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Quantum Mechanical Studies on the π-π Stacking Interactions of Aniline and Water-assisted Aniline in Gas and Aqueous Phases

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The quantum mechanical study of weak interactions such as π-π stacking interactions of aromatic molecules has been an important aspect, since high level methods have limitations for application to large molecules. The differences in the stacking energies of various aromatic molecular structures are found quite significant. It has also been found significant for identifying the most favoured stacked models of aniline and some of the substituted aniline molecules. There observed a remarkable change in interaction energies for both gas and solvent phases for the same stacked models. The effect of basis set in the stacking energies of the second order Møller-Plesset perturbation method (MP2) calculations is very small. The moderately accurate calculations, MP2 level of theories were found feasible for most of the simple aromatic systems such as benzene, pyridine, aniline etc. In our study, the investigation was on the π-π stacking interaction energies for stacked models of aniline and water-assisted aniline systems both in gas and aqueous phases.

Key words: Aniline, water, π-π stacking, interaction energy, MP2 method

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Computational Chemistry encompasses a growing number of fields and corresponding techniques. The traditional techniques for stationary-state quantum chemistry and equilibrium Monte Carlo [1] and Molecular Dynamics [2] are being expanded with Quantum Monte Carlo: Quantum Molecular Dynamics' Microdynamics [3] but also by research and computer programs on database, interactive animation, artificial intelligence and chemical knowledge processing [4]. Aromatic stacking interactions play an important role in chemistry and biology [5, 6]. They are fundamental for the geometric characteristics and stabilization energy of DNA molecules, the crystal packing of aromatic molecules, the formation of the tertiary structure of proteins, the control in the enzyme-nucleic acids recognition in regulating gene expression, intercalation of drugs into DNA, and so on. For that reason, the stacking interactions were, and still are, the subject of numerous works, with stacking in benzene dimers has been widely studied as a prototype of these interactions [6-8]. Stacking interactions play a significant role in the outcomes of stereoselectivity in synthetic organic reactions [9-10]. Not surprisingly, there has been widespread interest in the magnitude and origin of the interactions [2-5, 11-14]. Recently, experimental studies were reported which aimed at an energetic quantification and an improved understanding of non-covalent interactions involving aromatic rings [15-16]. Non-covalent or π-π interaction in aromatic systems is believed to play a vital role in stabilizing various complex chemical species [17]. In the field of medicinal chemistry, a lot of research work has been done in protein-protein, π-π stacking interactions etc., which also puts an emphasis on stacking interaction of aniline and water-assisted aniline systems [18]. C. Zhai *et al.* studied the interactions between -NH_2 group and H_2O molecule using experimental techniques, density functional theory (DFT) and atoms in molecules (AIM) analysis. Quantum chemistry calculations and AIM analysis further confirmed the existence of hydrogen bonding between H_2O molecules and the amide group [19]. In industrial chemistry, it has been observed that aniline systems show characteristic absorption phenomena among different gases. Dry aniline and water-assisted aniline systems play a major role in absorption due to the change in acid/base behaviour of the molecules [20]. Therefore, quantum mechanical study of π-π stacking in aniline and water-assisted aniline systems is an important aspect of research. In this work we compare the stacking energy afforded by *ab initio* methods, used to describe stacked complexes. Here, it has been investigated to study the different stacking interaction energies and the effect of change in conformation for pure and water-assisted aniline systems.

EXPERIMENTAL

Computational Method in our investigation

All the optimizations and single point calculations were carried out by using MP2 levels of theories with 6-

311++G(d,p) basis set in Gaussian 09. In the basis set 6-311++G(d,p), 6 represents the number of Gaussian functions (G) summed to describe the inner shell orbitals, 3 represents the number of Gaussian functions that comprise of the first Slater type orbital (STO) of first zeta and 1 and 1 are the number of Gaussian functions summed in the second and third STO respectively. It is supplemented by diffuse functions (++); 1 set of d function on heavy atoms and 1 set of p function on hydrogen [21-23]. The most favoured optimized and stable structures obtained from various methods are almost similar, and also comparable with that of more accurate Coupled Cluster single-double (triplet) method (CCSD(T)), but not exactly equal. The effect of basis set in the stacking energies of MP2 calculations is small. Nevertheless, the size of stacking complexes is usually large, and it is not practical to employ high level *ab initio* calculations to study them. Even, MP2 calculations are not always adequate to describe this kind of systems, as they usually overestimate complex stability.

Ab initio calculations have been shown useful for studying the non-bonded interactions of aromatic molecules [11-14, 24-26]. The various levels of theories and basis sets have been carefully chosen to calculate the interaction energies of aromatic π-π stacking and non-bonding, the types of interactions that are responsible for the stabilization of nucleobases. It is evident that the studies of molecular stacking require high level *ab initio* calculations. Many theoretical studies are reported to predict the preferred stacking interactions of benzene dimers, and thereby provoking the importance of dipole-dipole and quadrupole-quadrupole interactions [25-29]. Similar studies on the intermolecular interactions of cytosine dimers have been calculated with MP2/6-311++G(d,p) level. Comparison of different levels of theories used in certain investigations clearly indicates the choice of reasonably accurate methods that include proper basis set as well as electron correlation in the calculations. As we know, the London dispersion force is the instrumental binding of stacked molecules, which is not described by Hartree-Fock (HF) theory [6, 30-31]. Therefore, the correlated descriptions of electrons are a must to produce even a qualitatively accurate picture of weakly interacted molecules. It should be noted that several newly developed functional have shown to provide acceptable results for this type of intermolecular interactions [32-34].

However, this method is still rather expensive for large molecules, and it can only be feasibly applied to small molecules such as benzene dimers and its substituted dimers. The computational cost required for larger molecules does not permit the application of accurate *ab initio* methods. As we know that the interaction energies obtained from HF calculation include columbic, induction, exchange and some electron correlation energies, the intermolecular electron correlation necessary for the stabilization of these stacked molecules cannot be calculated with this method. However, the interaction energies obtained from this method may be taken for comparison with the MP2 results. The present studies focus on how the interaction energies can be improved with the inclusion of diffused functions in MP2 level of calculations. Our results showed that the interaction energies did not considerably vary with the inclusion of more diffuse functions in the basis set. The interaction energies obtained from MP2/6-311++G(d,p) calculations were found to be much better than any other computational methods [35].

Calculation of Interaction Energies

The interaction energies for the stacked models are computed from the following equation [36].

$$\textbf{Interaction energies} = \mathbf{E_{ST} - 2E_M}$$

Here, E_{ST} and E_M are the energies of stacked model and monomer. All the calculations are carried out with Gaussian 09 program code [37].

