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Thermodynamic Study and Total Energy Calculation for three systems of Enol↔Keto Tautomerism

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ABSTRACT

Using Hartree–Fock (HF) and Density Functional Theory (DFT) calculations the thermodynamic properties such as thermal energy , U_{th}^{0}, thermal enthalpy , H_{th}^{0}, thermal entropy , S_{th}^{0}, thermal Gibbs free energy , G_{th}^{0}, heat capacity ,C_v, and molecular structures of several species involving in keto↔enol tautomerism related to acetaldehyde (A), 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and acetylacetone (AA) have been investigated. In addition, the geometric structure of all stages intervening in enol ↔ keto conversion related to three above mentioned compounds have been investigated on ab initio calculation and DFT level by using STO-3G, 6-31G, 6-31++G and 6-31++G** basis sets. The results showed that the enol structure related to acetylacetone is more stable because of intramolecular hydrogen bond formation in the enol form while the keto structure is more stable in acetaldehyde and dimedone because of strong C=O bond existence in the keto tautomers. The computed HF/DFT results are in a good agreement with the experimental studies. Moreover,the values of ΔU_{th}^{0}, ΔH_{th}^{0}, ΔG_{th}^{0} and thermodynamic equilibrium constant, K_{th}, of tautomerization phenomenon related to acetaldehyde, dimedone and acetylacetone are calculated on the basis of DFT-IR method.

Keywords : keto ↔ enol; tautomerism; DFT; Hydrogenbonding; Thermodynamic equilibrium constant; Acetaldehyde ; Acetylacetone ; Dimedone

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INTRODUCTION

keto↔enol tautomerism *[>HC—C(=O) ↔ >C=C(OH)]* is one of the most common investigated subjects of isomerism respect to carbonyl compounds [1]. Generally, the keto form is more stable than the enol one for neutral systems. For example, acetaldehyde ($H_3C–CH=O$) or keto form is more stable than vinyl alcohol ($H_2C=CH–OH$) or enol form.Therefore, this enol↔ keto isomerization is highly exothermic. If an extra intramolecular stabilization takes place, the enol tautomer may be favoured. IR, NMR, and neutron studies on acetylacetone and its derivatives indicate that substitution of the methyl grops of AA has a drastic effect on both the position of keto → enol equilibrium and the strength of the intramolecular hydrogen bond [2, 3].

It has been shown that substitution of methyl groups in AA by phenyl groups increases the hydrogen bond strength [4].

The keto tautomer of AA has two carbonyl functional groups, whereas the enol tautomer has one carbonyl functional group and one hydroxyl group (fig.1).

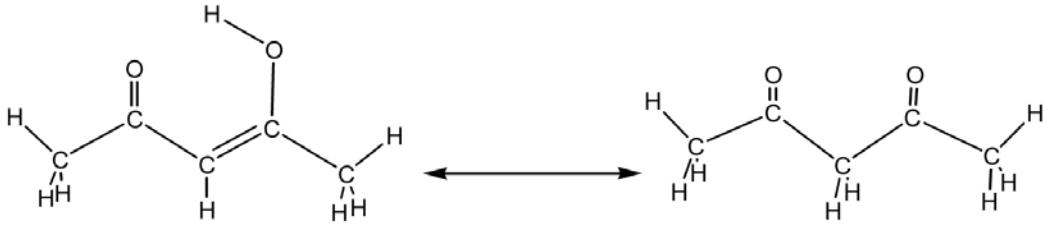


Fig.1. Chemical structures of enol and keto tautomers related to acetylacetone.

