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Quantum mechanical study of water-assisted effect of intramolecular proton transfer process in silarhodanine

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ABSTRACT

The global isomeric structure in the gas phase and with water-assisted in solution is predicated at B3LYP/6-31++G** // B3LYP/6-31G* levels of theory. The free energies, enthalpies of solvation and equilibrium constants are calculated at the same level of theory. Eight local minima structures (S1-S8) and nine hydrated structures (S1.H₂O-S8.H₂O) are extracted for silarhodanine molecule. The hydration processes are lowered the stabilization energy. S5 and S5.H₂O are the global minimum in the gas phase and in water respectively. The calculations predict an important catalytic effect since the activation barrier has been decreased to 21.19 kcal/mol of hydration of S1 molecule.

Keywords: Global minimum, silarhodanine, equilibrium constant and stability.

INTRODUCTION

Prototropic tautomerism of substituted thiazolidine and oxazolidine heterocycles were studied theoretically at the B3LYP/6-311G(2d,p) level. The thermodynamic parameters for the molecules were calculated in the gas phase and in two different solvent utilizing IPCM methods. The study revealed that the same tautomer is the most stable both in gas phase and in solution (DMSO and cyclohexane) [1]. The steady state absorption and emission studies of the rhodanine derivative ((5-(dimethylaminobenzylidene) rhodanine)) have been investigated. A dual fluorescence associated with an intramolecular charge transfer (ICT) phenomenon is reported. In support of the experimental results ab initio and DFT calculations have been performed. The theoretical calculations are also indicating that the chosen compound has significant non-linear optical (NLO) properties [2]. The electron paramagnetic resonance and the nuclear magnetic resonance parameters have been investigated by quantum mechanical methods, the calculations gave good agreement with the experimental data [3-4]. The structure of rhodanine has been determined by three dimensional Fourier and least squares methods using an I.B.M electronic computer the crystal structure showed that the molecule is planar, and there are two strong N...O hydrogen bonds around the center of symmetry, binding the molecules in pairs [5]. A novel use of cluster analysis is presented to compare the output from different levels of theory. The relative energies of the tautomer of methylidene rhodanine (5-methylene-2-thioxo-thiazolidin-4-one) computed by the semiempirical molecular orbital method AM1 are remarkable similar to ab initio values which involves effective core potentials augmented by polarization and diffuse function [6]. A new series of rhodanine based on phosphodiesterase-4 inhibitors is described. The structure-activity relationship directed toward improving potency led to the development submicromolar inhibitors. The replacement of rhodanine with structurally related heterocycles was also considered [7]. Recently, we are investigated the sila- and thio- derivative of formohydroxamic acid in the same manner [8-9].

1. Computational Details

The calculations were investigated the relative stabilities of the various tautomeric forms of Silarhodanine. The DFT calculations were performed with the B3LYP three parameter density functional, which includes Becke's gradient exchange correction [10] and the Lee–Yang–Parr correlation functional [11-12]. The geometries of all conformers, products and transition states were fully optimized at the B3LYP/6-31G(d) level of theory. The zero-point vibrational energy contribution is also considered. Single-point calculations were then performed at the B3LYP/6-31++G(d,p) level for the geometries optimized at the B3LYP/6-31G(d) level. The SCF = Tight option was used in these calculations. Free energy of solvation for the conformers was calculated using SCRF keyword with Tomasi's polarized continuum (PCM) model [13]. Mon-water molecules with dielectric constant ($\epsilon=78.36$) has been used as a solvent. Calculations were carried out using Gaussian 03 program package [14].

RESULTS AND DISCUSSION

Eight local minima structures (S1-S8) and nine hydrated structures (S1.H₂O-S8.H₂O) are investigated for silarhodanine molecule. The free energy of solvation for the structures was calculated using water as a solvent. The selected optimized structures of the hydrated molecules are presented in Figure 1. The major purpose from considering solvent effect is simulation of real system and determination of the differences between the gas phase and aqueous systems.

