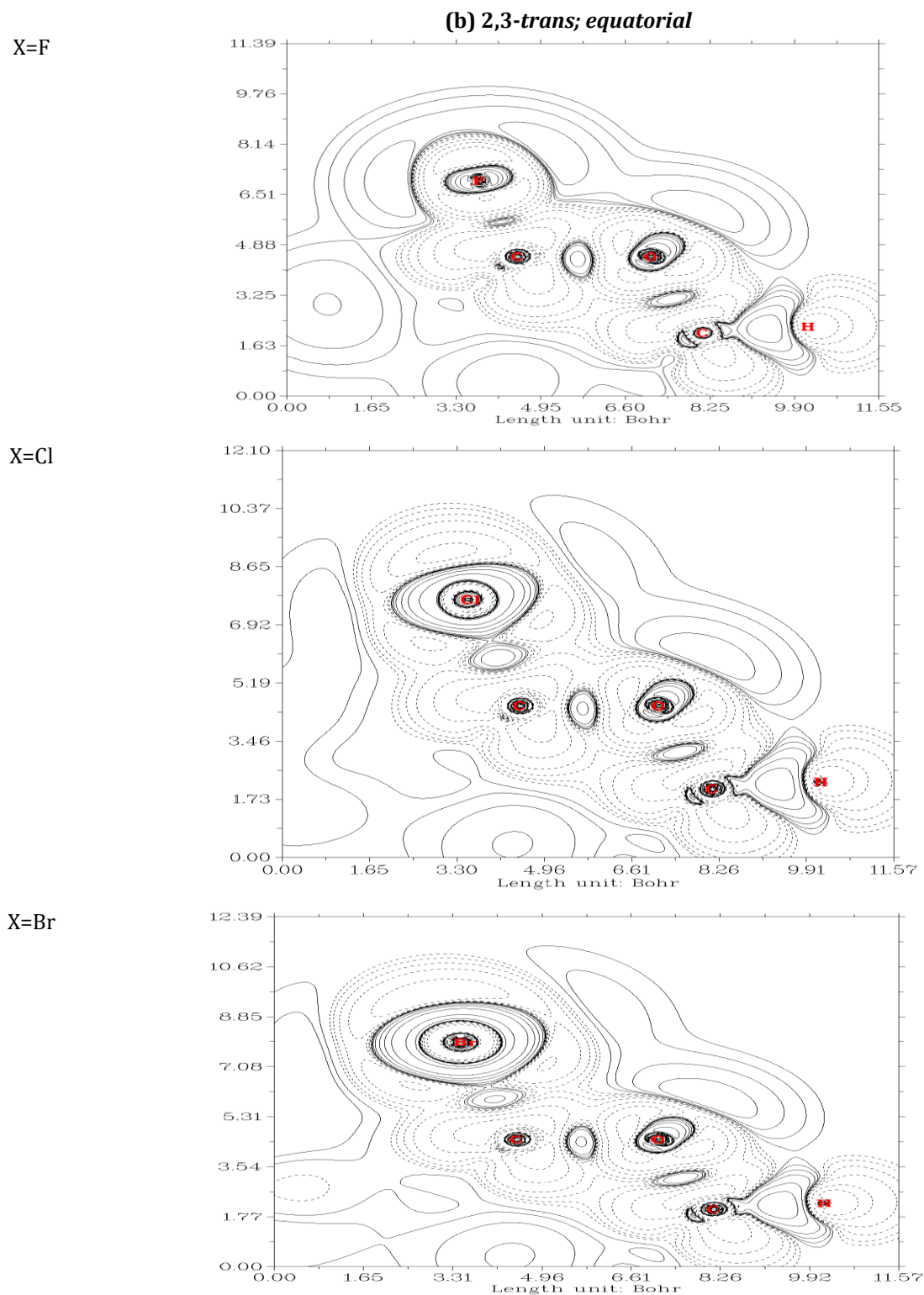


Figure 3. Electron deformation density for the (a) *axial* and (b) *equatorial* conformers of *trans*-2,3-dihalo-1,4-dioxanes molecules; section through O-C-X

Dipole moment

The dipole moment values of the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules are listed in Table 1. Directions of the dipole moments vectors of *axial* and *equatorial* conformers of *trans*-2,3-fluoro-1,4-dioxanes molecules are presented in Figure 4. Since the *trans*-2,5-dihalo-1,4-dioxane molecules are non-polar, their dipole moment values are zero. Non-zero dipole moment values of polar *trans*-2,3-dihalo-1,4-dioxanes molecules revealed the smaller dipole moment values for *axial* conformer compared to *equatorial* conformer. The obtained results are consistent with the lower dipole moment values for the higher stable conformers [36]. The highest dipole moment values can be found at the presence of the X=Br and X=F for *axial* and *equatorial* conformers, respectively.

