

Full Length Research Paper

DFT study of solvent effects on tautomerization of 4-(2-thiazolylazo)-resorcinol

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Here, the structural parameters of the enol and keto tautomers of the 4-(2-thiazolylazo)-resorcinol (TAR) were determinate. Also, tautomerization mechanism of the TAR was investigated, employing density functional theory and the polarizable continuum model (PCM). In addition to the gas phase calculations, the tautomerization mechanism of the TAR was investigated in the chloroform and dimethyl sulfoxide (DMSO) solutions for analysis of the solvent effects. More polar solvent results in higher activation energy for the keto-enol tautomerization, and larger amount of keto tautomer than the enol.

Key words: Density functional theory (DFT), 4-(2-thiazolylazo)-resorcinol, enol-keto tautomerism, polarizable continuum model (PCM), mechanism, solvent effects.

INTRODUCTION

For high sensitivity and selectivity, thiazolylazo compounds have attracted much attention as analytical reagents. The resorcinol-based dyes have been used for determination of many transition metals spectrophotometrically (Visser et al., 2000; Wen-Bin and Li-Zhong, 1985; Karipcin et al., 2009).

4-(2-thiazolylazo)-resorcinol (TAR) is a well-known chelating reagent in spectrophotometric determination and separation of metal ions (Ghasemi and Hashemi, 2011; Karipcin et al., 2009; Singh and Mishra, 2010; Soylak and Yilmaz, 2010) and acid-base titrations as an indicator (Ueno et al., 1992).

Theoretical investigations have much applicability in many areas of the chemistry, such as kinetics and mechanism investigations of the reactions, spectroscopic assignments, characterization of the molecular structures, etc., (Beyramabadi et al., 2008, 2009, 2011; Beyramabadi and Morsali, 2011; Chowdhury et al., 2010; Eshtiagh-Hosseini et al., 2010; Khaleghian et al., 2011; Pishkar et al., 2010; Wang et al., 2008).

Here, we have theoretically investigated the tautomerization mechanism of the TAR "in the gas phase chloroform and DMSO solutions". Also, the geometrical

structures and energy contents of the TAR conformers have been investigated.

THEORETICAL METHODS

All calculations have been performed by using the B3LYP hybrid functional (Lee et al., 1988) and the 6-311+G(d,p) basis set. The Gaussian 98 software package (Frisch et al., 1998) was employed. First, all degrees of freedom for all geometries were optimized. The optimized geometries were confirmed to have no imaginary frequency of the Hessian.

The frequency calculations were performed at the same computational level to the evaluation of the zero-point energies and the Gibbs free energies. The polarizable continuum model (PCM) (Tomasi and Cammi, 1995) has been employed for considering of solvent effects. The gas phase optimized geometries were used to apply the solvent effects in chloroform and DMSO as solvents.

RESULTS AND DISCUSSION

Geometries optimization

The TAR ligand could exist as two different conformers, the enol and keto, which their optimized geometries are shown in Figure 1. Some of the calculated structural parameters are gathered in Table 1. The calculated structural parameters are in good agreement with the corresponding values reported for similar compounds

