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Evaluation of axial and equatorial conformation stabilization of compounds 1, 3-dioxane by DFT

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Abstract: Saturated heterocyclic compounds like carbohydrates and alkaloids play a significant role in organic and inorganic chemistry. The structural parameters of compounds 1, 3- dioxane [X: F(**1**), Cl(**2**), Br(**3**), CN(**4**), CF_3(**5**), NO_2(**6**)] for axial and equatorial conformations with density functional theory (DFT) $B_3LYP/6\text{-}311+G^{**}$ were surveyed. Through analyzing natural bond orbital (NBO), the stabilization energies (E_2) associated with electron delocalization $LP_1O_1 \rightarrow \sigma^*_{C2\text{-}C5}$, $LP_2O_1 \rightarrow \sigma^*_{C2\text{-}C5}$, $LP_1O_3 \rightarrow \sigma^*_{C2\text{-}C5}$ and $LP_2O_3 \rightarrow \sigma^*_{C2\text{-}C5}$ and natural bond order (nbo) and dipole moment (μ) of compounds **1** to **6** were studied. Research indicated that the bond length (r) of O_1-C_2, O_3-C_2 the axial conformation is shorter than equatorial conformation, so more electron transfers are done. Stabilization energy differences ($\Delta E_{\text{axial}} - \Delta E_{\text{equatorial}}$) in compounds **1** to **6** were reported to be 0.08, 0.22, 0.22, 0.51, 0.37 and 0.62 kcal/mol^{-1} respectively. The tendency of the stabilization energy difference associated with electron delocalization is directly related to the dipole moment difference.

Keywords: 1,3- Dioxane, NBO, Dipole moment, Anomeric effect, Electron delocalization.

Introduction

The structural balance of alicyclic compounds has been studied for several years. The theoretical behavior of cycloalkanes corresponds to experimental values. The science of the structural properties of heterocyclic compounds is very important. Therefore, saturated heterocyclic compounds occupy a large share in organic and inorganic chemistry. These compounds are naturally involved in alkaloids and carbohydrates and regulate plant growth [1]. The conjugation effect is considered to be an important part of the intermolecular reaction between the ground state and the transition state. The importance of the conjugation reaction of ions, free radicals and excited compounds has increased significantly [2, 3]. The influence of the conjugation reaction on the parameterization of molecular mechanics is used to prove the nature of the covalent bond.

These interactions affect the equilibrium structure, such as the anomeric effect, the twisted barrier of ethane and other molecules [4]. The main controlling factor in the structure of carbohydrates and other compounds is the anomeric effect. In 2010, MO calculated the electrostatic reaction related to the dipole-dipole reaction dependent on the anomeric effect [5]. In 2007 and 2011, Liu and et. al proposed that electron delocalization and electrostatic reaction were not enough to produce the anomeric effect [6]. Studies have shown that the microwave spectrum, electron diffraction, and gas vibration spectrum are consistent with the 1, 3 dioxane chair conformation. The structure and thermodynamic behavior of 1, 3 dioxane compounds were studied by ab initio MO and DFT methods [7]. Praly and Lemieux mentioned the anomeric effect in six-membered saturated cyclic compounds and studied the difference between internal and external anomeric effects in equatorial and axial conformations [8]. According to Figure **1**, the electron

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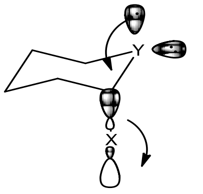
delocalization of the alone pair of Y atoms towards the C-X bond represents the stability of the axial conformation. Using this model, the bond length change can be well explained. Consistent with the anomeric effect, the electrons delocalization of the Y atom cause increases the length of the C-X bond and reduces the C-Y bond.