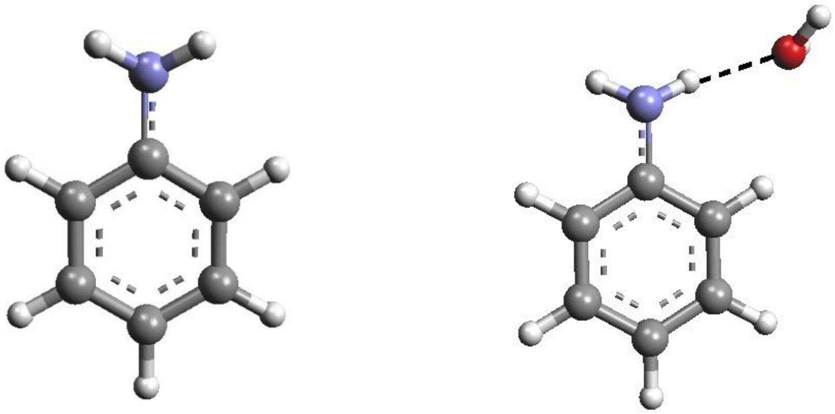


Figure 1. Optimized model of free and water-assisted (hydrated) aniline systems.

RESULTS AND DISCUSSION

In this research work, the π-π stacking interactions of pure aniline and water-assisted aniline dimers have been studied for different conformations in gas phase as well as in aqueous phase. First of all aniline and water-assisted aniline molecules were optimized by using Gaussian 09 (Figure 1). All the conformations for aniline and water-assisted aniline stacked systems were prepared with different dihedral angles: 0˚, 60˚, 120˚ and 180˚ (Figure 2-3). The eclipsed conformation, with dihedral angle 0˚ was prepared by placing one aniline ring parallel over the other ring with an internal separation of 3.6Å. Then, one aniline ring was horizontally shifted along either X, Y, or Z-axis (from positive to negative direction), keeping the other ring at a constant position, to get the most favoured minimized stacked model. In this case, the horizontal shifting for the stacked model was investigated along X-axis from -3 to +3Å. Similarly, all the staggered conformations for the stacked models of aniline systems were also prepared with dihedral angles 60˚, 120˚ and 180˚.

From the Interaction Energy plot (Interaction Energy vs Horizontal Separation), by looking at the trend, it was observed that there appeared two minima and one maximum at the centre of the plot. The maximum represented the highest repulsion in the stacked model, where one of the two monomers was just above the other, without any displacement at a vertical separation of 3.6Å. The point at the maximum gave less negative interaction energy value and the stability of the respective stacked model was also less than that of other models. In the stacked model, when one ring is horizontally shifted along positive or negative axis from the origin, we may get two minima on both sides. The points at the minima give more negative interaction energy values which represent the most stable stacked model [38]. Moreover, if we further shift the rings beyond 2.5Å, no such stacked interaction energy is observed.

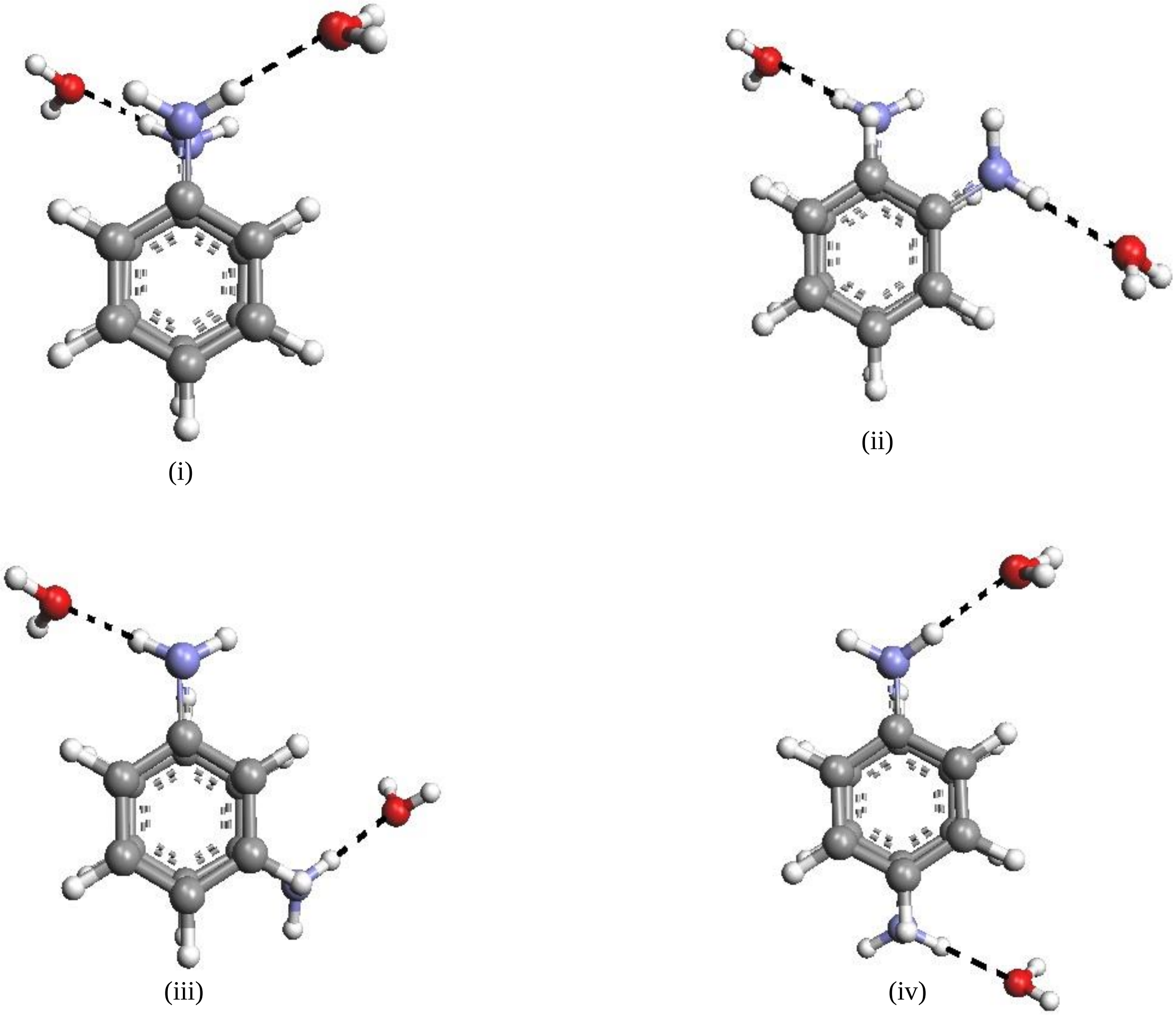
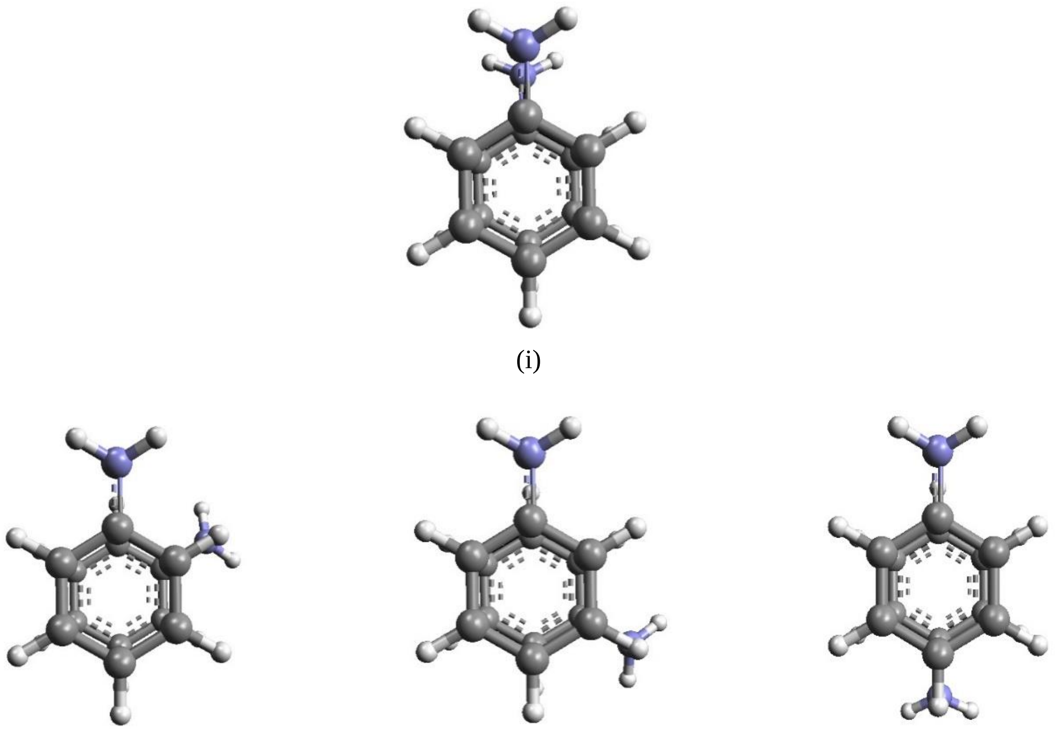

