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A computational study on Gauche Effect of $C_8H_{15}O$-X (X: OH, NH_2, CH_3) Conformers

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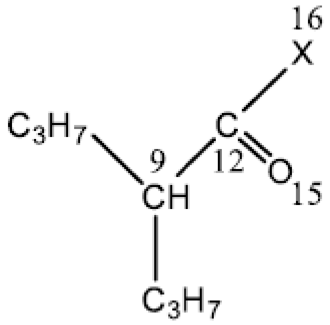
ABSTRACT

Theoretical calculations of chemical hardness and stability energy on $C_8H_{15}O$-X (X: OH, NH_2, CH_3) carried out by NBO at the B3LYP/6-311+G** level. $C_8H_{15}O$-X have been two distinguishable conformations: one CO-anti position, and the other CO-gauche position. This calculations confirm importance of LP2O16→ σ*C12-Y(Y=O, N, C) hyperconjugation interactions that can stable the CO-gauche conformers. Chemical hardness of CO-gauche conformers is in good agreement with the energy results. This results show that molecular interaction in the gauche geometries increases from compound with X=OH to X=CH_3. Actually, the gauche effect with hyperconjugation factor play important role in the stability of the gauche geometries.

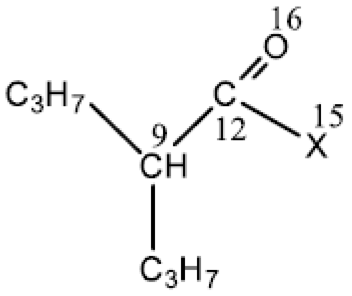
Keywords: Gauche Effect; Chemical Hardness; $C_8H_{15}O$-X (X: OH, NH_2, CH_3)

1. Introduction

The gauche effect is a tendency to conform to a structure that has the maximum number of gauche interactions between adjacent electron pairs or polar bands [1]. This effect characterizes any gauche-conformer which is more stable than the anti-conformer [2]. There are two main explanations for the gauche effect: hyperconjugation and bent bonds. In this work, we used $C_8H_{15}O$-X compounds with X= OH, NH_2, CH_3 and expected that $C_8H_{15}O$-X have been two distinguishable conformations: one CO-anti position, and the other CO-gauche position (Fig.1). The gauche- conformations were found to be more stable by hyperconjugation factor of the gauche effect. Also, in this study, Natural Bond Orbital (NBO) analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds [3]. Fig.2: The structures of $C_8H_{15}O$-X (X=OH, NH_2, CH_3) inconformation CO-gauche and CO-anti.



CO-anti



CO-gauche

2. Experimental

Computational method

This study was carried out by the Gaussian 09 program. Geometry optimizations of compounds [CO- gauche and CO-anti conformers] was performed at the B3LYP/6-311+G** level. Natural Bond Orbital analysis was also performed at the B3LYP/6-311+G** level of theory. NBO analysis was carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energy importance by second-order perturbation theory [4]. Chemical hardness is an important reactivity property of matter that is defined as the resistance towards electron cloud polarization or deformation of chemical species is a measure of stabilities and reactivates of molecules [5]. Global chemical hardness (η) was calculated as follows:

$$\eta = 0.5(\varepsilon LUMO - \varepsilon HOMO) \qquad (1)$$

3. Results and discussion

Table 1 shows the values of the chemical hardness of the CO-gauche and CO-anti conformers. In C8H15O-X geometries, hyperconjugation factor of the gauche effect increases the stability to gauche conformers. Also, there is a stereoelectronic preference for conformations in which the best donor lone pair is antiperiplanar to the best acceptor bond. Chemical hardness of gauche conformers decreases from compound with X=OH to X=CH3 and the E2 too. This results show that molecular interaction in the gauche geometries increases from compound with X=OH to X=CH3. Table 2 shows the stability energies of the CO-gauche and CO-anti conformers.

Table1: Chemical hardness for different compounds of C8H15O-X (X: OH, NH2, CH3)

compound	donor-accepter	E_2(stability energy)
$C_8H_{15}O$-OH,anti	$LP_2\, O_{16} \rightarrow \sigma^*C_{12}$-$O_{15}$	34.05
$C_8H_{15}O$-OH, gauche	$LP_2\, O_{16} \rightarrow \sigma^*C_{12}$-$O_{15}$	34.15
$C_8H_{15}O$-NH_2,anti	$LP_2O_{15} \rightarrow \sigma^*C_{12}$-$N_{16}$	24.88
$C_8H_{15}O$-NH_2,gauche	$LP_2\, O_{16} \rightarrow \sigma^*C_{12}$-$N_{15}$	25.61
$C_8H_{15}O$-CH_3,anti	$LP_2\, O_{15} \rightarrow \sigma^*C_{12}$-$C_{16}$	20.25
$C_8H_{15}O$-CH_3, gauche	$LP_2\, O_{16} \rightarrow \sigma^*C_{12}$-$C_{15}$	20.58

Table2: Molecular interaction and calculated energies (in Hartree) of the HOMO and the LUMO for different compounds of C8H15O-X (X: OH, NH2, CH3)

compound	ε_{LUMO}- ε_{HOMO}	η
$C_8H_{15}O$-OH,anti	32.7..0	0.136115
$C_8H_{15}O$-OH, gauche	32.7000	0.136940
$C_8H_{15}O$-NH_2,anti	0.24693	0.123465
$C_8H_{15}O$-NH_2,gauche	0.24515	0.122575
$C_8H_{15}O$-CH_3,anti	0.22304	0.11152
$C_8H_{15}O$-CH_3, gauche	0.22474	0.11237

4. Conclusions

The origin of the gauche effect in C8H15O-X is hyperconjugation. The gauche effect plays important role in the stability of gauche geometries. LP2O16→ σ*C12-Y(Y=O, N, C) interaction is responsible for gauche preference in C8H15O-X. The results show that chemical hardness of gauche geometries decrease from compound with X=OH to X=CH3, the stability energy (E2) is also same trend.

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