

Theoretical Investigations on the π - π Stacking Interactions in Phenol-Water Complexes

Shruti Sharma, Mrinal J Bezbaruah, Ibrahim Ali, Mahasweta Choudhury, Bipul Bezbaruah*

Department of Applied Sciences, Gauhati University, Guwahati, India

Email: *bipulbezbaruah@gmail.com

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Abstract

Non covalent interactions are quite common in all kinds of π -systems, such as π - π interactions, long range/short range van der waal force of interactions, ion- π interactions etc. *Ab initio* calculations are well established and account well for the experimental long range interaction energies for small clusters of aromatic molecules and most of the calculations were carried out using the MPn methods. If a reasonably large basis set is used to calculate the stacking interaction energies for a cluster (dimer, trimer etc.) of aromatic molecules then the electron-electron correlation energy may be properly calculated. Moreover, *ab initio* calculations for aromatic π -systems show that the calculated stacking interaction energies highly depend on the basis set used and the electron correlation energy. In this investigation, the electron correlation of the stacked hydrated phenol systems has been accounted at MP2 level of calculations. We have calculated the π - π stacking interaction energies of the hydrated phenolic systems with different conformations.

Keywords

Phenol, π - π Stacking, MP2, *Ab initio*, etc.

1. Introduction

Intermolecular interactions involving aromatic rings are common in many areas of chemistry and biology. In proteins, π - π stacking has been the subject of systematic search in crystal structures, showing that aromatic side chains preferentially interact in a parallelly-displaced orientation [1]. The stacking interaction for different aromatic molecules can also be easily estimated from the extent of the dispersion forces, very short range exchange repulsion forces and electrostatic interactions among the molecules of the system, while the extent of intermolecular electron correlation between aromatic rings is the core factor for cal-

culating the dispersion forces. However, it is often found that the less accurate force field methods, and even density functional methods have been successfully applied to large molecular systems [2] [3] [4]. The T-shaped structure, shown to arise as well in biomolecules, was found from high level *ab initio* calculations to be less stable than the parallel arrangement [5]. Moreover, the *ab initio* calculations with the inclusion of correlation effect at least at the MP2/6-31G* level of theories have been found successfully in some cases. The applications of correlated *ab initio* methods are limited for small molecules, and the Moller-Plesset perturbation theory (MPn) can be used for medium size molecules [6] [7].

During the last few years, there has been a significant progress in the methods of calculating interaction energies in aromatic complexes. It has been found that stacking stabilization energies computed by MP2 methods with extended basis sets are overestimated especially for stacked structures [8] [9] [10]. Phenol is a simple aromatic system and it can directly interact with each other to form dimer, trimer etc. as similar to water molecules. For sterically hindered phenols and other phenolic systems with bulky groups, it is very difficult to calculate the π - π stacking interactions accurately. π - π stacking interactions between hydrated phenol systems have been studied as an initial step to understand the change in hydrogen bonding interactions during pi-pi stacking interaction. Recent studies on phenol-water clusters put more emphasis on the geometries of clusters and the nature of hydrogen bonds [11]-[22]. Dimitrova *et al.* had investigated the structure and the stability of the hydrogen-bonded complexes of phenol molecule with one to four water molecules by using various levels of *ab initio* theory and it revealed that for phenol complex with two, three, and four water molecules, the most stable complex was a planar phenol ring [23]. A second-order Møller-Plesset (MP2) perturbation theoretic study using interaction-optimized polarization basis set has revealed the existence of three different minima in the phenol-water complex [24]. Benoit and Clary have studied phenol-water clusters using rigid-body diffusion quantum Monte Carlo method [25] [26]. Earlier studies suggested that the interaction involved in phenol-water clusters is similar in strength to the σ -hydrogen bond [27]. *Ab initio* calculations have also been carried out for the electronic ground state and the lowest excited state of phenol and complexes of phenol with water and ammonia and the corresponding cations [28]-[40].

The latter complex is highly interesting as the structure of the dimer is characterized by two different types of non-covalent interactions: The phenol water hydrogen bonding and the stacking of two aromatic rings. The hydrogen bonding is mainly of an electrostatic origin while the aromatic stacking is mainly due to London dispersion interactions, both of which participate in determining the equilibrium structure [41]. Phenol may serve as a basic unit of larger molecules, e.g., tyrosine residues in proteins. The hydrogen-bonded phenol complexes with simple solvent molecules are important models for investigation of H-bonding and proton transfer in proteins and nucleic acids [42]. The study of ionic hy-

drogen bonded clusters involving phenol and simple molecules, such as water or ammonia, has attracted considerable attention as models for studying numerous biological and chemical processes [43] [44] [45]. In this study, we have investigated the π - π interactions of hydrated phenol systems with different conformations in gas and aqueous phase.