(i) (ii) (iii) (iv)

Figure 2. Possible dihedral angles for stacked models of water-assisted aniline systems: (i) eclipsed (0°), (ii) staggered (60°), (iii) staggered (120°) and (iv) staggered (180°) conformations.



(i)

(ii) (iii) (iv)

Figure 3. Possible stacked models of pure aniline systems: (i) eclipsed (0°), (ii) staggered (60°), (iii) staggered (120°) and (iv) staggered (180°) conformations.

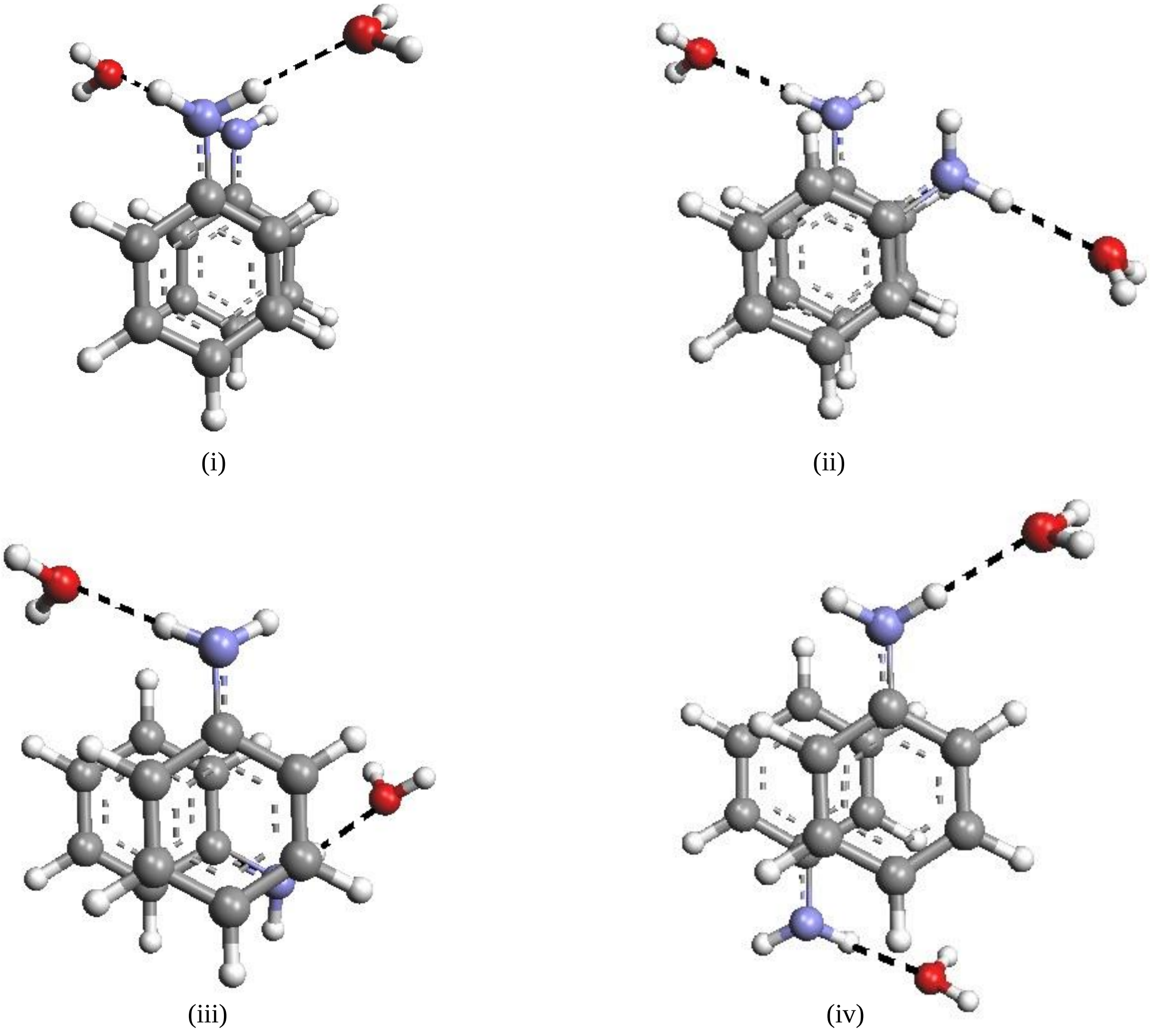
Among all the stacked models of aniline systems in gas phase, it has been observed that the stacking interaction energies of stacked aniline model with an eclipsed conformation (with dihedral angle = 0˚) was found to be with the most negative value (-16.0672 kcal/mol) (Table 1). The more negative stacking interaction energy value represent the more stable conformation and effective calculation of electron-electron correlation and dispersion forces [33]. On the other hand, the π-π stacking interaction energy for the staggered conformation with dihedral angle 120˚ was found to be -14.8118 kcal/mol (Table 1). In aqueous phase, the stacking interaction energy for the staggered conformation with dihedral angle 120˚ has been found to be the most negative (-6.1631 kcal/mol). But interestingly in the staggered conformation with dihedral angle 180˚, the stacking interaction energy decreased, as less electron-electron correlation and dispersion force existed. Figures 4-5 show the minimized stacked models for all the stacked aniline systems with different dihedral angles. The computed stacking energies of minimized structures with various levels of calculations in gas and aqueous phases are shown in Table 1.