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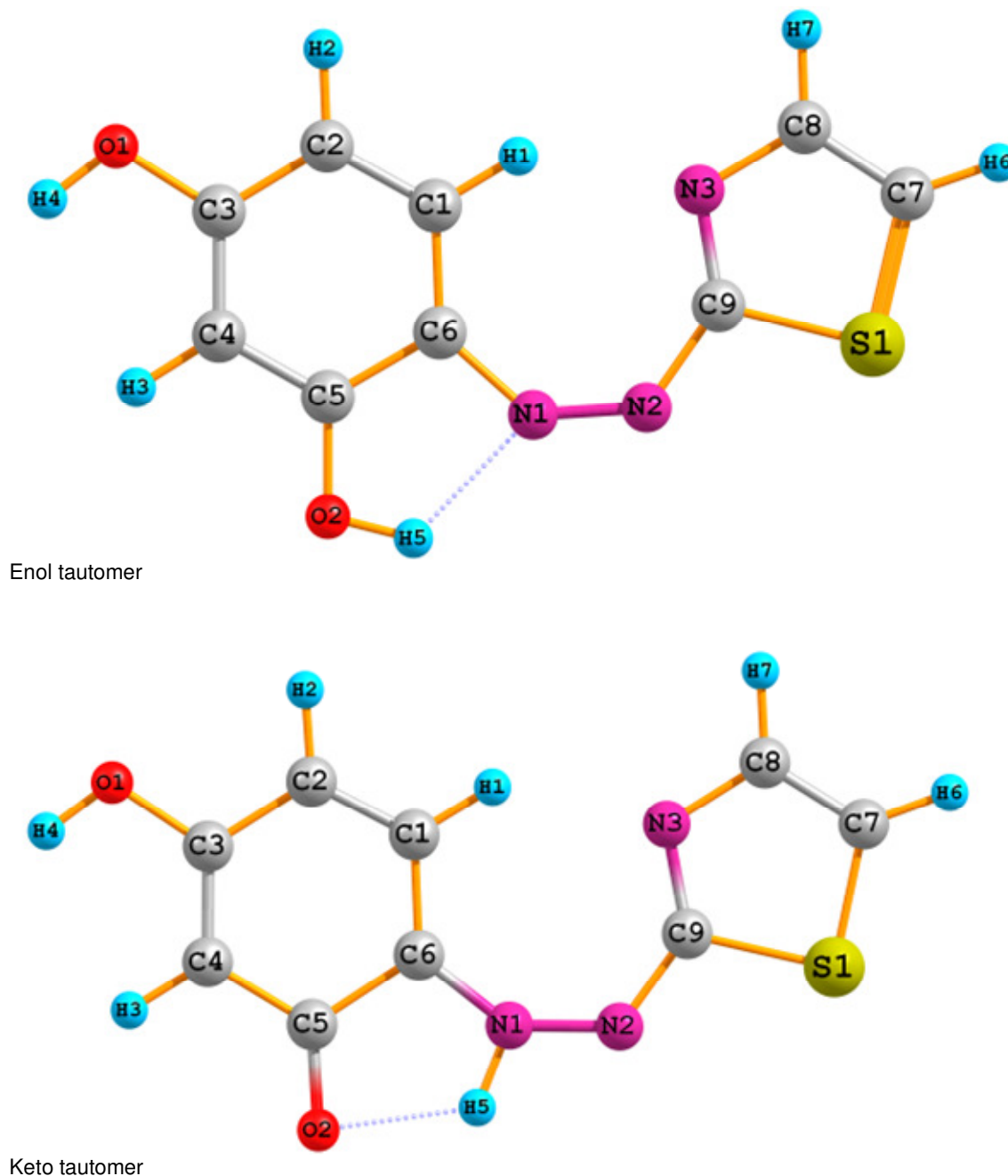


Figure 1. The optimized structures of the enol and keto tautomers of the TAR.

(Shepherd, 2003; Singh and Mishra, 2010; Soylak and Yilmaz, 2010).

The calculated dihedral angles demonstrate that both the keto and enol tautomers are planar. The intramolecular-hydrogen bond generates a five-membered ring in both the keto and enol tautomers. The intramolecular H-bonding is between O-H donor and imine N1 acceptor of the enol tautomer, but in the case of the keto tautomer, this interaction is between N-H donor

and phenolic O2 acceptor, where the hydrogen-bond lengths are about 1.9 Å. Therefore, the H-bonding interaction is relatively strong, which leads to a O2-N1 distance of about 2.56 Å. The calculated D-H5...A hydrogen-bond angles in the keto and enol tautomers are 119.91 and 119.37°, respectively.

