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Computational Study of the Keto-Enol Tautomerism of 3-Phenyl-2,4-Pentanedione in the Gaseous Phase and Solvents Using DFT Methods

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ABSTRACT

The study of tautomerics equilibria is of vital importance as tautomeric compounds reactivity highly depends on the proportion of each tautomer. Herein, the tautomeric equilibrium of the 3-phenyl-2,4-pentanedione was studied theoretically by the b3lyp/6-31+g(d)methods. The effect of four solvents was considered (water, methanol, carbon tetrachloride and Cyclohexane). The tautomeric equilibrium takes place through four-membered ring transition state. The barrier heights energies of the tautomerics equilibria reaction of the transition state with reference to Keto were found to be 31.26, 31.23, 30.84, 30.82 and 30.61 kcal mol^{-1} in water, methanol, carbon tetrachloride, Cyclohexane and the gas-phase, respectively. Furthermore, the electronics energies differences between the Keto-form and Enol-form were found to be -16.50, -16.55, -17.27, -17.34 and -17.89 kcal mol^{-1} in the same previous solvents respectively. The DFT calculations revealed that the Keto-form is more stable one in all investigations.

Keywords: 3-phenyl-2,4-pentanedione, Keto-Enol tautomeric equilibrium, four-membered ring transition state, Solvent effect, Density Functional Theory.

INTRODUCTION

In organic molecules, tautomerism of proton is a general occurrence, and has very important role in numerous areas of biological dynamics and the acid-base chemical reactions, which would be caused by the interaction of specific site like hydrogen bonding. The hydrogen bond in recent years has important role in chemistry, physics and biology. Also the hydrogen bond attracted more, and has more attention to the intra-molecular proton transfer (IPT)[1-18].

Tautomerism in organic chemistry has been extensively studied by chemists experimentally and theoretically due to its vast usage as organic reagents in medicinal and organic chemistry. The organic compounds that have carbonyl functional groups with alpha hydrogen atoms can be found at equilibrium as ketone or enol tautomeric continual isomers. These tautomers are crucial due to their unique

properties such as the presence of different hetero-heavy donor atoms and functional groups as well as their solubility in polar and nonpolar solvents. Thus, they facilitate their applications in chemistry to be intermediates in organic synthesis and chelating ligands of heavy metals. Furthermore, they have a key role in biology as an antitumor, antibacterial, anticonvulsant, antidepressant, and the dynamics of biological systems happened by the interactions of specific site like bond of hydrogen. Therefore, a profound understanding of the Keto-Enol tautomeric mechanism is vitally significant to be understood.

The stability of these two tautomeric forms of carbonyl compounds in different solvents has been detected in the condensed and gas phases by spectroscopic approaches such as nuclear magnetic resonance (NMR) and infrared techniques (IR). Therefore, the effect of solvents on the stability of keto and enol tautomeric forms for different dicarbonyl compounds such as β-diketones, β-Dicarbonyls[19], 3-phenylazo-2,4-pentanedione[20], pentan-2,4-dione, β-ketoester, β-diketones[21], β-ketonitrile, alpha-ketophosphonates, and acetylacetone have reported in the literature. Their results summary revealed that polar solvents stabilize the keto tautomer over the corresponding enol tautomer and this was attributed to the high polarity of the Keto-form compared to the Enol-form. Furthermore, when there is no interaction between the solvent and the keto and enol forms then the keto tautomer is more stable in solvents with high dielectric constants than the enol form. This was assigned to the formation of bonds of hydrogen between the keto isomer and solvent which is unfavorable in the case of the enol form. Therefore, the stability of tautomeric isomers in the solvent depends on the interaction between the solvent and the tautomer.