Table 1. Computed Stacking Interaction energies for minimized stacked models of aniline and water-assisted (hydrated) aniline systems (MP2 method).

ANILINE SYSTEMS	**Interaction Energies (kcal/mol) for Eclipsed and Staggered conformations**			
	0˚	**60˚**	**120˚**	**180˚**
		Gas Phase		
Pure Aniline	-16.0672	-14.6723	-14.8118	-14.0739
Hydrated Aniline	-6.7199	-7.4127	-7.8020	-7.2193
		Aqueous Phase		
Pure Aniline	-5.3027	-6.0716	-6.1631	-5.5697
Hydrated Aniline	-6.6411	-6.8577	-7.1511	-6.8648

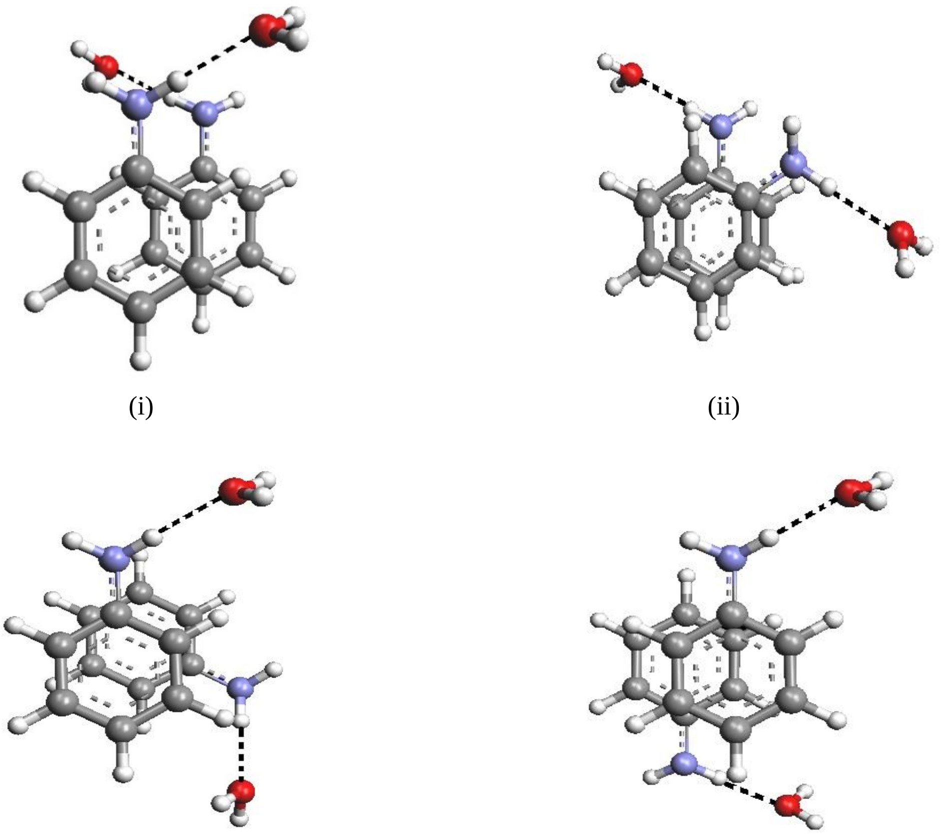
The study for water-assisted aniline stacking interactions showed effective π-π interaction and they were quite well stacked at dihedral angles of 0˚ and 120˚. For pure aniline in gas phase at 120˚ dihedral angle, the minimized energy showed the most negative value (-7.8020 kcal/mol) at a horizontal shifting of -1.0 Å. It is because of the water molecules of one aniline are far apart from the others which show minimum electron-electron repulsion. However, towards the positive horizontal shifting, the repulsive forces are maximum and therefore they show less negative values. Similar investigations were also done in aqueous phase with dihedral angles of 0˚, 60˚, 120˚ and 180˚. These models showed almost similar results and 120˚conformation gave the most negative value of -7.1511 kcal/mol [Figures 4-5].

For a neutral or unstacked molecule, the computed Mulliken charge density of all the atoms remains constant. But, during π-π stacking interaction, it shows a change in Mulliken charge density of each and every atom of the molecule [39]. More change in the Mulliken charge density in the stacked molecule, more is the effectiveness of the π-π stacking. Here, we computed the Mulliken charges for both the gas and aqueous phases for minimized stacked models as well as the unstacked aniline system to compare the change in electron charge density of aniline molecule.



(i) (ii) (iii) (iv)

Figure 4. Minimized stable stacked models of water-assisted aniline: (i) eclipsed (0°), (ii) staggered (60º), (iii) staggered (120°) and (iv) staggered (180°) in gas phase.