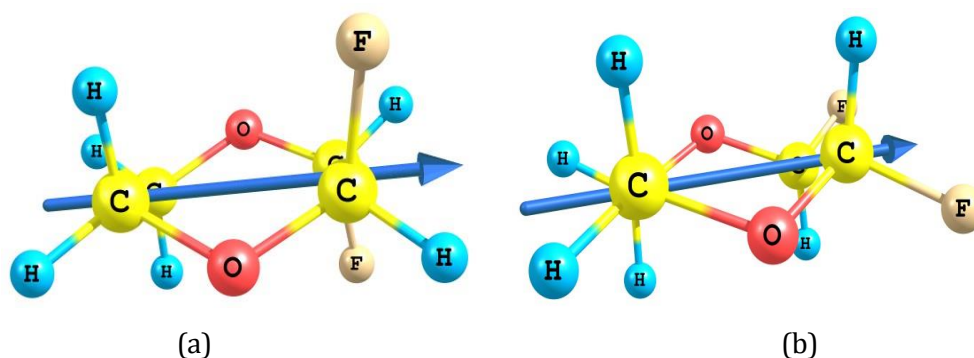


Figure 4. Directions of the dipole moments vectors of (a) *axial* and (b) *equatorial* conformers of *trans*-2,3-fluoro-1,4-dioxanes molecules

Thermodynamic analysis

Thermodynamic parameters of the isomerization for the studied conformers are presented in Table 2. The negative free energy changes values (ΔG) of the isomerization of *equatorial* conformer to *axial* conformer revealed that this isomerization is spontaneous. As demonstrated, this reaction is more appropriate at the presence of X=F. The negative enthalpy values (ΔH) for the isomerization of *equatorial* conformer to *axial* conformer revealed that this isomerization is exothermic. Also, the largest equilibrium constant values were observed when X=F.

Structural parameters

C2-H2 and C2-X2 bond distances of the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules are listed in Table 3. The variations of the C-X bond distances shows the longer bonds in *axial* conformer compared to *equatorial* conformer. This variation in bond distances is elucidated by a significant LP (2)O \rightarrow σ^* (C-X) negative hyperconjugation interaction between a pair of non-bonded electrons on oxygen and the adjacent C-X bond in *axial* conformer

(Figure 2). This interaction is the donation of electron density from a filled p -orbital of oxygen to a neighboring σ^* -orbital of the C-X bond. This phenomenon stabilizes the molecule. As a result, it reasons σ -bond elongation by increasing the electron density to its anti-bonding orbital.

The second order perturbation theory analysis of the Fock matrix in NBO basis of the LP (2)O $\rightarrow \sigma^*$ (C-X) interactions in the *equatorial* and *axial* conformers of the studied molecules are listed in Table 4. As seen, the stronger the interactions in the LP (2)O $\rightarrow \sigma^*$ (C-X), the more negative the hyperconjugation interaction in axial conformer than the equatorial conformer.

Table 2. Thermodynamic parameters values of the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules and isomerization of the *equatorial* conformer to *axial* conformer at LCBLYP/6-311+G(d,p) level of theory