This approach can be used to investigate the Keto-Enol tautomerization mechanism, using density functional theory (DFT) calculations. In this method, the thermodynamic functions of tautomerization can be calculated by computer simulation in different solvents and gas phases to explore the effect of solvents on the stability of Keto-Enol tautomeric forms. For example, Linear and Cyclic-Diketones[22], β-Diketones[23], α- and β β-Cyclodiones[24], Cyclohexanone[25], Acetylacetone[26], and 4(substitutedphenylazo)-3;5-diacetamido-1-H-pyrazoles[27], are reported in the literature. The common results of these studies are that the solvents that can destroy hydrogen bonds the enol form is unstable due to an unfavorable entropy of enolization but the keto form is stable due to the electrostatic interactions. This can lead to a reduction of enol forms in these solvents but a greater extent than expected because of the unfavorable entropy change. However, the keto form is more enthalpically stable in the solvents that can be acted as hydrogen bond protons acceptors and donors but is not stabilized as much as the eno1 tautomer. The entropy of enolization is unfavorable in these solvents, but due to the enthalpy stabilization of the enol tautomer the percentage of enol is greater than would be expected on the basis of dielectric constant.

This article will investigate keto-enol tautomerism of 3-phenyl-2,4-pentanedione in the gaseous phase and in solvents to see the effect of these solvents on the stability of ketol–Enol Tautomerism.

Computational Methods

Calculations of the title compound were carried out with Gaussian 09[28] using the Density Functional Theory calculations (DFT) B3LYP methods, to predict the molecular structure. Molecular geometries of tautomeric forms of 3-phenyl-2,4-pentanedione in the gaseous phase and in solvents were fully optimized using Density Functional Study (DFT) calculations and high level basis set 6-31+g(d). Also, the geometries of the Keto-form, transition state and Enol-form involved in the reactions were all fully optimized by using B3LYP/6-31+g(d). The vibrational analysis calculations were doing to molecular structures obtained, to characterize them as local minima or transition states. For the later structures, Intrinsic Reaction Coordinate IRC calculations[29] were doing along the vector of transition which explained by the mode of

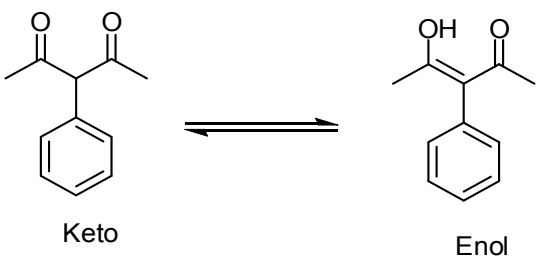
vibration of this imaginary frequency to check that the structure of the saddle point connected downhill the corresponding forward and backward minima. The investigation of the molecular structures of transition state through the reaction pathway can be allowed by the above mentioned methodology. In the Gaussian calculations the standard condition is 298 K temperature and 1 atm pressure.

The solvents effect on the tautomerics molecular structure parameters were studied by the self consistent reaction-field (SCRF) method of calculations depend on PCM solvation model developed by Tomasi and co-workers[28], as implemented in G09[28]. The solvents chosen for this work are polar solvent , water (the dielectric constant of liquid water, ε equal 78.40) and methanol (the dielectric constant of liquid methanol, ε equal 32.60), and nonpolar solvents like cyclohexane (ε equal 15.60) and carbon tetrachloride (ε equal 2.20).

RESULTS AND DISCUSSIONS

Tautomeric Isomers of the 3-Phenyl-2,4-Pentanedione

As Scheme1 shows the 3-Phenyl-2,4-Pentanedione remains in dynamic equilibrium between two tautomeric forms which are known as Keto and Enol isomers. The enolform can be generated as a consequence of shifting α-carbon atom hydrogen in any carbonyl group in the keto form of the molecule. As it is reported in the literature articles, the Enol-form is less stable than the Keto-form due to the high stability of C=O bonds compared to C=C bonds, but this is still a matter of debate due to the stability still depends on different factors such as the solvent.Therefore, this study is going to discuss the stability of Keto-Enol isomers of the 3-Phenyl-2,4-Pentanedione in different solvents.



