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Ab initio study on the variation of stacking interactions of aniline and hydrated aniline systems

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ABSTRACT

The use of appropriate level of theories for studying weak interactions such as π-π stacking interactions of aromatic molecules has been an important aspect, since the high level methods have limitations for application to large molecules. The differences in the stacking energies of various aromatic molecular structures are found significant. It is also very important for identifying the most favored stacked models of aniline and hydrated aniline molecules. The effect of basis set in the stacking energies of MP2 calculations is small. The values for HF and MP2 level of theories calculate less electron correlation energy whereas CCSD (T) methods may be used for the calculation of better electron correlation energy. 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 studies, it has been investigated to study the different π-π stacking interaction energies and the effect of change in conformations for aniline and hydrated aniline systems.

Keywords: π-π Stacking interactions, aniline, MP2.

INTRODUCTION

Computational chemistry surrounds a vast area of fields and computing techniques. The classical techniques used for stationary-state quantum chemistry and equilibrium Monte Carlo [1] and Molecular Dynamics [2] are being studied with Quantum Monte Carloas stated in Quantum Molecular Dynamics,' Microdynamics [3] but is also investigated by research and computer programs on data base, interactive animation, artificial intelligence, and chemical knowledge processing [4].

Aromatic stacking interactions have always played a very important role in both chemistry and biology [5,6]. They are crucial for the geometry characterization and calculating the stabilization energy of DNA molecules, the crystal structure packing of various aromatic molecules, the formation of the various tertiary structure of proteins, the control in the enzyme-nucleic acids, intercalation of drugs into DNA, and so on. For that reason, the stacking interactions still play a vital role in the subject of numerous works [3-8]. In synthetic organic reactions, stacking interactions have been reported to play a significant role in the outcomes of stereo selectivity [7-10]. Moreover, there has been vast interest in the magnitude and origin of

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*Corresponding author: bipulbezbaruah@gmail.com interactions. [2-5, 11-14] Recently experimental studies have been reported aiming at an energetic quantification of noncovalent interactions which involved aromatic rings [27, 28] .In this work we compare the stacking energy afforded by *ab-initio* methods, used to describe stacked complexes [23]. In our studies it has been investigated to study the different stacking interaction energies and the effect of change in conformations for aniline and hydrated aniline systems.

METHODOLOGY

Computational Methods in our investigation:

All the geometries of aniline and hydrated aniline systems are completely optimized by HF-method. All single point calculations were carried out using HF and MP2 methods with 6-311++G (d, p) as a basis set with Gaussian'09 program. The optimized geometries are used for constructing various stacked models of aniline and hydrated aniline systems using Join Molecule package of software. In all the models, one of the stacked configurations have been horizontally shifted over the other, along both positive and negative x-axis directions with a fixed vertical separation of 3.6 A°. The most favored optimized and stable structures obtained from various methods are almost similar. The effect of basis set in the stacking energies of MP2 calculations is small. Here, we have carried out only cc-pVQZ basis set for calculation the interaction energies because it is more compatible than that of CCSD methods of calculations. Whereas; the values for HF/6-311++G (d, p) and MP2/6-311+G(d, p) calculates less electron correlation energy.

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

Interaction energies = $E_{ST} - 2E_M$

E_{ST} and E_M are the energies of stacked model and monomer. All the calculations are carried out with Gaussian09 program code [29].

RESULTS AND DISCUSSION

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 hydrated aniline molecules. The calculated interaction energies with 6-311++G (d, p) basis set does not show much variation from that of 6-31+G(d, p) basis set (Table 1). The relative changes of the interaction energies of different stable stacked models of aniline molecules are shown in (Figures 1 & 2) and certain stable stacked structures are located from the minima in the interaction energy plots (Figure 5 & 6) i.e. it gives the most favored and stable stacked models. However, the corresponding interaction energy plots of HF calculations shown in (Figure 6) cannot properly explain the stacking stabilization of aniline molecules because this method could not calculate the electron correlation energy. The single point calculations of all stacked models have been performed in the study, since the complete geometry optimization may not be advantageous to locate the local optimum structures. The corresponding potential energy plot of HF Calculation shown in (Figure 6) cannot explain the stacking stabilization of stacked aniline molecules.