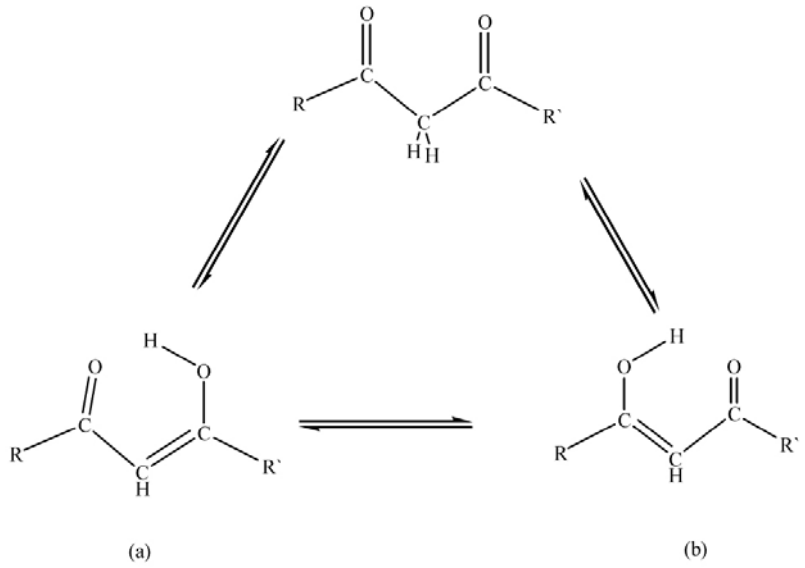


Fig.2. Keto and enol forms related to β- ketones.

Computational

Geometric optimization on the basis of ab initio method

The equilibrium molecular geometries related to keto↔enol tautomerism of A, AA and dimedone were computed with the GAUSSIAN 98 software system on the basis of a selection of modern density functionals BLYP and B3LYP where the selected exchange and correlation functionals were used for DFT Kohen-Sham calculations [9]. Also, the Becke's 1988, B, and the Becke's three-parameters (B3) exchange functionals with the correlation functional of Lee, Yang, and Parr, LYP were used in oder to carry out the calculations.Four basis sets including two pople's sets, small, the Slater-type orbital (STO-3G) basis set with DZ (Double Zeta without polarization) functions were used for the clusters and each functional [10]. Inner shells were treated within the frozen core approximation and 6-31G basis set,

RESULTS AND DISCUSSION

3-1. Preferred structures for isolated keto and enol forms

3-1-1. Acetaldehyde

Tautomerism refers to the equilibrium between two different structures of the same compound. Usually the tautomeric forms in organic compounds differ in the point of attachment of a hydrogen atom. One of the most common examples of a tautomeric system is the equilibrium between a ketone and its enol form.This is due to the flexibility of C=C—O chain in the enol form and convergence of the C—C=O chain in the keto form .Different structures related to enol↔keto mechanism for acetaldehyde are shown in fig.3.

Analyzing the system diagrammed in fig.4, is of especial challenge since the isomers (T1→T6) may be interconverted by intramolecular movement of a hydrogen atom from one oxygen to another over a small distance.

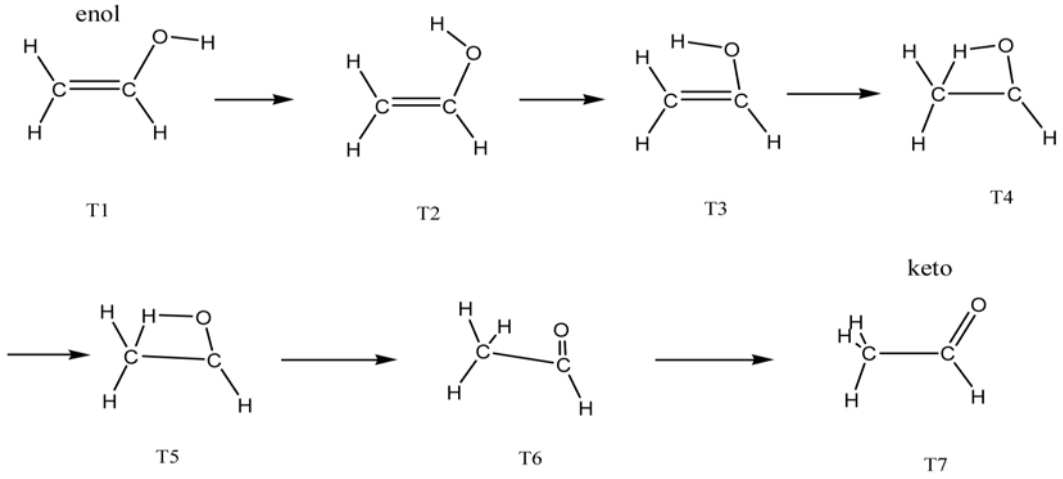


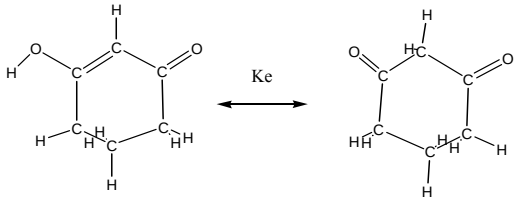
Fig.3. Proposed structures in enol↔ keto mechanism related to acetaldehyde.