Scheme 1. The possible tautomeric forms of the 3-Phenyl-2,4-Pentanedione at equilibrium

Geometries Analysis of Keto, Enol, and transition state

The b3lyp/ 6-31+g(d) optimized geometries of The gas phase of the Enol, Keto, and transition state of the 3-Phenyl-2,4-Pentanedione and their corresponding chosen molecular structural simulated parameters are displayed in Fig. 1 and Table 1, respectively. The reaction of internal proton transfer (IPT) of Enol ⟶ transition state ⟶ Keto was regarded, since an internal proton transfer (H_{17}) on (C_{12}) in the keto form to the carbonyl oxygen atom (O_{15}). This shift is attended by a rearrangement of the four-membered ring, not six-membered due to the 3-phenyl-2,4-pentanedione carbonyl groups are not planar. Therefore, the calculated geometric parameters in Table 1 are in good accordance with this statement. The distance between (C_{12}-H_{17}) increases and (H_{17}-O_{15}) decreases during an internal proton transfer (IPT) reaction. The (C_{12}-H_{17}) and (H_{17}-O_{15}) distances for transition state are 1.583 angstrom (Å) and 1.230 angstrom(Å), in gas phase respectively. According to the initial values, we can concluded that the (C_{12}-H_{17}) is broken and (H_{17}-O_{15})bond is formed through an internal proton transfer reaction of 3-phenyl-2,4-pentanedione. However, in the IPT in the reaction channel Enol ⟶ transition state ⟶ Keto, the (C_{12}-C_{13}) bond decreases, changing from a sigma bond in Keto form to a double bond in Enol form through transition state, and the (C_{13}-O_{15}) bond has increased, changing from double bond in keto form to sigma bond in Enol form in all phases. The A(17,12,13) bond angle decreases, while the (13,15,17) bond angle increases in Enol⟶ transition state ⟶ Keto transfer. Furthermore, the (12,13,15) bond angle increases, while the (15,17,12) bond angle decreases in Enol ⟶ Keto transfer in all phases. These results are consistent with the Keto–Enol tautomerisation of cyameluric acid reported literature article[30]. Since the single carbon nitrogen bond C–N was converted into double carbon nitrogen bond C=N after the transfer of hydrogen, while the double bond carbon oxygen C=O has been transformed from π to σ in Keto–Enol tautomerisation of cyameluric acid. This was accompanied by the bond angles nitrogen carbon oxygen (N–C–O) decrease in the intermediate after the Enol-form was formed[30]