(i) (ii)

(iii) (iv)

Figure 5. Minimized stable stacked models of water-assisted aniline: (i) eclipsed (0°), (ii) staggered (60º), (iii) staggered (120°) and (iv) staggered (180°) in aqueous phase.

Table 2. Computed Mulliken Charges of pure aniline system in gas and aqueous phases (MP2 method).

Stacked Model	**Conformation**	**Mulliken Charges**			
		Group	**Atoms**	**Unstacked**	**Stacked**
		Gas Phase			
PURE ANILINE	Eclipsed (0°)	NH_2	N	-0.3723	-0.3306
			H	0.2479	0.2495
	Staggered (60°)	NH_2	N	-0.3723	-0.3722
			H	0.2479	0.2516
	Staggered (120°)	NH_2	N	-0.3723	-0.3849
			H	0.2479	0.2483
	Staggered (180°)	NH_2	N	-0.3723	-0.3884
			H	0.2479	0.2479
		Aqueous Phase			
PURE ANILINE	Eclipsed (0°)	NH_2	N	-0.4356	-0.3857
			H	0.2793	0.2748
	Staggered (60°)	NH_2	N	-0.4356	-0.4527
			H	0.2793	0.2879
	Staggered (120°)	NH_2	N	-0.4356	-0.4495
			H	0.2793	0.2788
	Staggered (180°)	NH_2	N	-0.4356	-0.4019
			H	0.2793	0.2833

Table 3(a). Mulliken Charges of water-assisted (hydrated) aniline system in gas phase.

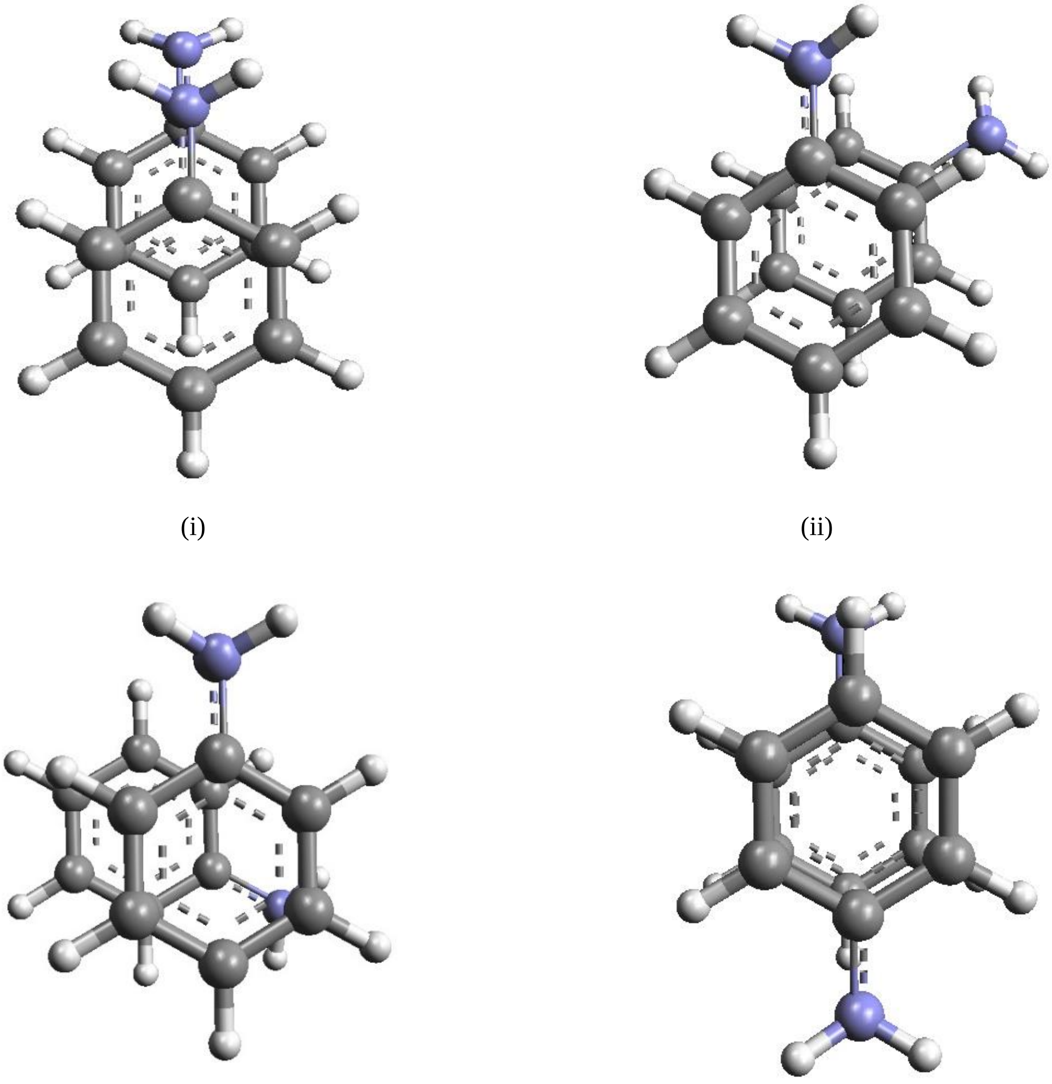
Stacked Model	**Conformations**	**Mulliken Charges**			
		Group	**Atoms**	**Unstacked**	**Stacked**
HYDRATED ANILINE	Eclipsed (0°)	NH_2	N	-0.4451	-0.4074
			H	0.3562	0.3653
		OH_2	O	-0.5639	-0.5425
			H	0.3562	0.3653
			H	0.2832	0.2751
	Staggered (60°)	NH_2	N	-0.4451	-0.4651
			H	0.3562	0.3596
		OH_2	O	-0.5639	-0.5365
			H	0.3562	0.3596
			H	0.2832	0.2710
	Staggered (120°)	NH_2	N	-0.4451	-0.4297
			H	0.3562	0.3598
		OH_2	O	-0.5639	-0.5388
			H	0.3562	0.3598
			H	0.2832	0.2729
	Staggered (180°)	NH_2	N	-0.4451	-0.4327
			H	0.3562	0.3632
		OH_2	O	-0.5639	-0.5391
			H	0.3562	0.3632
			H	0.2832	0.2721

Table 3(b). Mulliken Charges of water-assisted (hydrated) aniline system in aqueous phase.