As we know that the interaction energies obtained from HF calculation include columbic, induction, exchange and some electron correlation energies, and 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 how the interaction energies can be improved with the inclusion of diffused functions in the HF and MP2 level of calculations.

The computed interaction energies of various levels of calculations are summarized in (Table 1). The values are found significantly different, and the MP2/6-311++G (d, p) calculations could estimate more negative interaction energies. It is not surprising that the interaction energies of HF/6-31+G (d, p) and HF/6-311++G(d, p) calculations are all positive, which is definitely due to the lack of dispersion energies with these calculations. The series of results could provide prior necessity of dispersion forces for the stabilization of these stacked molecules. The results of HF and 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 interaction energies, where the increase of diffuse function in the basis set provides little change in the interaction energies. It may be noted that the difference of interaction energies obtained from HF/6-31+G and MP2/6-31+G calculations is significantly large, whereas values of MP2/6-311++G (d,p) is not so different (Table 1). However the most expensive method, MP4 level of theory is particularly used in most calculations on stacking interactions, but such high level calculations could not be performed. The change in interaction energies of stacked models as determined by MP2 method with 6-31+G (d,p) and 6-311++G(d,p) may be appropriate for qualitative explanations of these non-bonded weak interactions. Our results show that the interaction energies do 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 are found much better than any other computational methods[34].

In this study it has been found that the stacking interaction of hydrated aniline molecule is quite stable than that of free aniline-aniline stacking. The stacking interaction energy found in (Table 1) shows more negative HF and MP2 energies for the hydrated aniline-aniline stacked molecule, i.e. more negative interaction gives more stable stacked structure. Although the HF and other low level calculations cannot be used to calculate accurate interaction energies, it may be useful for predicting the position of counter molecules in stacked models. As we can see that both the HF and MP2 methods can locate almost similar minimized stacked structures.

CONCLUSION

As shown in (Table 1), the extent of dispersion energies included in the interaction energies of MP2/6-311++G(d,p) calculations of small molecules, whereas the HF/6-311++G (d, p) method cannot usually estimate dispersion energies. So the role of dispersion forces demonstrated in these calculations may be useful for studying stacking interactions of aromatic molecules. In conclusion, the MP2/6-311++G (d, p) are found feasible for explaining the π-π type of stacking interaction for both free and hydrated aniline-aniline stacking. But, the hydrated aniline-aniline stacking gives more favored stacking interaction than that of free aniline-aniline stacking. The high level computational methods with basis sets such as, CCSD (T) and cc-pVQZ may be applied to calculate the effective electron correlation energy to get more accurate calculations, but such high level calculations are quite expensive and time consuming. pi-pi stacking is observed in both aniline-aniline and hydrated aniline-aniline stacking and is favorable for the models (fig. 3 & 4).All the favored and stacked models can be observed from the minimum point of the graphs (fig. 5, 6 & 7).All the minima are observed for different basis sets (Table 1).