two Pople's sets, large, 6-311++G and 6-31++G** were used in order to carry out the calculations. Hartree-Fock results were also included in the comparison with all the basis sets.

3.1.3: 5, 5-dimethyl-1, 3-cyclohexanedione (dimedone)

The enol→ keto tautomerization of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) in the gas phase was studied with different methods of ab initio by using the Gaussian98package program. β-Dicarbonyl compounds have a strong tendency to

phototropic transformation. The keto↔enol tautomeric equilibrium of dimedone can be proposed as follows [16]:



Enol tautomer Keto tautomer

In liquid solvents, the equilibrium is very sensitive to solvent environments related to polar/ polarizability and hydrogen–bonding capability of solvents [17-18]. In this work, in order to avoid the solvent effects,we have studied the equilibrium in the gas phase and compared our results with experimental data(table 1) [19]. The six stages including seven forms respect to enol → keto conversion related to dimedone are shown in fig . 5.

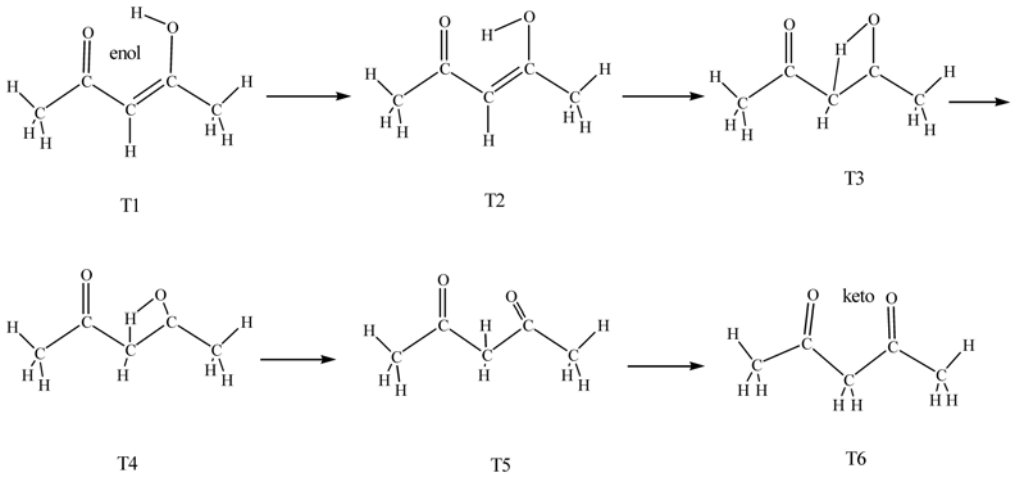


Fig.4. Proposed structures in enol↔ keto mechanism related to acetylacetone.