The keto and enol tautomers could be converted to each other via an intramolecular proton transfer (IPT) reaction. Some of structural parameters of the enol

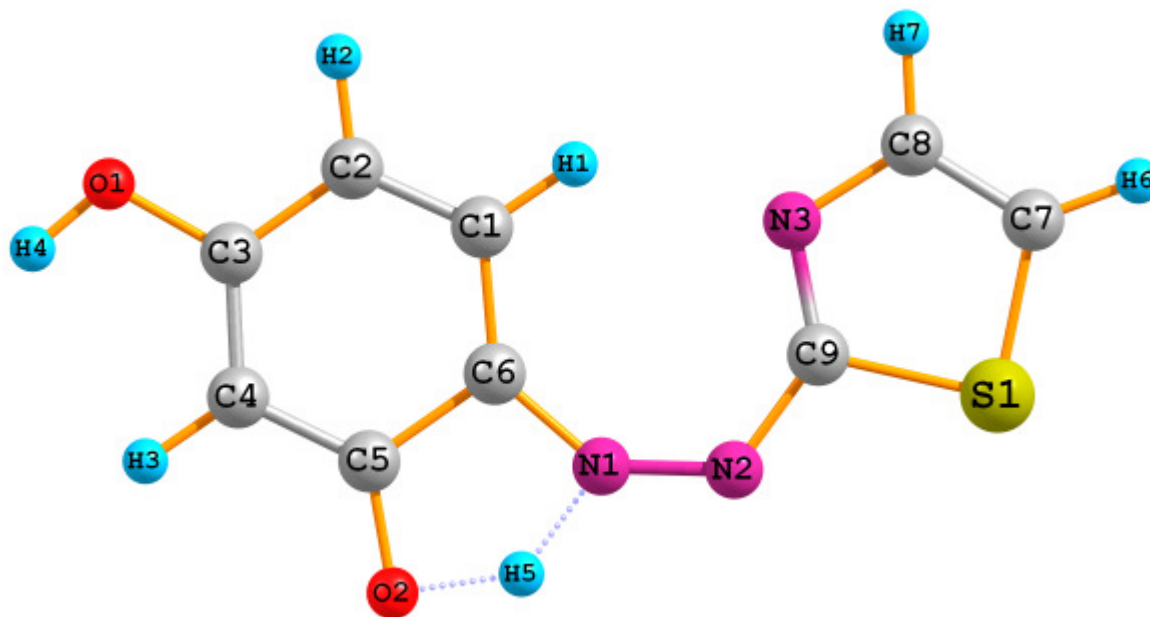


Figure 2. The optimized structure of the transition state (TS) of the enol-keto tautomerization.

form change in the enol \rightarrow keto IPT, the most important of which are: the C2-O1 bond length decreases from 1.3372 in the Enol form to 1.2429 Å in the keto form.

Solvent effects on the tautomerization

The tautomerization mechanism of the TAR ligand has been theoretically investigated in the gas phase, chloroform and DMSO solutions. In the gas phase, geometry of the transition state for the tautomerization reaction (TS) has been fully optimized, which is shown in Figure 2.

The obtained structure for the TS is planar (Table 1). Breaking of the O2-H5 bond together with formation of the N1-H5 bond are occurring in the optimized structure of TS.

The energy contents for the Enol-Keto tautomers and TS species were computed in the gas phase and solution (chloroform and DMSO). Obviously, the solvent molecules play an important role in chemical reactions. Here, the solvent effects were calculated by handling the PCM model, which is widely used for investigation of the solute-solvent interactions (Beyramabadi et al., 2008, 2009; Chowdhury et al., 2010).

In the gas phase, the enol tautomer is more stable than the keto one by 0.74 kcal/mol. However, considering the solvent effects prefers the keto tautomer in both the DMSO and chloroform solutions by 1.70 and 1.25 kcal/mol, respectively.

The solvation stabilizes all the species. The dipole moment increases during the enol to keto tautomerization.

Obviously, larger dipole moment leads to larger stabilization in solution phase. Moreover, the solvent with larger dielectric constant results in larger stabilization energy for the polar species. The computed dipole moments for the enol, keto and TS species are 4.17, 4.89 and 3.14 D, respectively. Hence, order of solvation energies is keto > enol > TS. Also, the stabilizing effect of the DMSO ($\epsilon = 46.7$) will be greater than the chloroform ($\epsilon = 4.9$). The solvent effects result in an exothermic enol \rightarrow keto tautomerization reaction in both DMSO and chloroform solvents.