| Molecule | <i>axial</i> | | <i>equatorial</i> | | <i>equatorial</i> \rightarrow <i>axial</i> | | |
|-------------------------|----------------|----------------|-------------------|----------------|--|--------------------------|--------------------|
| | G (a.u) | H (a.u) | G (a.u) | H (a.u) | ΔG (kcal/mol) | ΔH (kcal/mol) | K |
| 2,3-<i>trans</i> | | | | | | | |
| F | -505.1945 | -505.1561 | -505.1849 | -505.1463 | -6.02 | -6.13 | 2.60×10^4 |
| Cl | - 1225.6448 | - 1225.6050 | - 1225.6372 | - 1225.5971 | -4.75 | -4.92 | 3.03×10^3 |
| Br | - 5453.2054 | - 5453.1630 | - 5453.1971 | - 5453.1538 | -5.22 | -5.77 | 6.79×10^3 |
| 2,5-<i>trans</i> | | | | | | | |
| F | -505.1957 | -505.1573 | -505.1861 | -505.1476 | -5.98 | -6.05 | 2.41×10^4 |
| Cl | - 1225.6464 | - 1225.6059 | - 1225.6407 | - 1225.5999 | -3.59 | -3.76 | 4.26×10^2 |
| Br | - 5453.2067 | - 5453.1636 | - 5453.2008 | - 5453.1574 | -3.70 | -3.87 | 5.19×10^2 |

Table 3. C2-X2 and C2-H2 bond distances (\AA) of the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules at LCBLYP/6-311+G(d,p) level of theory

| Molecule | C2-X2 | | C2-H2 | |
|-------------------------|--------------|-------------------|--------------|-------------------|
| | <i>axial</i> | <i>equatorial</i> | <i>axial</i> | <i>equatorial</i> |
| 2,3-<i>trans</i> | | | | |
| F | 1.384 | 1.353 | 1.089 | 1.097 |
| Cl | 1.803 | 1.754 | 1.085 | 1.094 |
| Br | 1.970 | 1.909 | 1.083 | 1.093 |
| 2,5-<i>trans</i> | | | | |
| F | 1.385 | 1.357 | 1.090 | 1.097 |
| Cl | 1.800 | 1.757 | 1.086 | 1.093 |
| Br | 1.964 | 1.910 | 1.085 | 1.093 |

Table 4. Second order perturbation theory analysis of Fock matrix in NBO basis of LP (2)O \rightarrow σ^* (C-X) negative hyperconjugation interaction of the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules at LCBLYP/6-311+G(d,p) level of theory

| | <i>axial</i> | | | <i>equatorial</i> | | |
|-------------------------|--------------|----------------|-------------|-------------------|----------------|-------------|
| Molecule | E (2)* | E (NL)-E (L)** | F (L, NL)** | E (2)* | E (NL)-E (L)** | F (L, NL)** |
| 2,3-<i>trans</i> | | | | | | |
| F | 28.80 | 0.80 | 0.135 | 1.40 | 0.84 | 0.031 |
| Cl | 26.83 | 0.67 | 0.120 | 1.77 | 0.70 | 0.032 |
| Br | 29.35 | 0.61 | 0.119 | 1.92 | 0.65 | 0.031 |
| 2,5-<i>trans</i> | | | | | | |
| F | 26.48 | 0.80 | 0.130 | 1.43 | 0.83 | 0.031 |
| Cl | 24.95 | 0.68 | 0.116 | 1.70 | 0.70 | 0.031 |
| Br | 27.16 | 0.62 | 0.116 | 1.86 | 0.64 | 0.031 |

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

NBO analysis

In the current study, 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 5). 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 5. shows that the greater preference of the *axial* conformer when only considering the conjugation effects. Calculation of the total steric energy E (ST) was done through the NBO analysis. Table 5. further displays the more pronounced steric interactions occurring in the *equatorial* conformer compared to the *axial* conformer (except, 2,5-*trans*; X=Cl, 2,3-*trans*; X=Br). Calculations of the natural coulomb electrostatic energies E (NCE), and the total electronic energy and its Lewis components were conducted [37]. Table 5. reveals the more preferable *axial* conformer based on the NCE values (except, 2,5-*trans*; X=F).

¹H NMR parameters

The spin-spin coupling constant values of the C6-H6_{ax} and C6-H6_{eq} bonds (J(C6-H6)) for *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules are shown in Table 6. The results revealed the smaller J (C-H_{ax}) values compared to J (C-H_{eq}) in the studied molecules. This result has been explained in terms of an Lp (2)O \rightarrow σ^* (C-H) interaction between a pair of non-bonded electrons on oxygen and the *axial* adjacent C-H bond. This is due to the fact that, the double bond-no bond resonance [38] weakens the C-H_{ax} bond and decreases the Fermi contribution to the one bond

[13] C-¹H coupling constant [39-44]. In this regard, the stereoelectronic effects upon one-bond C-H coupling constants are named as “perlin effects” [41].

