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Study of Mechanism Keto-Enol Tautomerism (isomeric reaction) Structure Cyclohexanone by Using Ab initio Molecular Orbital and Density Functional Theory (DFT) Method with NBO Analysis

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Abstract

Initial quantum mechanic studies and density function theory (DFT) in the level of HF/6-311+G**, B3LYP/3-21+G* and B3LYP/6-311+G** on Keto-Enol Tautomerism (isomeric reaction) cyclohexanone structure, that results shows that activation energy for this reaction equal 64.6143(kcal.mol^{-1}) and transition state has the highest energy level equivalent whit -194354.27(kcal.mol^{-1}) that due to breaking of C-H bond and composing of O-H bond. The results of NBO analysis of showed that the bond π are in resonance condition with lone-pair electrons oxygen of and therefore providing enol state and the transition state in these reactions usually is the structure between ketone state and enol state. Bond order and density of electrons aren't the same in structures enol state, transition state and ketone state. Also tautomerism cyclohexanone structure is a kind of endothermic isomeric reaction.

Keywords: Ab initio, Cyclohexanone, DFT, NBO, Tautomerism

1. Introduction

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Tautomerism is the movement of an atom or a group of atoms in a molecular structure and providing the new from that may this new from more stable or more unstable than initial form . One of the most important of available processes in containing carbonyl groups is their tautomerism that it operated in neutral environment with less intensity in comparison with acidic and alkaline environments [1, 2]. There are two forms in ketone and enol tautomerism. That ketone is less stable than enol usually. In such usually suitable catalyst in such mechanics, is an acidic and alkaline catalyst. In balance mode, the most containing carbonyl groups compositions exist in ketone from and separation of pure enol is very difficult cyclohexanone is the composition that in room temperature has only 0.0001 percent enol form [3]. However separation of enol is very difficult and exist very minorly in balance mode, but because of their extensive reactionability, they play an important role in chemistry of containing carbonyl groups composition. Ofcourse, the condition for operation of tautomery is the existence of Hα in comparison with carbonyl operative group. In this research we studied on the structure and rate of levels of energy of cyclohexanone in tautomerism reaction by using initial quantum mechanic and DFT methods.

2. Calculation Method

The calculations of quantum mechanics in theory level by using UHF/6-311+G** theory method operated on the structure of cyclohexanone[4]. In order to this, firstly the structure of initial matter and product matter designed by using Chem Office 2008 software, and initial optimization operated by using Winmopac version 2.0 software and AM1 method [5]. The transition mode of structure simulate by using keyword SADDLE and then transition state GAUSSIAN 03W package program and keyword QST2 implemented on a pentum-PC computer with a 730 MHz processor, used for finalization[6,7]. Eventually, the final optimization and calculation of energy levels operated in theory of the levels HF/6-311+G**, B3LYP/3-21+G* and B3LYP/6-311+G**. Also NBO - version 03 program used for calculations of natural bond orbital.

3. Result and Discussion

Structure parameters reported for ketone, enol and transition state cyclohexanone structure in table 3. Obtained results indicate from difference in Bond lengths, Bond angles and torsion angles in three different structure of cyclohexanone. General stages of tautomerism reaction of cyclohexanone showed in figure 1. Calculated energies for tautomerism structure cyclohexanone has been shown in table 1. The results of Natural Bond Orbital (NBO) analysis showed in table 2, 4. In table 4 express that electron density of involved atoms in tautomerism reaction is not same and in transition state, structure of cyclohexanone exit from ketone state and approach to enol state. That O-H bond is composition and C-H bond is breaking and displacement of π electrons caused to composition of enol form. The results of table 2 indicated that this resonance of bonding electrons of π and none-bonding electron pair of oxygen with double bond. That cause to providing on easy and fast balance between cyclohexanone structure and cyclohexanol stericure, that of course enol form is more unstable because of its high energy level and less abundancy.

All tables should be numbered with Arabic numerals. Headings should be placed above tables, left justified. Leave one line space between the heading and the table. Only horizontal lines should be used within a table, to distinguish the column headings from the body of the table, and immediately above and below the table. Tables must be embedded into the text and not supplied separately. Below is an example which authors may find useful.

4. Conclusion

   Initial quantum mechanic studies and density function theory (DFT) in the level of HF/6-311+G**, B3LYP/3-21+G* and B3LYP/6-311+G** on Keto-Enol Tautomerism process cyclohexanone structure, that results shows that activation energy for this reaction equal 64.6143(kcal.mol^{-1}) and transition state has the highest energy level equivalent whit -194354.27(kcal.mol^{-1}), that due to breaking of C-H bond and composing of O-H bond. The process is a type of easy and fast balance that is more stabler of enol state. The results of NBO analysis of showed that the bond π are in resonance condition with pair electrons nonbonding oxygen and therefore providing enol state that is a kind of isomeric reaction and the intermediate in these reactions usually is the structure between ketone and enol state. Bond angles and density of electrons aren't the same in structures enol state, transition state and ketone state. Also tautomerism is a kind of endothermic isomeric reaction.