Y: O, N
X: F, Cl, Br and EWG

Figure 1: The process of electron delocalization from alone pair electron Y atom in the 6-membered ring to the anti-bonding orbital

Results and discussion

Structural parameter

Table **1** indicates the bond lengths and bond angles of compounds **1** to **6** with axial and equatorial conformations calculated by the B$_3$LYP method with the base set 6-311+G**. During the investigation, it is estimated that the bond lengths O$_1$-C$_2$ and O$_3$-C$_2$ in the axial conformation are shorter than the equatorial conformation the due to electrons delocalization in the ring from oxygen. The C$_2$-C$_5$ bond length in the axial conformation is longer than in the equatorial conformation. Table **1** shows the bond angles of compounds **1-6** O$_1$C$_2$C$_5$ and O$_3$C$_2$C$_5$ in the axial and equatorial conformations.

Table 1. Calculated structural parameters of axial and equatorial conformation of compounds **1** to **6**.

Compounds	**1**		**2**		**3**		**4**		**5**		**6**	
	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq
Bond lengths(A^0)												
r_{1-2}	1.4213	1.4217	1.4205	1.4210	1.4208	1.4210	1.4186	1.4196	1.4196	1.4199	1.4184	1.4192
r_{3-2}	1.4214	1.4217	1.4206	1.4211	1.4208	1.4211	1.4187	1.4197	1.4197	1.4202	1.4184	1.4192
r_{2-5}	1.5444	1.5441	1.5439	1.5445	1.5444	1.5443	1.5455	1.5441	1.5457	1.5442	1.5462	1.5441
Bond angles(^{0})												
θ_{125}	110.94	111.11	111.01	111.15	110.95	111.16	110.96	111.30	110.92	111.25	110.92	111.37
θ_{235}	110.94	111.11	111.02	111.15	110.96	111.17	110.97	111.30	110.96	111.28	110.92	111.37

Anomeric effects and stabilization energies:

Electron delocalization has a significant impact on the structural parameters and stabilization energy of the axial and equatorial conformations of compounds 1 to 6. In the NBO analysis process, the energy difference between the various forms of molecules comes from charge transfer between the antibonding-nonbonding and antibonding-bonding [12-14]. The NBO analysis explained by the B3LYP/6-311+G** calculation method that the reaction transfer electron pairs alone O atom of compounds 1 to 6 with axial and equatorial conformations to the anti-bonding orbital (LP O→σ*). Table **2** shows the delocalization energy LP1O1 and LP2O1, LP1O3 and LP2O3, and σ*C2-C5.

It can be seen from the Table **2** that the delocalization energy in the axial conformation is greater than the delocalization energy in the equatorial conformation. The anomeric effect is obtained from the difference between the sum of the anomeric effects in the axial and equatorial conformations [15].

$$\text{Anomeric effect ax-eq} = \Sigma\ (\text{Anomeric effect})\ \text{ax} - \Sigma\ (\text{Anomeric effect})\ \text{eq} \qquad \text{Eq2}$$

Anomeric effect of electron delocalization compounds **1** to **6** is directly related to the dipole moment. As shown in Table **2**, the energy of the donor (i) and acceptor (j) orbitals is given. According to Equation 1, the energy difference between the donor and acceptor orbitals is inversely proportional to E2. Table **2** shows that the orbital overlap in the axial conformation is greater than the orbital overlap in the equatorial conformation. Therefore, the axial conformation is more stable than the equatorial conformation.

Table 2. Second order stability energy calculated by NBO-B$_3$LYP/6-311+ G** (E$_2$; kcal/mol^{-1}), ΔE (kcal/mol^{-1}), orbital energy (ε; Hartree), orbital energy difference (Δε; Hartree), off-diagonal elements (Fij; Hartree), axial and equidistant structures of **1** to **6** compounds.