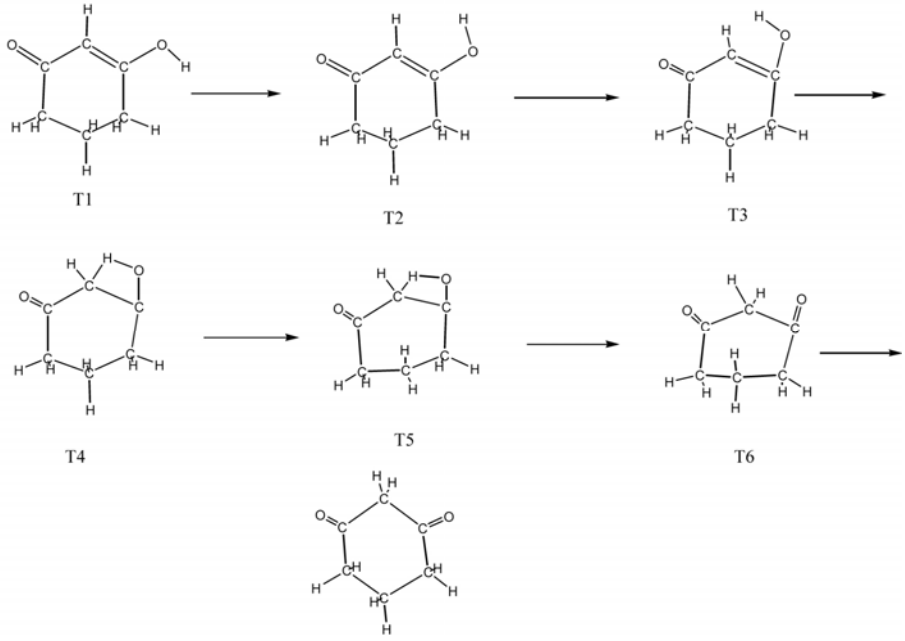


Fig.5. Proposed structures in enol↔ keto mechanism related to dimedone.

Discussion

The transition states related to the conversion of enol isomer to keto form are shown in figs.3-5 for acetaldehyde, acetylacetone and 5,5-dimethyl-1,3-cyclohexanedione (dimedone). The total energy difference for all stages have been calculated by HF & DFT methods with STO-3G, 6-31G, 6-31++G and 6-31++G** basis sets, table(1). Single point calculations were performed with B3LYP, BLYP/6-31++G** method on the geometric reference [14-19, 20-21]. The enol↔keto isomerization is highly endothermic respect to acetylacetone tatumerism but is exothermic for acetaldehyde and dimedone, table(1).

The total calculated energies are different in all stages. The stability order for the selected keto and enol structures is as follows: The keto (T7) structure is more stable for both acetaldehyde and dimedone while the enol (T1) structure is more stable for acetylacetone. The T5 and T4 structures are transition states reffering to enol→keto tautomerization which are shown in figs. 6-8.

Thermodynamic properties of enol→keto tautomerization respect to three mentioned compounds are calculated with BLYP/6-31++G** and B3LYP/6-31++G** methods. Under the isochoric condition, the thermodynamic functions such as, thermal energy (U_{th}^{0}), thermal enthalpy (H_{th}^{0}), total enthalpy (H_{total}^{0}), thermal entropy (S_{th}^{0}), thermal Gibbs free energy (G_{th}^{0}), total Gibbs free energy (G_{total}^{0}) and heat capacity (C_v) were calculated by freq methods (DFT-IR) upon the Gaussian 98 package program.

The results are shown in Tables 2-4. The ΔU_{th}^{0}, ΔH_{total}^{0}, ΔS_{th}^{0} and ΔG_{total}^{0} for keto↔enol interconversion related to acetaldehyde, dimedone and acetylacetone have been calculated by B3LYP\6-31++G** and BLYP\6-31++G** basis sets, table(6).

Thermodynamic equilibrium constant, K, for every keto↔enol tautomerization was calculated by the related standard Gibbs free energy difference (ΔG_{total}^{0}):

$keto \leftrightarrow$ enol: K

$$K = \exp\left(-\Delta G_{total}^{0} / RT\right) \quad (1)$$

For ordinary ketones, K is usually very small, but in β-Dicarbonyls due to the possibility of intramolecular H-bonding formation the enol form may be much more favorable. The values of K can be determined quite easily by using BLYP/6-31++G** and B3LYP/6-31++G** methods (Tables 2-4). According to our results the keto structure is the most stable form respect to acetaldehyde and dimedone but the enol structure is the most stable form respect to acetylacetone . The equilibrium constant for keto↔enol is defined as follow:

$$K = \frac{[enol]}{[keto]} \quad (2)$$

where [enol] and [keto] represent the molar concentration of the enol and keto tautomers, respectively.