Stacked Model	**Conformations**	**Mulliken Charges**			
		Group	**Atoms**	**Unstacked**	**Stacked**
HYDRATED ANILINE	Eclipsed (0°)	NH_2	N	-0.5013	-0.4821
			H	0.3667	0.3698
		OH_2	O	-0.6038	-0.5818
			H	0.3667	0.3698
			H	0.3090	0.2997
	Staggered (60°)	NH_2	N	-0.5013	-0.5401
			H	0.3667	0.3651
		OH_2	O	-0.6038	-0.5782
			H	0.3667	0.3651
			H	0.3090	0.2970
	Staggered (120°)	NH_2	N	-0.5013	-0.4984
			H	0.3667	0.3638
		OH_2	O	-0.6038	-0.5790
			H	0.3667	0.3638
			H	0.3090	0.2975
	Staggered (180°)	NH_2	N	-0.5013	-0.5007
			H	0.3667	0.3699
		OH_2	O	-0.6038	-0.5804
			H	0.3667	0.3699
			H	0.3090	0.2988

Since, the electron charge density is greatly affected by the $–NH_2$ group of the aniline ring both in stacked and unstacked models, hence we have investigated the variation of the Mulliken charges only for the H_2O and $–NH_2$ group (Tables 2-3). This also gives a brief idea about the effectiveness of π-π stacking interaction in aniline system.

Although we have done our calculations for π-π stacking interaction both in the gas and aqueous phases, but the results revealed that no such major changes have been found in the stability of the stacked models for water-assisted aniline as shown in the plots in Figures 8(a)-(d). Moreover, it has been observed that in the aqueous phase the π-π stacking interaction of water-assisted aniline molecule was found to be more stable than that of free aniline-aniline stacking. This is due to the fact that in the aqueous phase the polarity of water molecules can stabilize the electron charge density of the stacked models of water-assisted aniline system, resulting in a more favoured stacking interaction. On the other hand, the stacking interaction energies in Table 1 show more negative MP2 energies for the water-assisted aniline-aniline stacked molecule, i.e. more negative interaction gives more stable stacked structure.



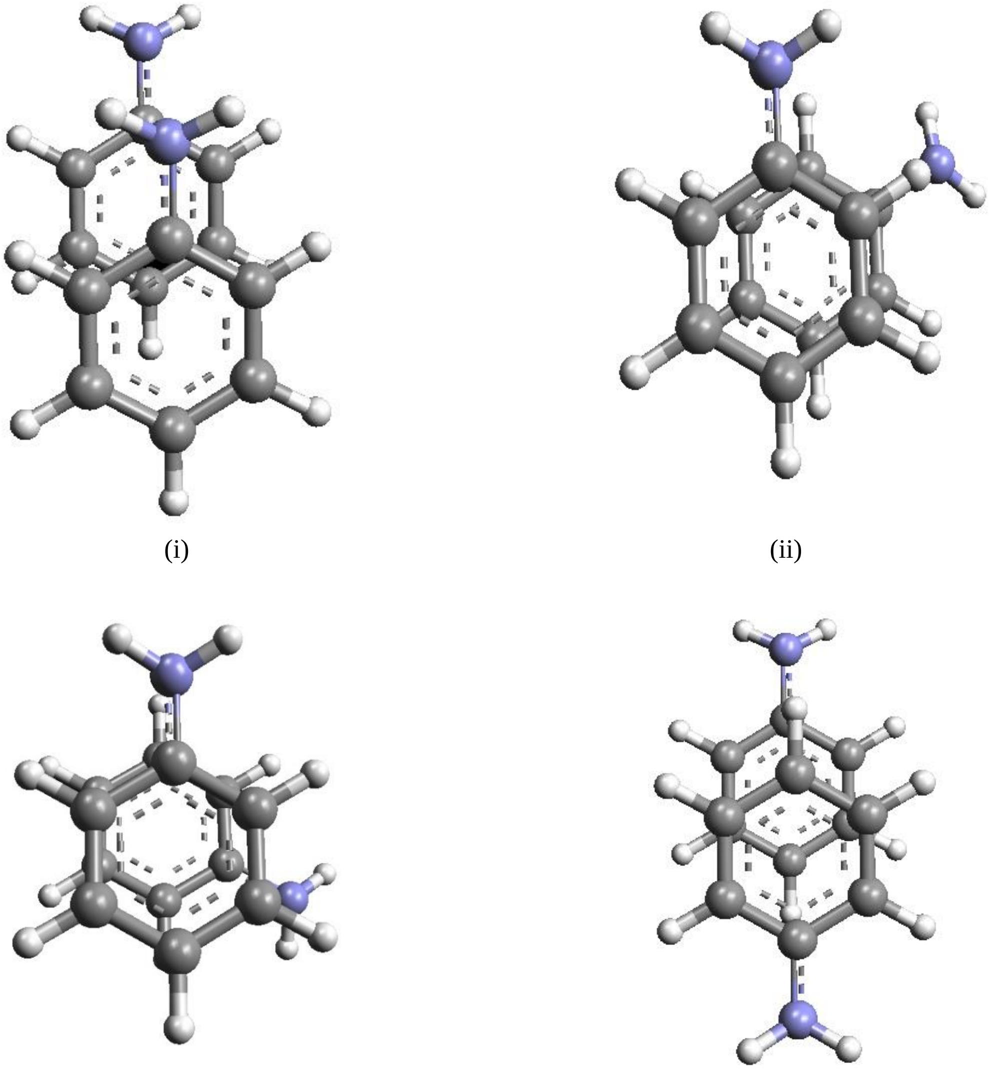
(i)

(ii)

(iii)

(iv)

Figure 6. Minimized stable stacked models of pure aniline: (i) eclipsed (0°), (ii) staggered (60º), (iii) staggered (120°) and (iv) staggered (180°) in gas phase.



(i) (ii)

(iii) (iv)

Figure 7. Minimized stable stacked models of pure aniline: (i) eclipsed (0°), (ii) staggered (60º), (iii) staggered (120°) and (iv) staggered (180°) in aqueous phase.

The single point MP2 calculations with 6-311++G(d,p) basis set have been found useful in describing the stability of stacked aniline and water-assisted aniline molecules. The relative changes of the interaction energies of different stable stacked models of aniline molecules are shown in Figures 4-7 and certain stable stacked structures are located from the minima in the interaction energy plots (Figures 8(a)-(d)), i.e. they give the most favoured and stable stacked models.