Compounds	**1**		**2**		**3**		**4**		**5**		**6**	
	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq
E$_2$												
LP$_1$O$_1$→σ*C$_2$-C$_5$	2.1	2.14	2.12	2.14	2.13	2.13	2.15	2.14	2.14	2.14	2.16	2.14
LP$_2$O$_1$→σ*C$_2$-C$_5$	5.43	5.35	5.5	5.37	5.49	5.38	5.68	5.44	5.60	5.42	5.75	5.46
LP$_1$O$_3$→σ*C$_2$-C$_5$	2.1	2.14	2.12	2.14	2.13	2.13	2.15	2.14	2.14	2.13	2.16	2.14
LP$_2$O$_3$→σ*C$_2$-C$_5$	5.43	5.35	5.5	5.37	5.49	5.38	5.68	5.43	5.61	5.43	5.75	5.46
Σ	15.06	14.98	15.24	15.02	15.24	15.02	15.66	15.15	15.49	15.12	15.82	15.20
AE(ax)- AE(eq)	0.08		0.22		0.22		0.51		0.37		0.62	
energy												
LP$_1$O$_1$	-0.559	-0.055	-0.560	-0.561	-0.560	-0.561	-0.568	-0.568	-0.565	-0.565	-0.570	-0.570
LP$_2$O$_1$	-0.312	-0.312	-0.313	-0.313	-0.313	-0.314	-0.321	-0.321	-0.317	-0.317	-0.323	-0.323
LP$_1$O$_3$	-0.559	-0.559	-0.560	-0.561	-0.560	-0.561	-0.568	-0.568	-0.564	-0.565	-0.570	-0.570
LP$_2$O$_3$	-0.031	-0.312	-0.313	-0.313	-0.313	-0.314	-0.321	-0.321	-0.317	-0.317	-0.323	-0.323
σ*C$_2$-C$_5$	0.370	0.372	0.368	0.371	0.367	0.370	0.355	0.363	0.359	0.366	0.350	0.361
Ej-Ei												
LP$_1$O$_1$→ σ*C$_2$-C$_5$	0.93	0.93	0.93	0.93	0.93	0.93	0.92	0.93	0.92	0.93	0.92	0.93
LP$_2$O$_1$→ σ*C$_2$-C$_5$	0.68	0.69	0.68	0.68	0.68	0.69	0.68	0.68	0.68	0.68	0.67	0.68
LP$_1$O$_3$→ σ*C$_2$-C$_5$	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.97	0.93	0.92	0.93
LP$_2$O$_3$→ σ*C$_2$-C$_5$	0.68	0.69	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.67	0.68
F$_{ij}$												
LP$_1$O$_1$→ σ*C$_2$-C$_5$	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040
LP$_2$O$_1$→ σ*C$_2$-C$_5$	0.055	0.054	0.055	0.054	0.055	0.055	0.056	0.055	0.055	0.055	0.056	0.055
LP$_1$O$_3$→ σ*C$_2$-C$_5$	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040
LP$_2$O$_3$→ σ*C$_2$-C$_5$	0.055	0.054	0.055	0.054	0.055	0.055	0.056	0.055	0.055	0.055	0.056	0.055

Bond orders

The anomeric effect associated with electron delocalization pair O$_1$-C$_2$ and O$_3$-C$_2$ and C$_2$-C$_5$ is effective for compounds **1** to **6** in axial and equatorial conformations. The order of the bonds is taken as the sum of squares off the diagonal of the density matrix of elements between atoms in the Weiberg bond index [16]. In this work, due to the electron delocalization LP$_1$O$_1$→ σ*C$_2$-C$_5$ and LP$_2$O$_1$→σ*C$_2$-C$_5$, LP$_1$O$_3$ → σ*C$_2$-C$_5$ and LP$_2$O$_3$→σ*C$_2$-C$_5$, the bond lengths of compounds **1** to **6** in the axial conformation are O$_1$-C$_2$ and O$_3$-C$_2$ It is expected to be shorter than the equatorial conformation. Furthermore, the length bond of C$_2$-C$_5$ in the axial conformation is longer than in the equatorial conformation. Therefore, bond order the O$_1$-C$_1$ and O$_3$-C$_2$ bonding sequence in the axial conformation is more than the equatorial conformation, and the C_2-C_5 bonding sequence in the axial conformation is fewer than the equatorial conformation.