4. CONCLUSIONS

Experimental and computational investigations have provided a more definitive understanding of tautomerism respect to acetaldehyde, dimedone and acetylacetone. All proposed stages have been constructed on the basis of bond or angle changing around the CO—CH, CH=C and C—OH bonds respectively. However, no spectroscopic data have been shown for all stages of keto↔enol tautomerism. The equilibrium constants and thermodynamic properties of acetaldehyde, acetylacetone and dimedone tautomerization have been investigated in the gas phase upon HF and DFT methods based on the GAUSSIAN 98 package. The enol form of β-diketones in acetylacetone is stabilized by a relatively strong intramolecular hydrogen bond formation, as is shown on the BLYP and B3LYP theories by using 6-31++G** basis sets. On the other hand, the results of our calculations, show that the keto structure is stabilized in acetaldehyde tautomerism and dimedone.

Table1. The calculated ΔE^{0}_{total} (kJ mol^{-1}) for enol↔ keto interconversion related to acetaldehyde, dimedone and acetylacetone, on the basis of different methods and different basis sets

Species	method	Basis set			
		STO-3G	6-31G	6-31++G	6-31++g**
Acetaldehyde	HF	86.9	48.9	42.2	52.5
	BLYP	79.3	60.4	54.2	48.0
	B3LYP	80.6	56.4	50.1	46.5
	$\Delta E^{0}_{total} = E^{0}_{total,\ enol\ \text{form}} - E^{0}_{total,\ \text{keto form}}$, Experimental value [20, 21] **47.0 kJ mol^{-1}**				
Dimedone	HF	63.7	21.3	19.7	27.4
	BLYP	53.7	26.2	23.8	17.9
	B3LYP	54.4	22.9	20.5	16.8
	$\Delta E^{0}_{total} = E^{0}_{total,\ enol\ \text{form}} - E^{0}_{total,\ \text{keto form}}$, Experimental value [19] **17.6 kJ mol^{-1}**				
Acetylacetone	HF	48.7	-4.9	-11.1	-3.6
	BLYP	37.5	1.3	-5.6	-12.8
	B3LYP	39.6	-0.7	-7.5	-12.6
	$\Delta E^{0}_{total} = E^{0}_{total,\ enol\ \text{form}} - E^{0}_{total,\ \text{keto form}}$, Experimental value [14] **-13.2 kJ mol^{-1}**				

Table2. Calculated thermal energy, thermal enthalpy, total enthalpy, thermal entropy, thermal Gibbs free energy, total Gibbs free energy, and heat capacity for seven (T1→T7) forms involving in acetaldehyde taotumerism by DFT-IR method

form	Method	U^{0}_{th} kJ/mol	H^{0}_{th} kJ/mol	H^{0}_{total} kJ/mol	S^{0}_{th} J/mol K	G^{0}_{th} kJ/mol	G^{0}_{total} kJ/mol	Cv J/mol K
T1	BLYP/ 6-31++G**	152.1	154.6	-402949.4	253.8	78.9	-403025.1	45.4
	B3LYP/ 6-1++G**	155.1	157.5	-403090.9	252.3	82.3	-403166.1	42.9
T2	BLYP/ 6-1++G**	158.6	160.9	-402855.7	255.4	84.8	-402931.8	49.3
	B3LYP 6-31++G**	161.9	164.4	-403004.6	252.7	89.1	-403079.9	45.7
T3	BLYP/ 6-1++G**	149.1	151.5	-401874.3	248.9	77.4	-401948.5	39.1
	B3LYP/ 6-31++G**	153.7	156.2	-402016.2	259.5	78.8	-402093.6	44.8
T4	BLYP/ 6-1++G**	159.1	161.6	-401612.3	254.1	85.8	-401688.1	44.6
	B3LYP/ 6-31++G**	163.9	166.4	-401752.7	263.4	87.9	-401831.2	50.2
T5	BLYP/ 6-31++G**	143.7	146.2	-401129.1	245.2	73.1	-401202.1	31.3
	B3LYP/ 6-31++G**	145.2	147.6	-401271.7	244.5	74.8	-401344.6	30.3
T6	BLYP/ 6-31++G**	171.1	173.6	-400342.8	248.9	99.4	-400417.1	34.8
	B3LYP/ 6-31++G**	172.5	174.9	-400506.8	246.5	101.5	-400580.2	33.3
T7	BLYP/ 6-31++G**	151.4	153.9	-402998.2	252.9	78.5	-403073.5	41.7
	B3LYP/ 6-31++G**	154.2	156.7	-403138.3	251.8	81.6	-403213.3	39.9