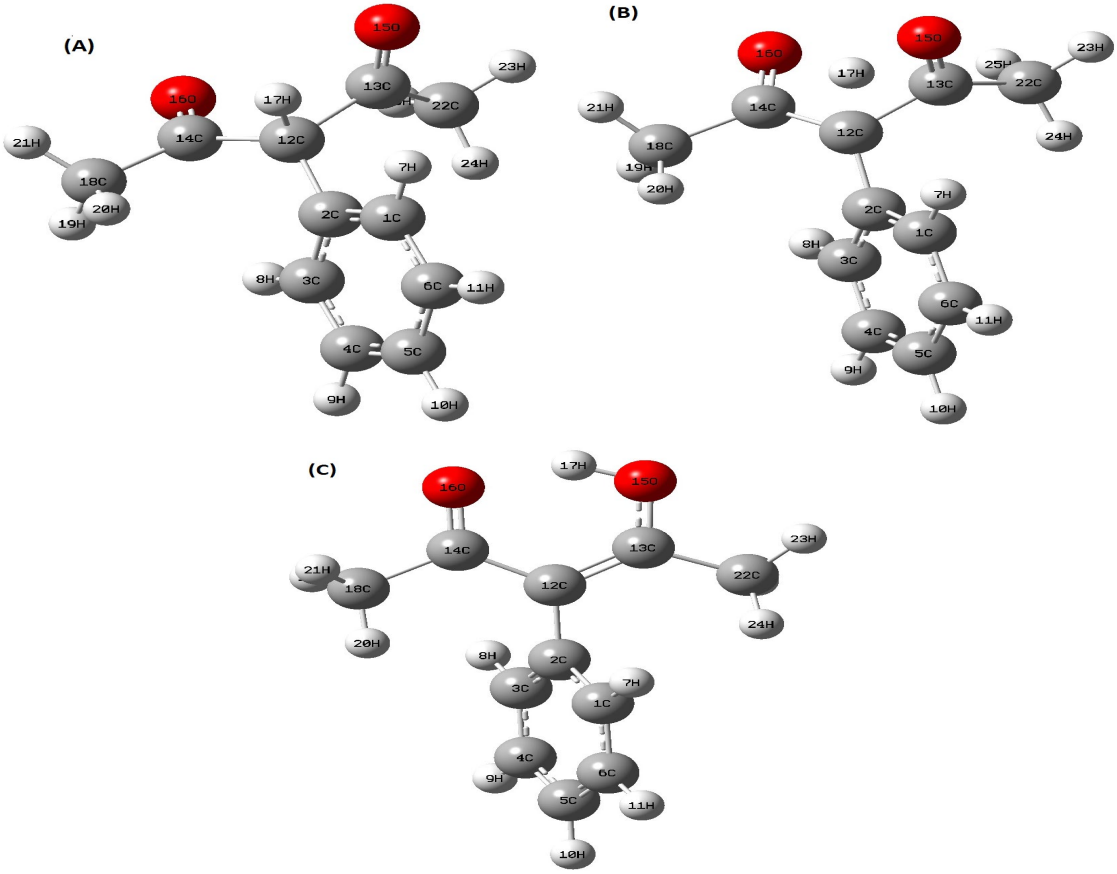


Fig. 1. Optimized geometries of different tautomers of 3-phenyl-2,4-pentanedione in the gaseous phase, (a) keto, (b) transition state, and (c) Enol form using b3lyp/6-31+g(d) method

Table 1: Chosen bond lengths and bond angles as obtained from b3lyp/6-31+g(d) geometrical optimization of 3-phenyl-2,4-pentanedione in solution and gaseous phase

Solvent	Bond	Bond lengths (Å) Keto	Transition state	Enol	Angle	Bond angles (o) Keto	Transition state	Enol
Gas phase	C_{12}-H_{17}	1.186	1.583	2.045	A(17,12,13)	080.60	065.28	058.48
	C_{12}-C_{13}	1.493	1.479	1.442	A(12, 13,15)	108.02	107.86	110.92
	H_{17}-O_{15}	1.688	1.230	0.990	A(13, 15,17)	071.39	082.79	100.85
	C_{13}-O_{15}	1.245	1.271	1.308	A(15,17, 12)	099.65	103.97	089.70
Cyclohexane	C_{12}-H_{17}	1.181	1.575	2.040	A(17,12,13)	080.97	065.52	058.62
	C_{12}-C_{13}	1.493	1.460	1.445	A(12,13,15)	107.84	107.64	110.56
	H_{17}-O_{15}	1.694	1.234	0.990	A(13,15,17)	071.33	082.63	101.03
	C_{13}-O_{15}	1.246	1.273	1.307	A(15,17,12)	099.45	104.91	089.71
Carbon tetrachloride	C_{12}-H_{17}	1.180	1.574	2.040	A(17,12,13)	081.02	065.55	058.62
	C_{12}-C_{13}	1.493	1.460	1.445	A(12,13,15)	107.82	107.61	110.52
	H_{17}-O_{15}	1.694	1.234	0.990	A(13,15,17)	071.32	082.61	101.05
	C_{13}-O_{15}	1.246	1.273	1.306	A(15,17,12)	099.44	104.10	089.72
Methanol	C_{12}-H_{17}	1.174	1.563	2.033	A(17,12,13)	081.53	065.87	058.84
	C_{12}-C_{13}	1.493	1.480	1.449	A(12,13,15)	107.59	107.34	110.05
	H_{17}-O_{15}	1.703	1.241	0.989	A(13,15,17)	071.21	082.36	101.22
	C_{13}-O_{15}	1.249	1.274	1.305	A(15,17,12)	099.13	104.24	089.77
Water	C_{12}-H_{17}	1.174	1.563	2.033	A(17,12,13)	081.56	065.89	058.85
	C_{12}-C_{13}	1.492	1.480	1.448	A(12,13,15)	107.58	107.32	110.03
	H_{17}-O_{15}	1.704	1.241	0.989	A(13,15,17)	071.20	082.34	101.22
	C_{13}-O_{15}	1.249	1.274	1.305	A(15,17,12)	099.12	104.24	089.79

For numbering of atoms, see Fig. 1, Bond angles in degrees, bond distances in Angstrom.