2. Computational Methodology

The most effective method for studying the non-covalent long range interactions of simple aromatic systems is the *ab initio* method. The study of π - π stacking interactions has now become much easier due to the quantum mechanical theoretical calculations. The interaction energies for the hydrated phenol systems have been calculated by using Gaussian09 program, using MP2 level of theories and all the hydrated phenol systems have been optimized with the basis set 6-311++G(d,p) (Figure 1). These calculations are useful for small clusters of molecules as these explain the binding energies of the smaller molecules in a much effective way. However, the *ab initio* calculations for studying the π - π stacking interaction energies highly depend on the electron correlation energy of the molecules and the type of basis set used for calculation. So, the various levels of theories and basis sets have been carefully chosen to calculate the interaction energies of the non-covalent type of interactions and aromatic π - π stacking, which are primarily responsible for stabilization of different π -systems.

All the optimized geometries are used for constructing the stacked models of hydrated phenol systems using JoinMolecule package of software. Arguslab/GaussView was also used to visualize and observe the different stacked models. The completely optimized geometries of hydrated phenol systems were taken for calculating the single point energies with MP2/6-311G++(d,p) basis set. Phenol water complexes may directly stack with one another either in eclipsed conformation or staggered conformation. The eclipsed conformation of phenol-water complex shows exact sandwich form at a dihedral angle of 0° . On the other hand, the staggered conformation for phenol-water complex may suitably stacked at different dihedral angles, preferably 60° , 120° and 180° .

The individual models in a stacked conformation are separated at a fixed vertical separation of 3.6 \AA , as among all the vertical separation ranging from 2.8 to 3.6 \AA , between the constructed models, 3.6 \AA shows the most favorable conformations of hydrated phenol systems.

Similarly, for all the stacked models, the single point calculations have also been performed. The eclipsed and the staggered forms with different dihedral angles have been taken for constructing various stacked models of hydrated phenol system by shifting one hydrated phenol ring horizontally along the plane of the other. The interaction energies are computed from the following equation:

$$\text{Interaction energy} = E_{\text{stacked}} - 2E_{\text{single}}$$

here, E_{stacked} = Energy of the stacked model and E_{single} = Energy of the single molecule. All the calculations were carried out with Gaussian 09 program code [45].

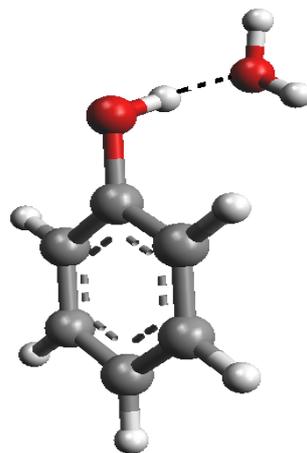


Figure 1. Optimized models of hydrated phenol.