Table3. Calculated thermal energy, thermal enthalpy, total enthalpy, thermal entropy, thermal Gibbs free energy, total Gibbs free energy, and heat capacity for seven (T1→T7) forms involving in dimedone taotumerism by DFT-IR method

form	Method	U_{th}^{0} kJ/mol	H_{th}^{0} kJ/mol	H_{total}^{0} kJ/mol	S_{th}^{0} J/mol K	G_{th}^{0} kJ/mol	G_{total}^{0} kJ/mol	Cv J/mol K
T1	BLYP/ 6-31++G**	354.5	356.8	-1005708.2	341.4	255.1	-1005809.9	107.1
	B3LYP/ 6-31++G**	364.0	366.3	-1006073.1	339.5	265.1	-1006174.3	109.5
T2	BLYP/ 6-31++G**	355.8	358.1	-1005701.1	342.8	255.9	-1005803.3	108.3
	B3LYP 6-31++G**	362.9	365.2	-1006065.2	330.6	266.7	-1006163.7	102.8
T3	BLYP/ 6-31++G**	338.3	340.6	-1005045.5	318.3	245.7	-1005140.4	92.4
	B3LYP/ 6-31++G**	347.3	349.6	-1005386.1	327.4	252.0	-1005483.7	95.9
T4	BLYP/ 6-31++G**	327.9	330.2	-1004365.2	317.9	235.4	-1004459.9	81.6
	B3LYP/ 6-31++G**	333.5	335.8	-1004707.6	312.0	242.8	-1004800.6	78.0
T5	BLYP/ 6-31++G**	359.4	361.7	-1003097.9	312.2	268.7	-1003190.9	83.7
	B3LYP/ 6-31++G**	365.6	367.9	-1003475.6	308.2	276.1	-1003567.4	79.1
T6	BLYP/ 6-31++G**	364.0	335.6	-1004567.4	338.7	235.1	-1004661.9	109.6
	B3LYP/ 6-31++G**	363.4	353.8	-1004975.3	324.5	257.6	-1005068.6	91.9
T7	BLYP/ 6-31++G**	351.4	354.9	-1005728.1	329.5	256.7	-1005826.2	102.2
	B3LYP/ 6-31++G**	359.2	364.4	-1006091.7	345.9	261.4	-1006194.8	105.2

Table4. Calculated thermal energy, thermal enthalpy, total enthalpy, thermal entropy, thermal Gibbs free energy, total Gibbs free energy, and heat capacity for seven (T1→T7) forms involving in acetylacetone taotumerism by DFT-IR method

form	Method	U_{th}^0 kJ/mol	H_{th}^0 kJ/mol	H_{total}^0 kJ/mol	S_{th}^0 J/mol K	G_{th}^0 kJ/mol	G_{total}^0 kJ/mol	Cv J/mol K
T1	BLYP/ 6-31++G**	327.6	329.9	-905838.2	329.7	231.6	-905936.5	94.4
	B3LYP 6-31++G**	336.1	338.6	-906160.9	333.9	239.1	-906260.4	97.6
T2	BLYP/ 6-31++G**	336.8	339.3	-903322.3	311.4	246.5	-903415.1	74.7
	B3LYP/ 6-31++G**	341.7	344.2	-903677.1	305.6	253.1	-903768.2	70.8
T3	BLYP/ 6-31++G**	328.8	331.3	-904722.8	318.2	236.5	-904817.7	81.5
	B3LYP/ 6-31++G**	334.5	336.9	-905058.6	310.0	244.6	-905151.0	77.0
T4	BLYP/ 6-31++G**	332.0	334.5	-903913.4	304.9	243.6	-904004.3	70.0
	B3LYP/ 6-31++G**	336.7	339.2	-904246.1	300.9	249.5	-904335.7	66.3
T5	BLYP/ 6-31++G**	356.5	358.9	-903102.2	317.7	264.3	-903196.8	75.1
	B3LYP/ 6-31++G**	361.2	363.7	-903451.7	311.2	270.9	-903544.5	71.7
T6	BLYP/ 6-31++G**	324.6	327.1	-905828.2	318.6	232.1	-905923.1	90.4
	B3LYP/ 6-31++G**	330.9	333.3	-906153.6	313.7	239.9	-906247.1	85.9