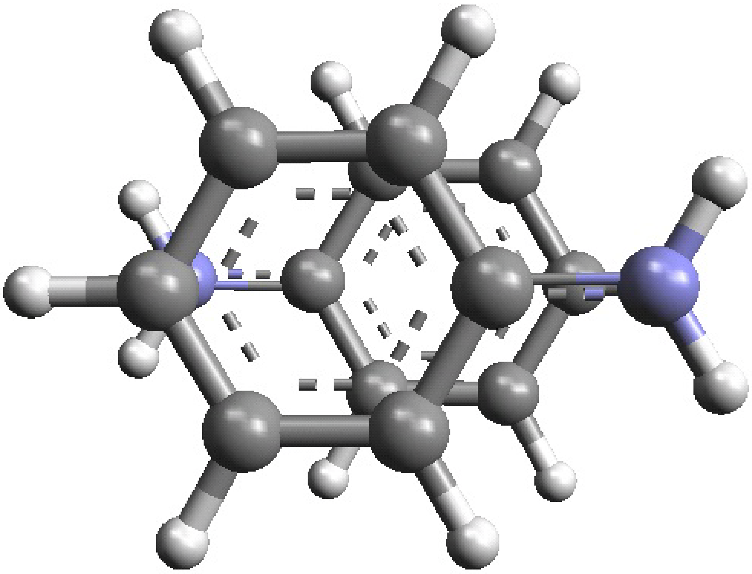


Fig. 1. Minimized aniline-aniline stacked model.

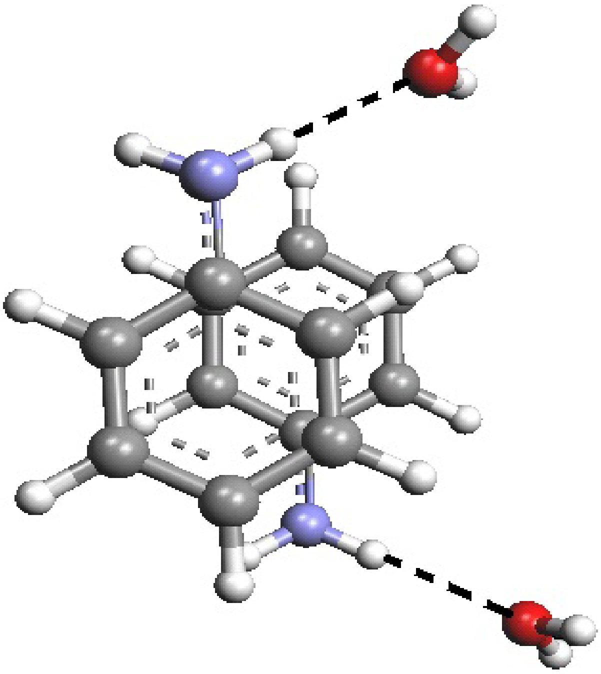


Fig. 2. Minimized hydrated aniline-aniline stacked model.