Dipole moments

Generally, in the gas phase, the energy of a conformation with a lower dipole moment is more stable of another conformation with a higher dipole moment [17]. Therefore, the lower the dipole moment, the higher the stability of the compound. According to the obtained results, the dipole moments of the axial and equational conformations of compounds **1** to **6** are shown in Table **3**. B_3LYP/6-311+G** method analysis shows that the dipole moment of the axial conformation is smaller than the dipole moment of the equatorial conformation. Dipole moment obtaine difference between the axial and equatorial conformations of compounds **1** to **6** is $\Delta\mu = (\mu)_{eq} - (\mu)_{ax}$. Calculations show that ΔE and Δμ are directly related.

Table 3. NBO-B_3LYP/6-311+G** computed bond order (Wiberg Bond Index; WBI), Dipole moment (μ; in Debye), axial and equatorial conformations of compounds **1** to **6**.

Compounds	**1**		**2**		**3**		**4**		**5**		**6**	
	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq	ax	eq
nbo												
O_1-C_2	0.9044	0.9042	0.9052	0.9049	0.9052	0.9050	0.9074	0.9071	0.9068	0.9066	0.9083	0.9077
O_3-C_2	0.9043	0.9042	0.9051	0.9049	0.9052	0.9050	0.9073	0.9070	0.9068	0.9063	0.9083	0.9077
C_2-C_5	0.9542	0.9543	0.9538	0.9543	0.9534	0.9544	0.9518	0.9541	0.9518	0.9543	0.9513	0.9540
μ	2.208	4.121	2.292	4.3512	2.2737	4.3924	4.8048	7.6297	3.2033	5.893	5.0652	7.9495
Δμ	1.91		2.05		2.11		2.82		2.68		2.88	

Computational Details

Using Gaussian 09W software [9] based on B_3LYP density theory and basis set 6-311+G** [10] Compounds **1-6** of the axial and equatorial conformation were optimally performed. Using NBO analysis, the stabilization energy electron delocalization associated to $LP_1O_1 \rightarrow \sigma^*C_2$-$C_5$, $LP_2O_1 \rightarrow \sigma^*C_2$-$C_5$, $LP_1O_3 \rightarrow \sigma^*C_2$-$C_5$ and $LP_2O_3 \rightarrow \sigma^*C_2$-$C_5$ and structural parameters such as bond length and bond angle, dipole moments and bond order were studied. The stability energies related to the anomeric effect in the axial and equatorial conformations of compound **1-6** were studied, and the relationship between the stability energies, related electron delocalization and dipole moments was analyzed. Stabilization energy electrons delocalization associate of the donor (i) and acceptor (j) electron orbitals. Overlap of the orbitals (Fij) and the energy difference (εj-εi) between the donor and acceptor orbitals are studied [11]. Stabilization energy electron delocalization associate of the i→j is estimated according to Equation 1. The anomeric effect with natural bond sequence is reasonable.

$$E_2 = \Delta E_{ij} = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i} \qquad \text{Eq.1}$$

Where:

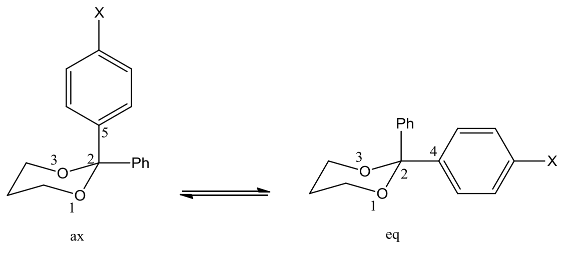
E_2: Second order stability energy (SE) of electron delocalization from electron donor i to electron acceptor j orbitals

q_i: Number of electron donor orbitals

ε_i: Energy of electron donor orbitals (diagonal element)

ε_j: Energy of electron acceptor orbitals (diagonal element)

F_{ij}: Secular determinant (off-diagonal elements)



X: F(**1**), Cl(**2**), Br(**3**), CN(**4**), CF_3(**5**), NO_2(**6**)

Figure 2: Axial and equatorial conformation conversion process of compounds **1- 6**.

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