The computed interaction energies of various levels of calculations are summarized in Table 1. The values were found to be significantly different, and the MP2/6-311++G(d,p) calculations estimated more negative interaction energies. The series of results could provide prior necessity of dispersion forces for the stabilization of the stacked molecules. The results of MP2 level of theories reflected the extent of dispersion energies accounted in all the calculations. Indeed, the electron correlations included in MP2 level with diffused function in the basis set could estimate more negative interaction energies, where the increase of diffuse function in the basis set provided little change in the interaction energies. It could be noted that the differences of interaction energies obtained from MP2/6-311++G(d,p) calculations were significantly large (Table 1).

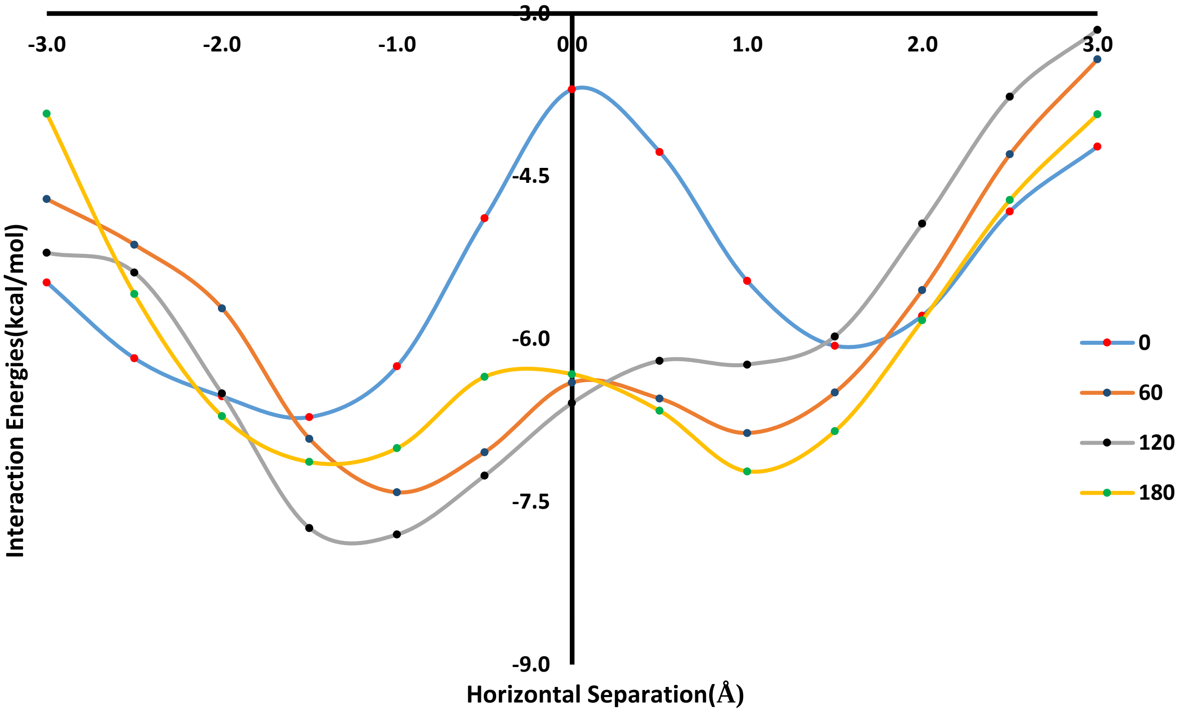


Figure 8(a). Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of water-assisted (hydrated) aniline in gas phase

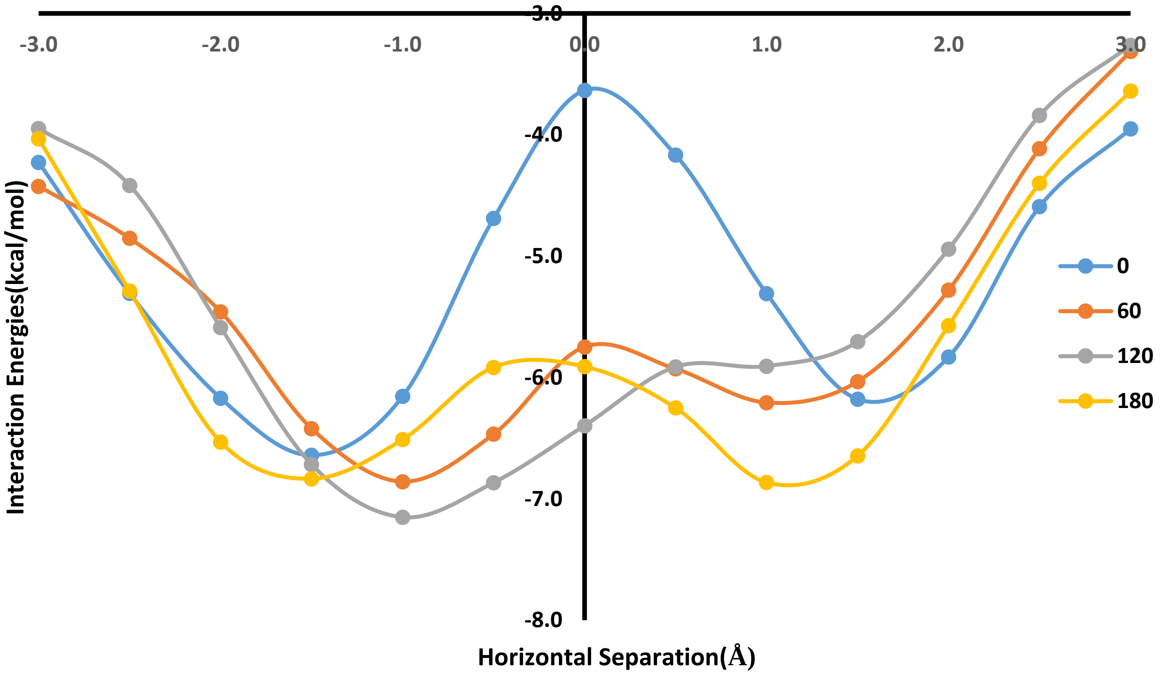


Figure 8(b). Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of water-assisted (hydrated) aniline in aqueous phase.