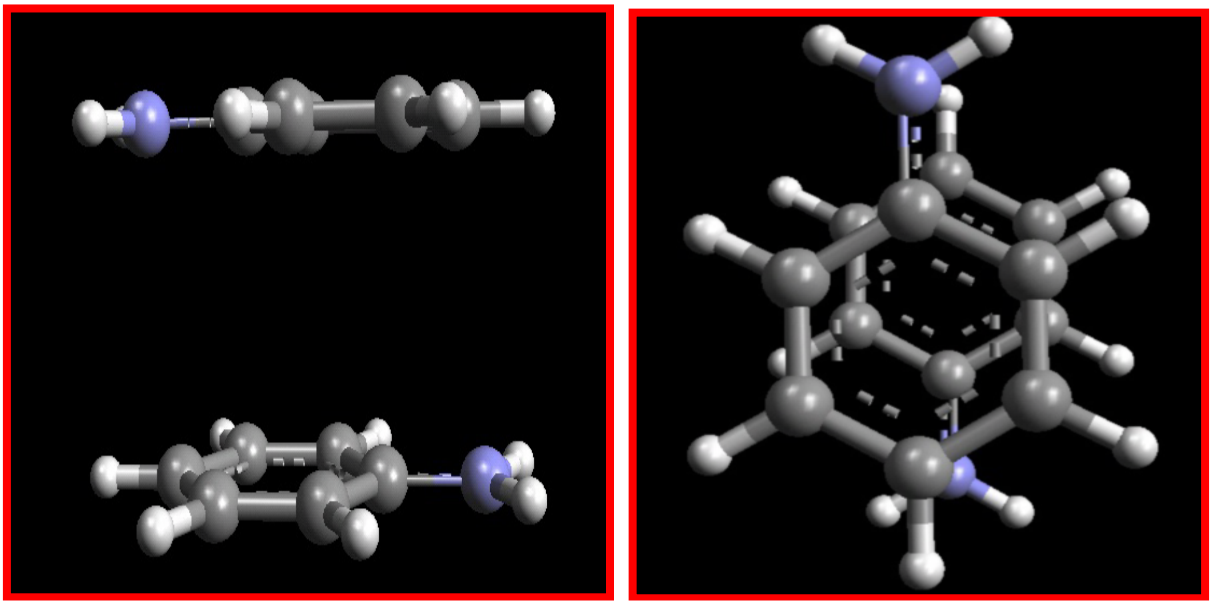


Fig. 3. Highly stable, minimized and favoured models for (a) aniline-aniline stacked model (*front view*) (b) aniline-aniline stacked model (*side view*).