Table 5. 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 the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules at LCBLYP/6-311+G(d,p) level of theory

| Molecule | E (steric) | ΔE (steric) | E (NCE) | ΔE (NCE) | E (NL) | ΔE (NL) |
|-------------------|------------|-------------|----------|----------|----------|---------|
| <i>axial</i> | | | | | | |
| <i>2,3-trans</i> | | | | | | |
| F | 252.18 | 0.00 | -0.31841 | 0.00 | -319.963 | 0.00 |
| Cl | 254.83 | 0.00 | -0.15763 | 0.00 | -307.684 | 0.00 |
| Br | 250.50 | 0.00 | -0.14937 | 0.00 | -300.871 | 0.00 |
| <i>2,5-trans</i> | | | | | | |
| F | 252.92 | 0.00 | -0.33999 | 0.00 | -319.878 | 0.00 |
| Cl | 255.23 | 0.00 | -0.15988 | 0.00 | -304.603 | 0.00 |
| Br | 248.73 | 0.00 | -0.15128 | 0.00 | -296.650 | 0.00 |
| <i>equatorial</i> | | | | | | |
| <i>2,3-trans</i> | | | | | | |
| F | 254.07 | 1.89 | -0.31647 | 1.217368 | -311.823 | 8.14 |
| Cl | 257.37 | 2.54 | -0.15436 | 2.051956 | -294.912 | 12.772 |
| Br | 249.91 | -0.59 | -0.14753 | 1.154617 | -285.522 | 15.349 |
| <i>2,5-trans</i> | | | | | | |
| F | 253.52 | 0.6 | -0.34989 | -6.21234 | -309.420 | 10.458 |
| Cl | 254.52 | -0.71 | -0.15863 | 0.784387 | -292.957 | 11.646 |
| Br | 249.23 | 0.5 | -0.15111 | 0.106677 | -284.086 | 12.564 |

* in a.u

Table 6. Spin-spin coupling constant values (J, Hz) values of C-H_{ax} and C-H_{eq} in the the *axial* and *equatorial* conformers of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules at LCBLYP/6-311+G(d,p) level of theory

| Molecule | C-H _{ax} | C-H _{eq} |
|-------------------|-------------------|-------------------|
| <i>axial</i> | | |
| <i>2,3-trans</i> | | |
| F | 128.57 | 128.87 |
| Cl | 127.90 | 129.04 |
| Br | 127.85 | 129.24 |
| <i>2,5-trans</i> | | |
| F | 126.80 | 132.51 |
| Cl | 126.24 | 134.66 |
| Br | 125.77 | 135.11 |
| <i>equatorial</i> | | |
| <i>2,3-trans</i> | | |
| F | 124.65 | 128.88 |
| Cl | 124.67 | 128.53 |
| Br | 124.79 | 128.54 |
| <i>2,5-trans</i> | | |
| F | 125.52 | 132.57 |
| Cl | 128.04 | 133.97 |
| Br | 128.85 | 134.20 |

Conclusion

The stabilities of *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes conformers were investigated at the LC-BLYP/6-311+G(d,p) theory level. The obtained results are as following.

1. The *axial* conformer was more stable than *equatorial* conformer in the studied molecules. Moreover, the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes molecules were iso-energetic.
2. The dipole moment of the more stable conformation (*axial*) of the *trans*-2,3- and *trans*-2,5-dihalo-1,4-dioxanes compounds was smaller than its corresponding *equatorial* conformation.
3. Based on the thermodynamic analysis of the isomerization of *equatorial* conformer to *axial* conformer, the ΔG and ΔH values were negative. Therefore, this isomerization is spontaneous and exothermic.
4. Structural parameters revealed that the C-X bonds of *axial* conformer are longer compared to *equatorial* conformer. These variations in bond distances are elucidated in terms of a dominant LP (2)O $\rightarrow \sigma^*$ (C-X) negative hyperconjugation interaction in *axial* conformer than *equatorial* conformer.
5. The J (C-H_{ax}) values were found to be smaller compared to J (C-H_{eq}) in the studied molecules.

Conflict of Interest

We have no conflicts of interest to disclose.

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