The TS has lower dipole moment than both the enol and keto tautomers, which results in higher barrier energy in the polar solvents than the gas phase. Because of more polarity, the E_a is greater for DMSO than the chloroform solution. "In the gas phase chloroform solution and DMSO solution", the calculated E_a s for the keto \rightarrow enol tautomerism are 4.88, 7.35 and 8.52 kcal/mol, respectively.

Considering the equilibrium between the enol and keto tautomers, the value of the tautomeric equilibrium constant (K) is calculated by using:

$$K = \exp\left(-\frac{\Delta G}{RT}\right) \quad (1)$$

where ΔG , R and T are the Gibbs free energy difference between the keto and enol tautomers, the gas constant and temperature, respectively (Beyramabadi et al., 2008). In both the chloroform and DMSO solutions, the ΔG s are in favor of the keto tautomer by 1.34 and 1.83 kcal/mol,

Table 1. Selected theoretical structural parameters for the keto and enol tautomers of TAR and transition state (TS) of tautomerization.

Parameter	E form	K form	TS
Bond length (Å)			
O1-C3	1.3569	1.3567	1.3549
C5-C6	1.4382	1.5009	1.4716
C6-N1	1.3829	1.3498	1.3584
N1-N2	1.2693	1.3011	1.2779
N2-C9	1.3863	1.3546	1.3701
C9-N3	1.3110	1.3155	1.3128
C7-C8	1.3700	1.3690	1.3698
C7-S1	1.7195	1.7240	1.7222
C5-O2	1.3372	1.2429	1.2868
O2-H5	0.9841	1.8901	1.2550
H5-N1	1.9190	1.0362	1.2898
O2-N1	2.5563	2.5626	2.5595
Angle (°)			
C1-C2-C3	120.06	120.73	120.51
H5-O2-C5	104.17	85.35	91.59
C1-C6-N1	133.36	130.25	135.81
N1-N2-C9	129.07	125.45	124.64
N2-C9-N3	135.23	133.39	132.84
N2-C9-S1	111.40	113.15	113.41
C9-S1-C7	89.04	88.80	88.78
C7-C8-N3	116.01	116.31	116.15
Dihedral angle (°)			
H5-O2-C5-C6	-0.00	0.00	0.00
C1-C2-C4-C5	0.00	0.00	0.00
O2-C5-C6-N1	0.00	0.01	0.01
C6-N1-N2-C9	-0.02	-0.01	-0.02
N2-C9-S1-C7	180.00	179.99	179.97
S1-C7-C8-N3	-0.01	0.01	0.04
N1-H5-O2-C5	0.00	-0.01	-0.11
C7-C9-C1-C4	179.99	-179.99	179.99
C3-C6-N3-S1	179.99	179.98	-179.98

respectively. Using the Equation 1, the percentage of the enol form in the chloroform and DMSO solutions are 10.42 and 4.55%, respectively.

Conclusions

The TAR could undergo enol-keto tautomerization. In this work, structural parameters and energetic characters of both the enol and keto tautomers of the TAR as well as its tautomerization mechanism have been theoretically studied in the gas phase and PCM model.

The density functional theory (DFT) calculations showed

that the enol tautomer is more stable than the keto tautomer in the gas phase, while solute-solvent interactions favor the keto tautomer in polar solvents. Also, by increasing of the polarity of the solvent, stability and percentage of the keto tautomer increases in comparison with the enol tautomer. This arises from order of dipole moment for the species as keto > enol > TS. As expected, more polar solvents lead to higher barrier energy (E_a) for the tautomerization reaction of TAR. "In the gas phase chloroform solution and DMSO solution", the calculated E_a s for the keto \rightarrow enol tautomerism are 4.88, 7.35 and 8.52 kcal/mol, respectively.

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