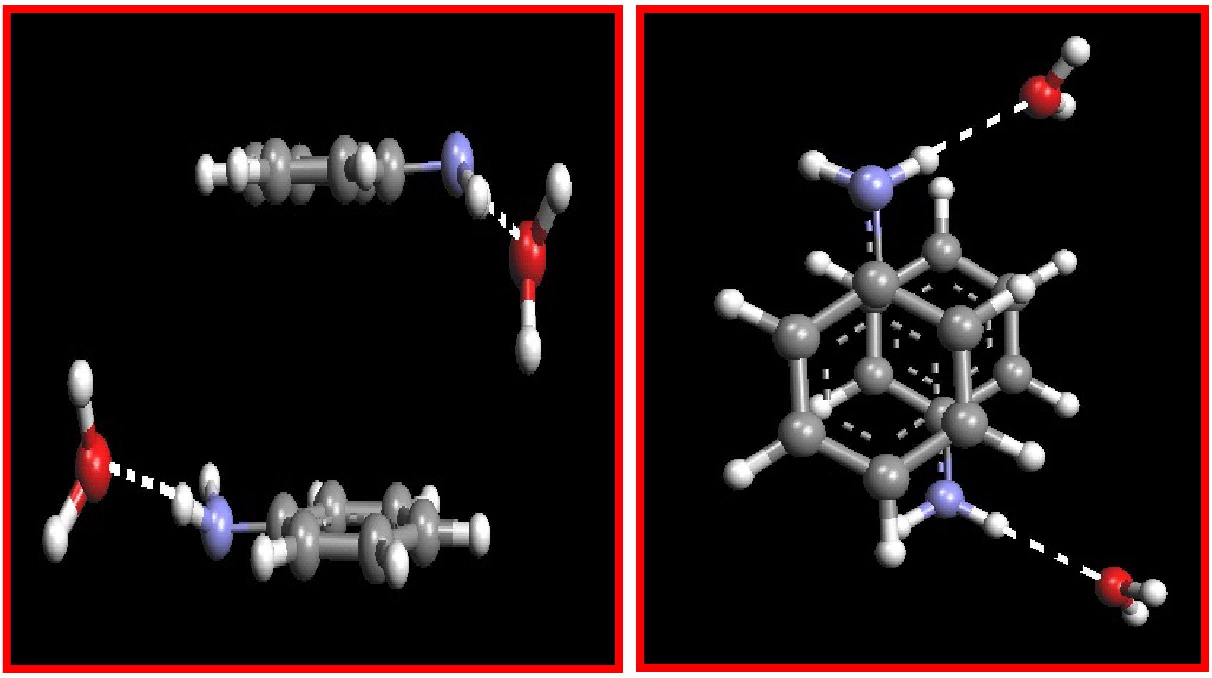
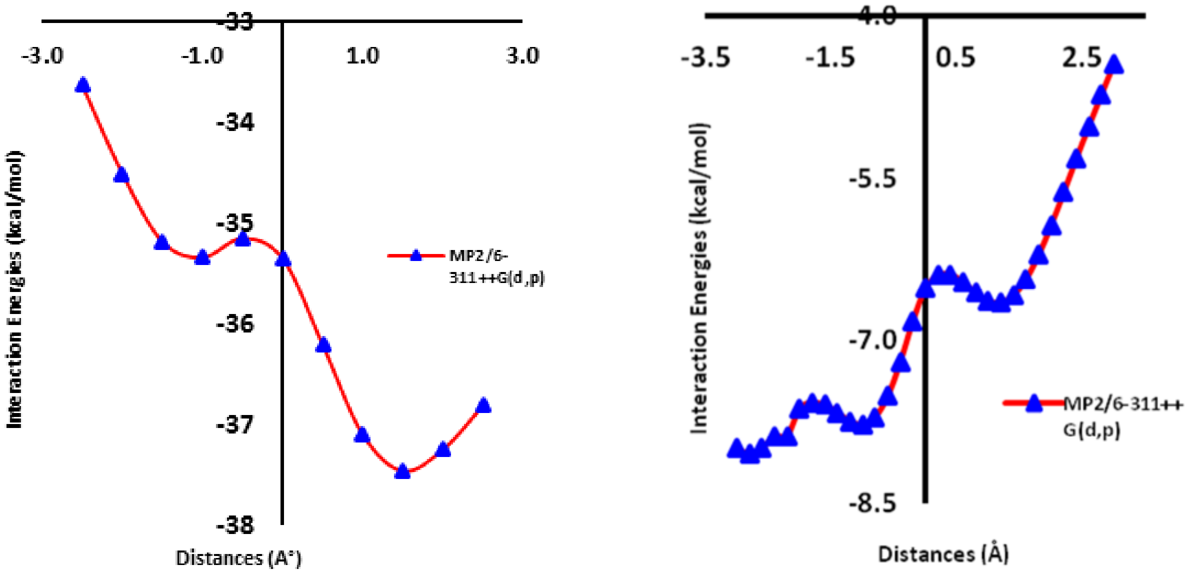
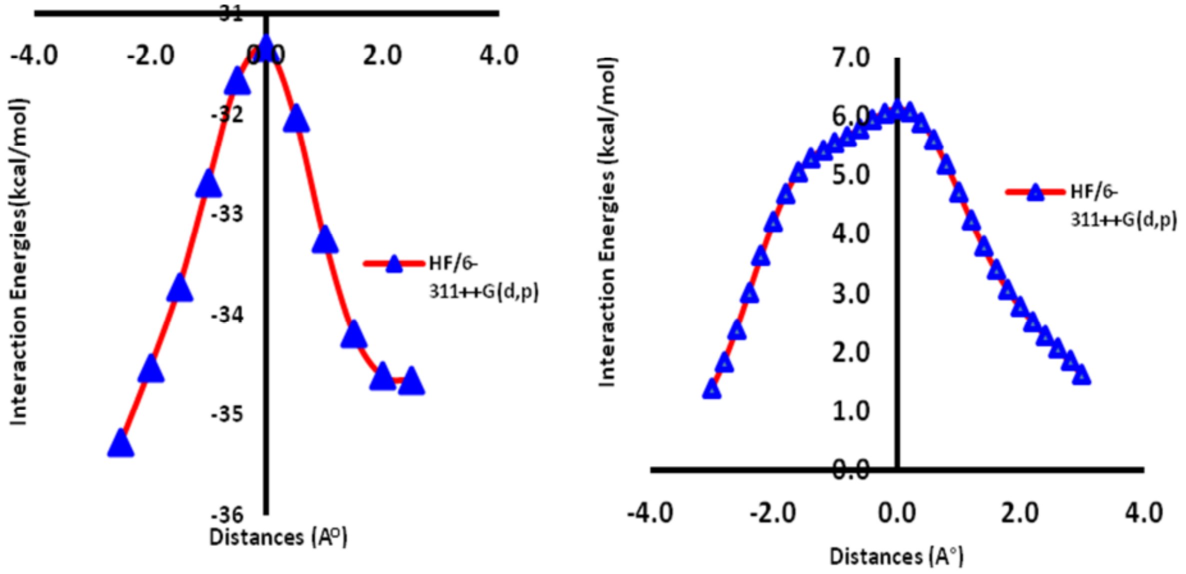