3. Result and Discussion

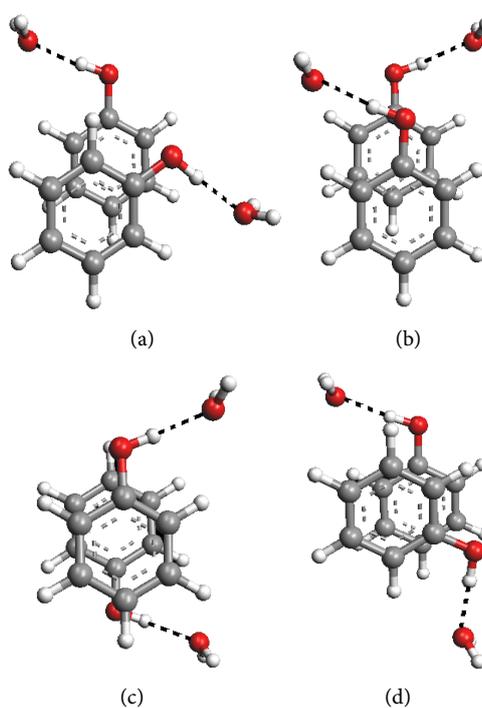
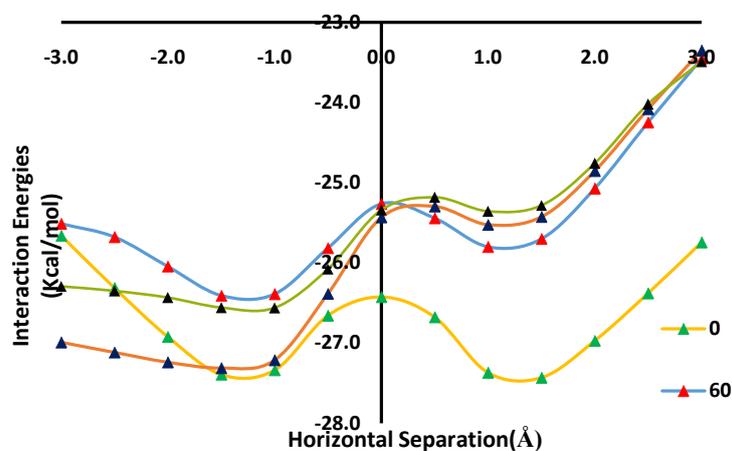
In this research work, the non-covalent π - π stacking interactions of water assisted phenolic dimers have been studied for different conformations in gas phase and aqueous phase. All the conformations for phenol water stacked systems were prepared with different dihedral angles— 0° , 60° , 120° and 180° . The eclipsed conformation, with dihedral angle 0° was prepared by placing one phenol ring parallelly over the other ring with an internal separation of 3.6 \AA . Then one water assisted phenol ring has been horizontally shifted along either X, Y or Z-axis (from positive to negative direction), keeping the other ring at constant position, to get the most favored minimized stacked model. In this case, the horizontal shifting for the stacked model was investigated along X-axis from -3 to $+3 \text{ \AA}$. Similarly, all the staggered conformations for the stacked models of phenol water systems were also prepared with dihedral angles 60° , 120° and 180° respectively.

The relative changes for the π - π stacking interaction energies in gas phase, with MP2 methods for different stacked hydrated phenol conformations are shown in **Table 1** and certain stable structures are located from the local minima in the potential energy curves shown in **Figure 2** and **Figure 3**. The intermolecular separation between the stacked models plays an important role in the calculation of effective π - π stacking interaction energy. The results of MP2 level of theories reflect the extent of dispersion energies accounted in all these calculations. Indeed, the electron correlations included in MP2 level with diffused function in the basis set could estimate more negative stacking energies, where the increase of diffuse function in the basis set provides little change in the energy values.

Among all the stacked models of hydrated phenol systems, it has been observed that the stacking interaction energies of stacked hydrated phenol model with an eclipsed conformation (with dihedral angle = 0°) is found to have the most negative value ($-27.4314 \text{ kcal/mol}$) (**Table 1**). The more negative stacking

Table 1. Stacking Interaction Energies for minimized stacked models of hydrated phenol systems (Basis set MP2/6-311++G(d,p)).

Phenol-Water System	Interaction Energies (Kcal/mol) for Eclipsed and Staggered conformations (<i>At</i> 298 K)			
	0°	60°	120°	180°
Gas Phase	-27.4314	-26.4084	-27.3121	-26.5610
Aqueous Phase	-24.4211	-24.4787	-25.3121	-24.6658

**Figure 2.** Minimized stacked models of hydrated phenol systems (a) eclipsed (0°); (b) staggered (60°); (c) staggered (120°) and (d) staggered (180°) conformations.**Figure 3.** Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of hydrated phenol (in gas phase) for the basis set 6-311++G(d,p).

interaction energy values represent the most stable conformation and effective calculation of electron-electron correlation and dispersion forces. On the other hand, the π - π stacking interaction energy for the staggered conformation with dihedral angle 120° is found to be -27.3121 kcal/mol (Table 1). Figure 2 shows the minimized stacked models for all the hydrated phenol systems with different dihedral angles. The computed stacking energies of optimum structures with various levels of calculations in gas phase are summarized in Table 1.

Above studies for hydrated phenol stacking interactions, show effective π - π interaction and they are quite well stacked at a dihedral angle of 0° and 120° . In gas phase at 0° dihedral angle the minimized energy shows the most negative value (-27.4314 kcal/mol) at a horizontal shifting of -1.5 Å, it is because of the water molecules of one phenol are far apart from the other which shows minimum electron-electron repulsion, but without any horizontal shifting (at 0 Å) it show maximum repulsion. On the other hand, at 120° dihedral angle, the minimized stacked model shows more negative value (-27.3121 kcal/mol) at a horizontal shifting of -1.5 Å which represents the minimum repulsion between the phenol water stacked model. However, towards the positive horizontal shifting, the repulsive forces are maximum and therefore they show less negative values. Similar investigations were also done for stacked hydrated phenol systems with dihedral angle of 60° and 180° . These models shows almost same results and they are less stable as compared to the 0° and 120° dihedral angle. We also computed the Mulliken Charges for both gas phase and aqueous phase for minimized stacked models as well as the unstacked phenol system to compare the change in electron charge density of phenol ring. Since, the electron charge density is greatly affected by the -OH group of the phenol ring both in staked and unstacked models, hence we have investigated the variations of Mulliken charges only for the -OH group (Table 2 and Table 3).