Table5. The calculated ΔU_{th}^0, ΔH_{total}^0, ΔS_{th}^0 and ΔG_{total}^0 for keto ↔enol interconversion related to acetaldehyde, dimedone and acetylacetone by DFT-IR method

Species	method	ΔU_{th}^0 $(kJmol^{-1})$ $U_{th,enol\ form}^0 - U_{th,keto\ form}^0$	ΔH_{total}^0 $(kJmol^{-1})$ $H_{total,enol\ form}^0 - H_{total,keto\ form}^0$	ΔS_{th}^0 $(Jmol^{-1}\ K^{-1})$ $S_{th,enol\ form}^0 - S_{th,keto\ form}^0$	ΔG_{total}^0 $(kJmol^{-1})$ $G_{total,enol\ form}^0 - G_{total,keto\ form}^0$
Acetaldehyde	BLYP\6-31++G**	0.7	48.7	0.9	48.4
	B3LYP\6-31++G**	0.9	47.4	0.5	47.2
Dimedone	BLYP\6-31++G**	-9.5	19.9	2.7	16.3
	B3LYP\6-31++G**	0.6	18.6	15.0	20.5
Acetylacetone	BLYP\6-31++G**	3.0	-10.1	11.1	-13.4
	B3LYP\6-31++G**	5.3	-7.3	20.2	-13.3

Table6. Calculated thermodynamic equilibrium constant, *K*, by DFT- IR method.

$keto \leftrightarrow$ enol: $K = [enol]/[keto]$

Species	Method	
	B3LYP/6-31++G**	BLYP/6-31++G**
Acetaldehyde	5.4×10^{-9}	3.3×10^{-9}
Dimedone	2.6×10^{-4}	1.4×10^{-3}
Acetyl acetone	215.8	219.0

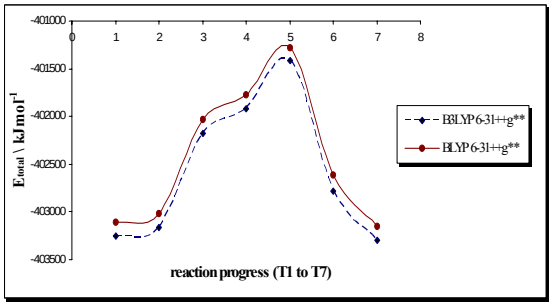


Fig.6. The calculated total energy (kJ mol^{-1}) of the geometric forms involved in enol↔ keto related to acetaldehyde interconversion

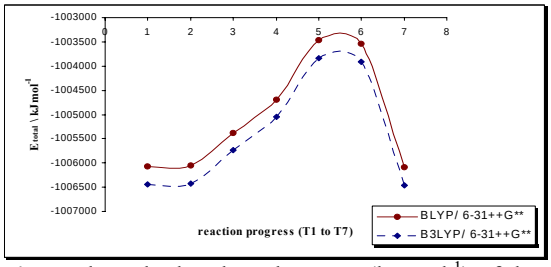


Fig.7. The calculated total energy (kJ mol^{-1}) of the geometric forms involved in enol↔ keto related to dimedone interconversion.

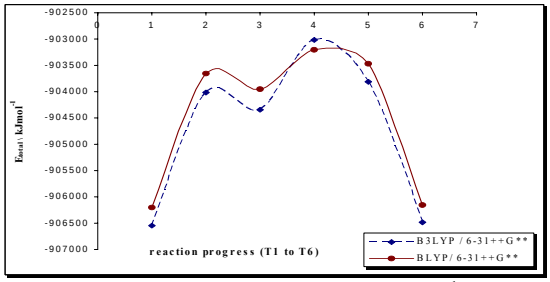


Fig.8. calculated total energy (kJ mol^{-1}) of the geometric forms involved in enol↔ keto related to acetylacetone interconversion.

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