Energies of Keto, Enol, and transition state

The relative energies of the 3-phenyl-2,4-pentanedione as depicted in Fig. 2 were calculated from the total energy difference between transition states and the Keto- forms, and the data were summarized in Table 2 for all given phases. The results revealed that relative energies of the transition state for Keto were found to be 30.61, 30.82, 30.84, 31.23, and 31.26 kcal mol^{-1} in the gaseous phase, cyclohexane, carbon tetrachloride, methanol, and water, respectively. Similarly, the total electronics energy differences between the two tautomers were -17.89, -17.34, -17.27, -16.55, and -16.50 kcal mol^{-1} in the gaseous phase, cyclohexane, carbon tetrachloride, methanol, and water, respectively. From these results, we obtained that in the gas and solution phases, the Keto-form is more stable than Enol-form, since IPT reaction between the two tautomers has a similar attitude. Furthermore, Fig. 2b shows increases of the barrier height on going from the gas phase to cyclohexane to carbon tetrachloride to methanol to water phase. These trends can be explained by the internal proton transfer reaction barriers being decreased as accordance with a decrease in the dipole moment of the solvents used. Therefore, in a polar protic solvent like water and alcohol, the lone pairs are involved in hydrogen bonding with the solvent which makes them less available to hydrogen bond in the Enol form. This is also in good agreement with reported literature on the effect of the solvent polarity on the keto form stability in the polar fluids where the Keto-form has larger dipole-moment was more favorable one[31]. The relative stability of keto form relative to enol one was found to be exist regardless of the solvent used[32]. On the other hand, the size of the substituent group in beta diketone increases[33], and the equilibrium shifts to favor of the keto tautomer due to steric hindrance of the phenyl-group attached on third-carbon of 2,4-pentanedione. Steric hindrance of bulky groups was reported to be the force of driving able to shift from the more common Keto-Enol tautomers to the β-beta-diketo[34]. According to the valence bond theory(VBT), the interaction between the lone pair of electrons of carbonyl oxygen as an acceptor-atom and the C-H orbital is responsible for proton transfer(PT). Therefore, the angle carbon hydrogen oxygen (C-H…O) and, the distance oxygen hydrogen(O…H) may be play an important role in the proton-transfer reactions.