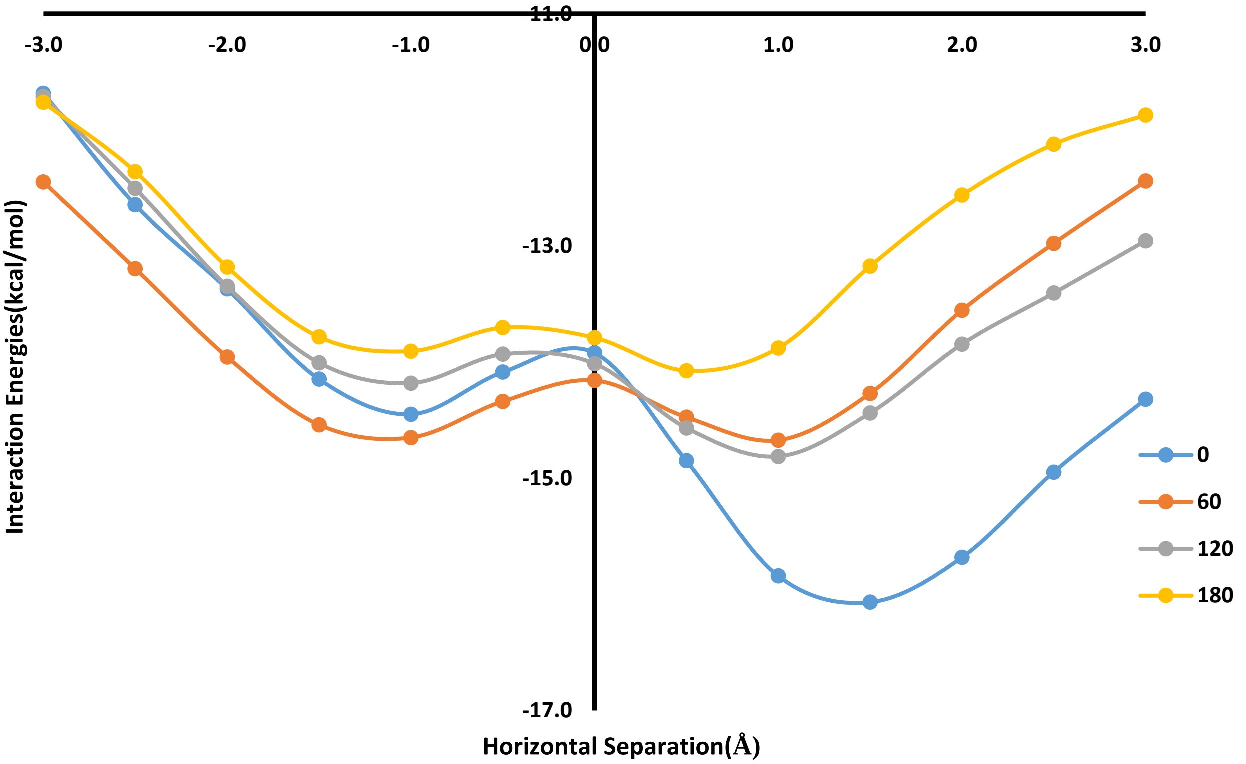


Figure 8(c). Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of pure aniline in gas phase.

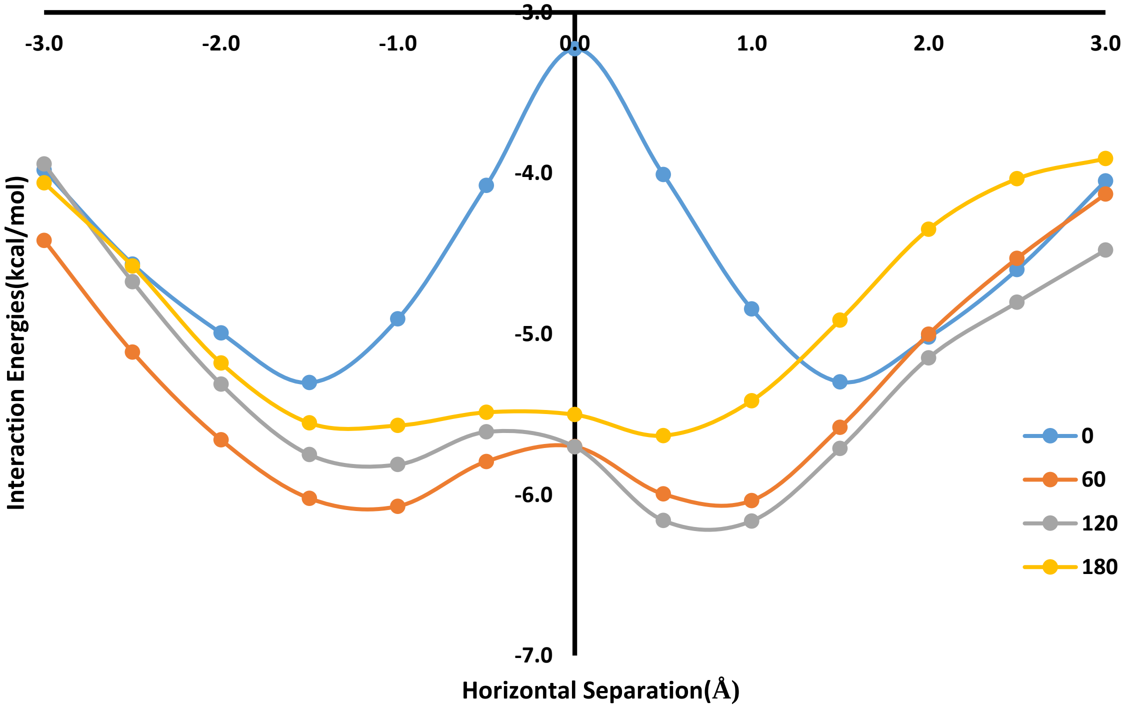


Figure 8(d). Plot of interaction energies (MP2 single point) versus stacking positions (Å) for different conformations of pure aniline in aqueous phase.

The order of stability of the stacking interactions of aniline and water-assisted (hydrated) aniline with respect to different dihedral angles is given below:

For Aniline-Aniline stacking:
180º< 60º ~ 120º < 0º (Gas phase)
0º< 180º < 60º ~ 120º (Aqueous phase)
For Water-assisted Aniline-Aniline stacking:
0º< 180º < 60º < 120º (Gas phase)
0º < 60º ~ 180º < 120º (Aqueous phase)

CONCLUSION

From the above studies, we can conclude that MP2/6-311++G(d,p) basis set is found to be more feasible for computing the π-π stacking interaction energies in pure aniline-aniline and water-assisted (hydrated) aniline-aniline system. Although, π-π stacking interaction is very common in both systems, the water-assisted aniline-aniline stacking interaction gives more favoured stacked models than that of pure aniline-aniline stacking in aqueous phase. In aniline systems, π-π stacking interaction energy is also dependent on the intermolecular rotation of the stacked models.

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