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Table 1. Calculated energies (in Hartree) for the important geometries of keto- enol tautomerism structure cyclohexanone

Method	B3LYP/6-311+G**			B3LYP/3-21+G*			HF/6-311+G**		
Geometry	Ketone State	Transition State	Enol State	Ketone State	Transition State	Enol State	Ketone State	Transition State	Enol State
ZPE^b	0.150301	0.143996	0.150261	0.151953	0.145217	0.150871	0.160465	0.153707	0.160664
E_{ele}	-309.981203	-309.87192	-309.96417	-308.238108	-308.123918	-308.21836	-307.9847007	-307.84711	-307.9638
E_0	-309.830902	-309.72793	-309.81391	-308.086155	-307.978701	-308.06749	-307.824236	-307.69340	-307.8031
ΔE^a_0	0.102971 (64.6143025)^C			0.107454 (64.427385)^C			0.13083200 (82.097080)^C		

^{a} Relative to the most stable geometry

^{b}Corrected by multiplying by a scaling factor (0.9135)

^{c}Numbers in parenthesis are the corresponding values in kcal mol^{-1}

Table 2. Calculated resonance energies (E2) of structure keton state, enol state and transition state

Method	NBO-B3LYP/6-311+G**		
Structure	Donor	acceptor	E_2(kcal.mol^{-1})
Ketone State	$\pi\ c_1\text{-}o_7$	$\pi^*\ c_2\text{-}c_3$	1.08
	$\pi\ c_1\text{-}o_7$	$\pi^*\ c_5\text{-}c_6$	1.08
	Lp o_7	RY* c_6	17.31
	$\pi\ c_1\text{-}o_7$	$\sigma^*\ c_2\text{-}H_8$	1.92
	Lp o_7	$\pi^*\ c_1\text{-}c_2$	19.97
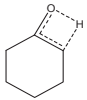
	Lp o_7	π^* c_1-c_6	19.97
Transition State	σ c_2-c_8	σ^*c_1-c_6	14.31
	σ c_2-c_8	π^* c_1-o_7	33.52
	π c_1-o_7	σ^* c_2-H_8	13.64
	Lp o_7	π^* c_6-c_7	18.89
	Lp o_7	σ^* c_2-H_8	94.12
	Lp o_7	σ^*c_1-c_2	10.77
	Lp o_7	σ^*c_5-c_6	3.43
Enol State	π c_1-c_2	RY^*o_7	1.24
	π c_1-c_2	π^* c_1-c_2	0.77
	Lp o_7	π^* c_1-c_2	29.25
	Lp o_7	σ^*c_1-c_2	5.69

Table 3. B3LYP/6-311+G** Calculated structural parameters

Method	B3LYP/6-311+G**		
Compound	Ketone	Transition	Enol
Bond Lengths(Angstrom)	State	State	State
r 1-2	1.5215	1.4195	1.3375
r 1-6	1.5215	1.4925	1.5025
r 1-7	1.2125	1.2865	1.3765
r 2-3	1.5425	1.5245	1.5105
r 2-8	1.0915	----	----
r 2-9	1.0995	1.0925	1.0895
r7-8	----	----	0.9645
Bond angles (degree)			
θ123	112.0	119.0	122.9
θ128	108.6	59.40	96.00
θ129	107.2	111.0	119.4
θ178	93.60	76.80	176.1
θ216	115.3	125.6	124.3
θ217	122.4	110.4	124.2
θ617	122.4	123.9	111.5
Torsion angles (degree)			
φ9216	118.5	-118.7	-0.800
φ8216	-5.9	-108.7	-2.700
φ7129	-35.80	65.3	-1.700
φ7128	3.5	-10.20	1.300
φ6178	-176.6	61.40	177.1

Table 4. Calculated bonds occupancies by using natural bond analysis (NBO) by B3LYP/6-311+G** method orbital

Method	B3LYP/6-311+G**		
	Occupancy		
Compounds	Ketone State	Transition State	Enol State
σ_{1-2}	1.97389	1.32946	1.98300
π_{1-2}	----	----	1.95522
σ_{1-7}	1.99618	1.99523	1.99323
π_{1-7}	1.98371	1.94756	----

$\sigma_{2\text{-}8}$	1.98094	1.71172	----
$\sigma_{2\text{-}9}$	1.95946	1.92335	1.97528
$\sigma_{7\text{-}8}$	----	----	1.98667
$\sigma_{2\text{-}3}$	1.98365	1.98660	1.98441
$\sigma_{3\text{-}4}$	1.98365	1.98038	1.98249
$\sigma_{4\text{-}5}$	1.97389	1.97680	1.97514
$\sigma_{5\text{-}6}$	1.98269	1.98082	1.98300
$\sigma_{6\text{-}1}$	1.98269	1.97433	1.97227