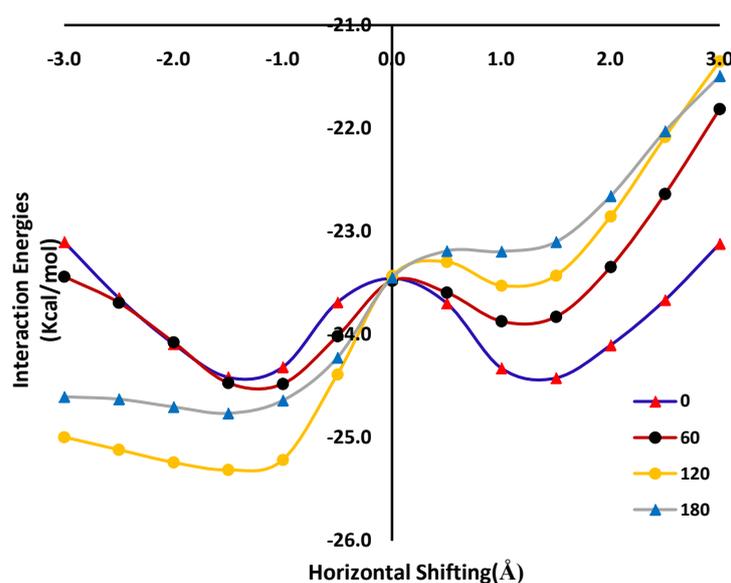
It also gives an idea about how effectively it shows the π - π stacking interaction. Although, we have done our calculations for π - π stacking interaction both in gas and aqueous phase, but the results reveal that no such major changes have been found in the stability of the stacked models for hydrated phenol as shown in the plots Figure 3 and Figure 4.

Table 2. Mulliken Charges of hydrated phenol systems in gas phase.

System	Conformation	Mulliken Charges			
		Group	Atoms	Unstacked	Stacked
HYDRATED PHENOL	Eclipsed (0°)	-OH	O	-0.3376	-0.3025
			H	0.2834	0.2939
	Staggered (60°)	-OH	O	-0.3376	-0.3025
			H	0.2834	0.2939
	Staggered (120°)	-OH	O	-0.3376	-0.3025
			H	0.2834	0.2939
	Staggered (180°)	-OH	O	-0.3376	-0.3025
			H	0.2834	0.2939

Table 3. Mulliken Charges of hydrated phenol systems in aqueous phase.

System	Conformation	Mulliken Charges			
		Group	Atoms	Unstacked	Stacked
HYDRATED PHENOL	Eclipsed (0°)	-OH	O	-0.3269	-0.2965
			H	0.2768	0.2854
	Staggered (60°)	-OH	O	-0.3269	-0.2965
			H	0.2768	0.2854
	Staggered (120°)	-OH	O	-0.3269	-0.2965
			H	0.2768	0.2854
	Staggered (180°)	-OH	O	-0.3269	-0.2965
			H	0.2768	0.2854

**Figure 4.** Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of hydrated phenol (in aqueous phase) for the basis set 6-311++ G(d,p).

4. Conclusion

Among the different stacked hydrated phenol systems, it has been observed that minimized π - π stacking interaction energy of the eclipsed conformation (dihedral angle 0°) gives more negative interaction energy values as shown in **Table 1** and **Table 2**. It has been observed that most of the phenolic systems give effective π - π stacking interaction (since all the stacked models give negative stacking interaction energies). Although, some phenolic systems are not always structurally symmetric, but they show effective π - π stacking between aromatic phenol rings. Therefore, in hydrated phenolic system, eclipsed conformation (dihedral angle = 0°) of stacked models show better π - π stacking interaction than that of other staggered (dihedral angle 60°, 120° and 180°) models and it happens due to less repulsive forces. Again, among all the staggered models, stacking models with dihedral angle 120° shows better π - π stacking interaction.

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