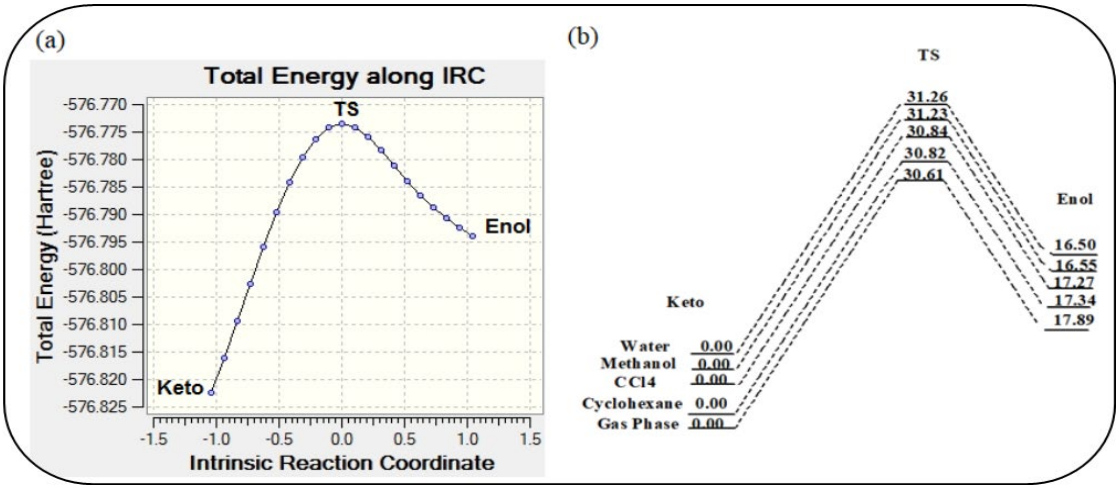


Fig. 2(a). Analysis of Intrinsic Reaction Coordinate (IRC) of four membered ring transition state of IPT, (b) Energy diagram of the proton-transfer process in different solvents and gaseous phase of 3-phenyl-2,4-pentanedione working with b3lyp/6-31+g(d)methods

Table 2: Total Electronic Energies (E, in Hartrees) of the 3-phenyl-2,4-pentanedione structural forms in the Gaseous Phase and Solutions at 298 K temperature and 1 atm pressure

	$E_{Gas\ phase}$	$E_{Cyclohexane}$	$E_{Carbon\ tetrachloride}$	$E_{Methanol}$	E_{Water}
Enol	-576.7938	-576.7995	-576.8002	-576.8086	-576.8091
Transition state	-576.7735	-576.7780	-576.7786	-576.7852	-576.7856
Keto	-576.8223	-576.8272	-576.8277	-576.8350	-576.8354

Table 3: Solvation Energies $\Delta E_S = E_{solv} - E_{gas}$ in kcal/mol of the 3-phenyl-2,4-pentanedione

	$E_{Cyclohexane}$	$E_{Carbon\ tetrachloride}$	$E_{Methanol}$	E_{Water}
Enol	-3.597	-4.039	-9.303	-9.618
Transition state	-2.839	-3.183	-7.337	-7.580
Keto	-3.045	-3.415	-7.956	-8.224

To further explain the stability of the keto tautomer in different solvents the bond angles were used. The results revealed that angles (12, 17, 15) are 99.65°, 99.45°, 99.44°, 99.13°, and 99.12° in the gaseous phase, cyclohexane, carbon tetrachloride, methanol, and water solutions, respectively. The hydrogen bond lengths of Keto-tautomer H_{17}.... O_{15} are 1.688 Å, 1.694 Å, 1.694 Å, 1.703 Å and 1.704 Å in the gas phase, cyclohexane, carbon tetrachloride, methanol, and water solutions, respectively. We conclude that the hydrogen bond is most alike in all phases and therefore it is suitable to see almost the same energy barrier internal proton transfer reaction process in all phases. This can be interpreted as was reported in the literature that an intramolecularly H-bonded keto structure highly predominates among pyruvic acid isomers. Moreover, in a similar study, it was found that the transition states of the tautomerism between the keto-enol form were 4-membered ring conformations and the keto form was more stable[30]. The finding in this study agrees with what has been mentioned before for neutral system, the Enol-form is less stable than the Keto-form[35,36].

CONCLUSION

We have studied the keto-enol tautomerisation reaction of 3-phenyl-2,4-pentanedione by the density functional theory method in gas phase as well as in different solvents. We found that the total electronics energies differences between the keto and enol are -17.89, -17.34, -17.27, -16.55, and -16.50 kcal mol^{-1} in the gase phase, cyclohexane, carbon tetrachloride, methanol, and water, respectively. Therefore, the Keto-form is more stable than the enol form in the gase phase and solution using b3lyp/6-31+d(d) levels of theory. The internal proton transfer reaction process between Enol-tautomers and Keto-tautomers follows almost similar way in gase phase and solutions. As a result of that, the internal proton transfer reaction barrier process is decreases with the decrease in the dipole moment of the solvent used. Furthermore, the size of substituent group in beta diketone increases, and the equilibrium shifts would favor the keto tautomer because of the steric hindrance of the phenyl group attached to the third carbon in 2,4-pentanedione.

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Conflict of interest

The author declares that we have no conflict of interest.

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