$\Delta E \text{ (kcal.mol}^{-1}) = \begin{cases} 64.6143025 \text{ (B3LYP/6-311+G**)} \\ 67.427385 \text{(B3LYP/3-21+G*)} \\ 82.097080 \text{ (HF/6-311+G**)} \end{cases}$

$E_0 \text{ (Hartree)} = \begin{cases} -309.727931 \text{ (B3LYP/6-311+G**)} \\ -307.978701 \text{ (B3LYP/3-21+G*)} \\ -307.693404 \text{ (HF/6-311+G**)} \end{cases}$

Transition State

Enol State

$E_0 \text{ (Hartree)} = \begin{cases} -309.813918 \text{ (B3LYP/6-311+G**)} \\ -308.067497 \text{ (B3LYP/3-21+G*)} \\ -307.803144 \text{ (HF/6-311+G**)} \end{cases}$

ΔE

Ketone State

$E_0 \text{ (Hartree)} = \begin{cases} -309.830902 \text{ (B3LYP/6-311+G**)} \\ -308.086155 \text{ (B3LYP/3-21+G*)} \\ -307.824236 \text{ (HF/6-311+G**)} \end{cases}$
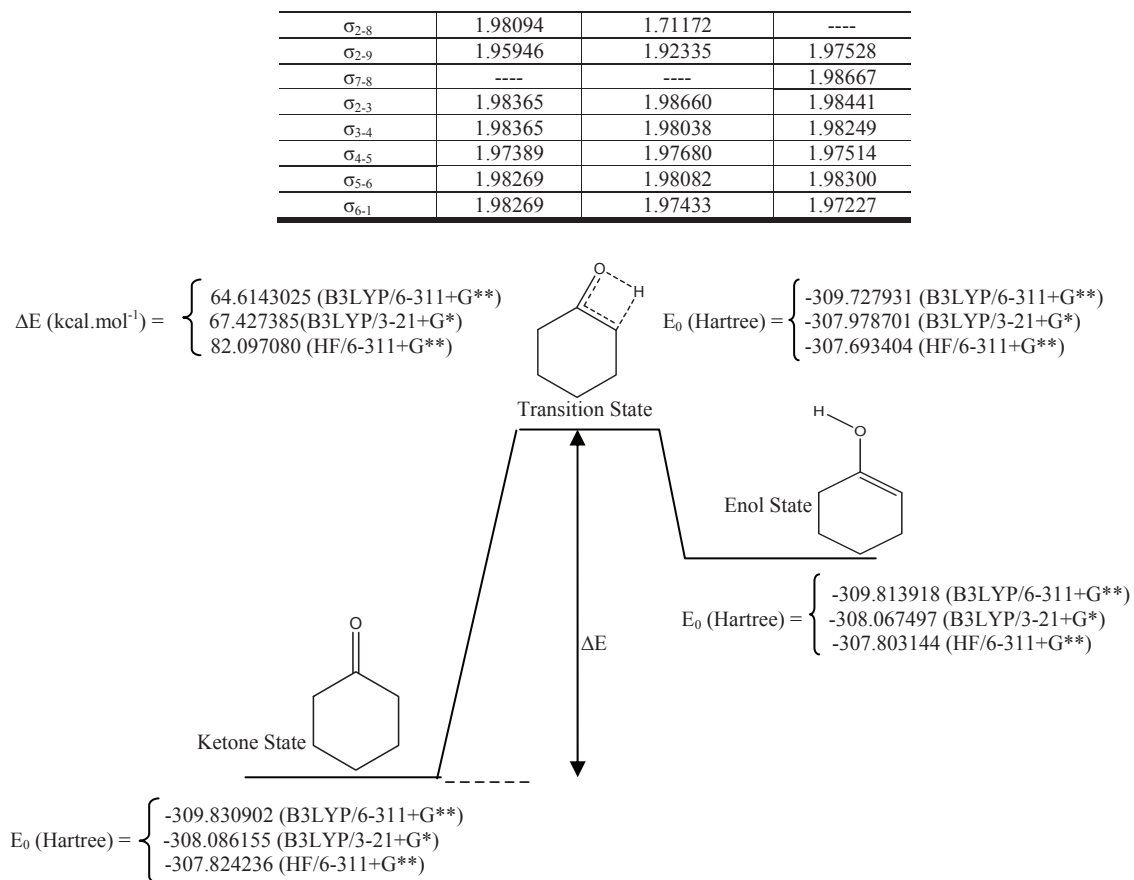
Fig. 1. Calculated HF/6-311+ G**, B3LYP/3-21+G* and B3LYP/6-311+ G** profile for Tautomerism structure Cyclohexanone.