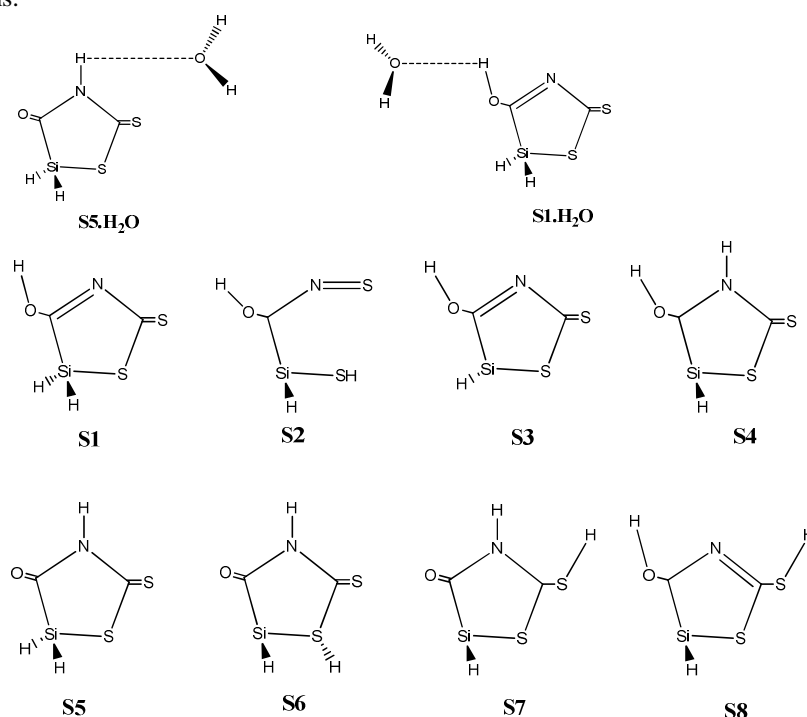


Figure 1: The eight minima structures and two hydrated molecules.

Table 1: The relative energies, enthalpies and free energies in solution.

Molecules	ΔE	ΔH	ΔG
S1.H ₂ O	16.95	19.030	8.97
S2.H ₂ O	38.59	41.60	40.35
S3.H ₂ O	32.69	33.68	30.12
S4N.H ₂ O	28.93	30.35	23.09
S4O.H ₂ O	26.23	26.28	18.574
S5.H ₂ O	0.00	0.00	0.00
S6.H ₂ O	41.48	42.902	41.54
S7.H ₂ O	27.42	28.47	28.36
S8.H ₂ O	29.43	30.56	31.69

Table 2: The enthalpies, free energies and equilibrium constants for the hydration reactions.

The reaction	ΔH	ΔG	K_{eq}
S1 + H ₂ O → S1.H ₂ O	-13.15	-4.55	2.17E+3
S2 + H ₂ O → S2.H ₂ O	-12.69	-3.42	3.21E+2
S3 + H ₂ O → S3.H ₂ O	-13.72	-4.15	1.10E+3
S4N + H ₂ O → S4N.H ₂ O	-12.06	-2.21	4.17E+1
S4O + H ₂ O → S4O.H ₂ O	-16.13	-6.35	1.07E+1
S5 + H ₂ O → S5.H ₂ O	-10.29	-0.70	3.26E0

$S6 + H_2O \rightarrow S6.H_2O$	-11.88	-1.84	2.23E+1
$S7 + H_2O \rightarrow S7.H_2O$	-13.17	-2.89	1.31E+2
$S8 + H_2O \rightarrow S8.H_2O$	-13.27	-3.12	1.94E+2

The energies, total energies, enthalpies, free energies, energies in solution, total free energy and the related energies and free energies in solution of the calculated structures are listed in Tables 1,2. The relative energies enthalpies and relative free energies of the hydrated molecules are given in Figure 2.

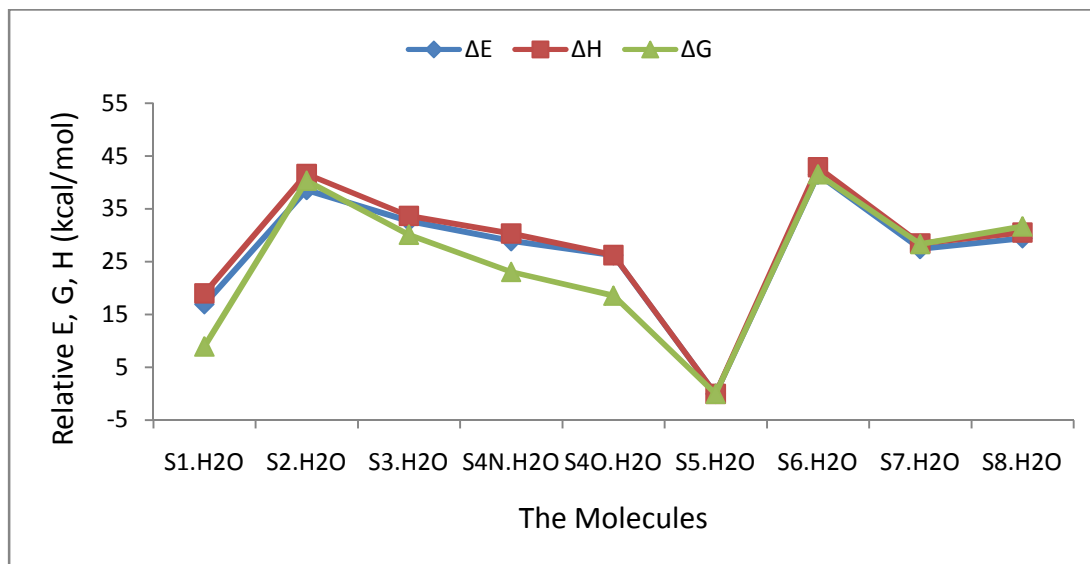


Figure 2: The Relative energies (ΔE), enthalpies (ΔH) and free energies of solvation (ΔG) for the hydration reactions.