Fig. 4. Highly stable, minimized and favoured models for (a) Hydrated aniline-aniline repulsive stacked model (*front view*) (b) Hydrated aniline-aniline stacked model (*side view*).



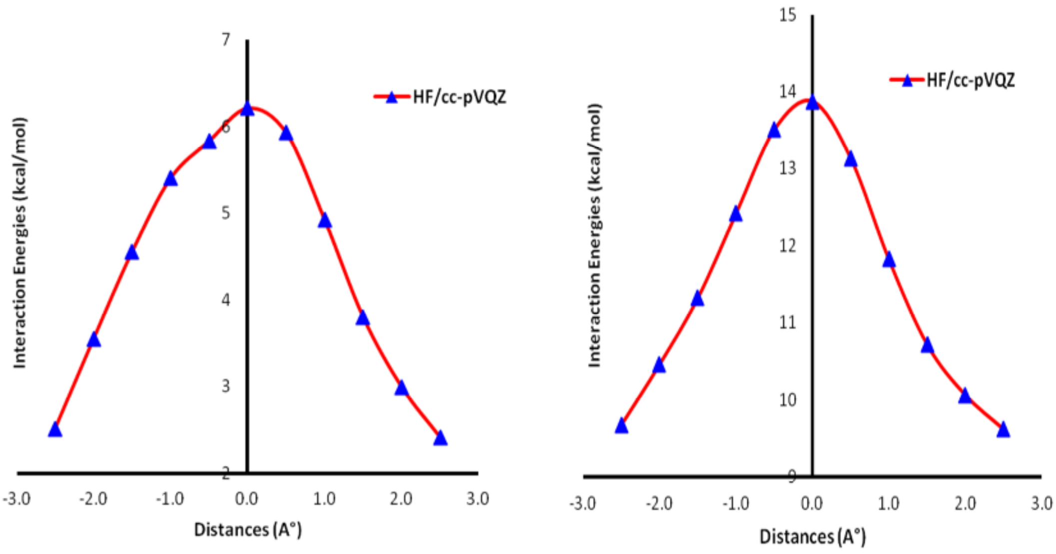
(a) (b)

Fig. 5. (a) Plot for stacked hydrated aniline-aniline molecules for the basis set MP2/6-311++G(d,p) ; (b) Plot for stacked aniline-aniline molecules for the basis set MP2/6-311++G(d,p).



(a) (b)

Fig. 6. (a) Plot for stacked hydrated aniline-aniline molecules for the basis set HF/6-311++G(d,p); (b) Plot for stacked aniline-aniline molecules for the basis set HF/6-311++G(d,p).



(a) **(b)**

Fig. 7. (a) Plot for stacked hydrated aniline-aniline molecules for the basis set HF/cc-pVQZ ; (b) Plot for stacked aniline-aniline molecules for the basis set HF/cc-PVQZ.

Table 1. Interaction Energies (kcal/mol) for the stable stacked models of aniline and hydrated aniline with different basis sets

BASIS SETS	**INTERACTION ENERGIES (kcalmol^{-1})**	
	Aniline-aniline	**Hydrated aniline**
HF/6-31+G(d,p)	2.2771	8.3085
HF/6-311++G(d,p)	2.9301	-34.6120
MP2/6-311++G(d,p)	-7.7736	-37.4590
HF/cc-pVQZ	6.2105	13.8741

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