The equilibrium constants of hydrated reactions were calculated from Gibbs free energies using $\Delta G = -RT \ln K_{eq}$. The equilibrium constant at 298.15 K of the hydration reactions are listed in Table 2, all the hydration reactions showed a high equilibrium constant values which means that the reactions at this temperature favor the products.

Table 1: The relative energies, enthalpies and free energies in solution.

Molecules	ΔE	ΔH	ΔG
S1.H ₂ O	16.95	19.030	8.97
S2.H ₂ O	38.59	41.60	40.35
S3.H ₂ O	32.69	33.68	30.12
S4N.H ₂ O	28.93	30.35	23.09
S4O.H ₂ O	26.23	26.28	18.574
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$S3 + H_2O \rightarrow S3.H_2O$	-13.72	-4.15	1.10E+3
$S4N + H_2O \rightarrow S4N.H_2O$	-12.06	-2.21	4.17E+1
$S4O + H_2O \rightarrow S4O.H_2O$	-16.13	-6.35	1.07E+1
$S5 + H_2O \rightarrow S5.H_2O$	-10.29	-0.70	3.26E0
$S6 + H_2O \rightarrow S6.H_2O$	-11.88	-1.84	2.23E+1
$S7 + H_2O \rightarrow S7.H_2O$	-13.17	-2.89	1.31E+2
$S8 + H_2O \rightarrow S8.H_2O$	-13.27	-3.12	1.94E+2

Although, the hydration process has no effect in the order of stability, the calculations predict an important catalytic effect since the activation barrier has been decreased to 21.19 kcal/mol by hydration of S1 molecule. The transition state (TS) energy has been applied for activation barrier calculation. The activation barrier S1-TS-S2 is 53.59 kcal/mol while for S1.H₂O-TS-S2.H₂O is 32.40 kcal/mol. The S1 + H₂O reaction is quantitative and has the largest value (2.17E+3). The Gibbs free energy difference (ΔG) between hydrated isomers at B3LYP/6-311++G(d,p) level of theory lie between -6.35 and -0.70 kcal/mol. From the free energies of various structures in aqueous solution it was found that the values for S5.H₂O, S6.H₂O and S4N.H₂O are -0.70, -1.84 and -2.21 kcal/mol, whereas the values

for S1.H₂O, S3.2H₂O and S2.3H₂O are -4.55, -4.15 and -3.41 kcal/mol respectively at 298.15 K and 1 atmosphere pressure. Therefore, the S5.H₂O is the not favored in aqueous solution as expected since S5 is the most stable structure. On contrast the S1 isomer is very reactive with water molecule and the formation of S1.H₂O species will be favored. The calculated enthalpies for hydration process in one water molecule is added; The S4 molecule has two sites available for binding with water molecule, one site through OH giving the S4O.H₂O and the other site through NH giving the S4N.H₂O. The enthalpy of S4O.H₂O is the lowest (-16.13 kcal/mol) Thus, hydrogen binding with water stabilized S4O.H₂O to greater extent than S4N.H₂O structure. The high stability of S5 structure is clearly detectable since the S5.H₂O molecule possessed the highest enthalpy. The enthalpies were estimated by adding the thermal corrections to the energy to account for translational, vibrational and rotational motion at 298.15 K and 1 atmosphere pressure.

REFERENCES

- [1] Tahmassebi D, *J. Mol. Struct.* **2003**, 638, 11.
- [2] Ray J, Panja N, Nandi P K, Martin J J, Jones-Jr W E, *J. Mol. Struct.* **2008**, 874, 121.
- [3] Lin J Z, Xiao P, *Der Chemica Sinica* **2012** 3(3) 527.
- [4] Babanegad S A, Ashrafi F, Ghasemi A S, Ashrafi E, *Der Chemica Sinica* **2012** 3(1) 124.
- [5] Van der Helm D, Lessor A E, Merritt-Jr L L, *Acta Cryst.* **1962**, 15, 1227.
- [6] Boyd D B, *J. Mol. Struct.* **1997**, 401, 227.
- [7] Irvin M W, Patrick G L, Kewney J, Hastings S F, MacKenzie S J, *Bioorg. Med. Chem. Lett.* **2008**, 18, 2032.
- [8] Ahmed A A, *Der Chemica Sinica* **2012** 3(4) 989.
- [9] Ahmed A A, *Der Chemica Sinica* **2012** 3(4) 884.
- [10] A. D. Becke, *Phys. Rev.*, **1988**, 38, 3098.
- [11] Lee C, Yang W, Parr R G, *Phys. Rev. B*, **1988**, 37, 785.
- [12] Miehich B, Savin A, Stoll H, Preuss H, *Chem. Phys. Lett.*, **1989**, 157, 200.
- [13] Mietrus S, Scrocco E, *J. Phys. Chem.*, **1981**, 55, 117.
- [14] Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford CT, **2004**.