



Research Article

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Quantum Chemical Studies on hydrogen bonding interaction of Pyrimidine and Water

Neha Shukla and Devendra Kumar Singh*

Department of Physics, Udai Pratap (Autonomous) College, Varanasi-221002

ABSTRACT

Structure and stability of the complexes formed between pyrimidine and water molecules have been completely investigated in the present study using by second order Moller-Plesset (MP2) and density functional theory (DFT) on the basis set 6-311++G(d,p). Nine reasonable geometries on the potential energy hyper surface of the pyrimidine and water are considered: two each are with two, three and four water molecules and one each with one, five and six water molecules. Optimized geometries and hydrogen binding energies for various structures have been estimated. Hydrogen binding energies and bond distances as well as the vibrational characteristics show that as the number of water molecules increases stability of the complexes increases and the bond length between N and H decreases. The ring-breathing mode ν_1 of the reference system Pd was chosen as a marker band to probe the degree of hydrogen bonding.

INTRODUCTION

Pyrimidine (Pd) is the parent heterocyclic of a very important group of compounds that have been studied extensively because of their occurrence in living systems. The pyrimidine ring system provides a potential binding site for metals and hence any information on their coordinating property is important for understanding the role of metal ions in biological systems, which are extremely vital for many life processes.

Hydration is a universal phenomenon in nature, many biological processes occur in aqueous media. Water plays a crucial role in directing the conformational preferences of molecules of biological relevance. Pyrimidine is a model structure for the representation of biologically relevant N-heterocycles. Pyrimidine has numerous different receptor/binding sites and water molecule are likely to be present in these binding sites and may play a role in the way in which pyrimidine interacts with water. Hydrogen bonding is an extensively investigated phenomenon, especially due to its importance for biological system. Quantum Chemistry provides the concepts to achieve an understanding of the fundamental nature of chemical bonds in general and hydrogen bonds in particular. Besides ab-initio methods, density functional theory (DFT) has become very popular recently owing to its good performance and reasonable computational efforts. Binary ionic complexes, complexes of small organic molecules with water, and some other systems have been examined by various authors [1-6]. Vibrational spectroscopic analysis of hydrogen-bonding between pyrimidine and water both experimentally and theoretically studies recently by Schlucker et al.[7]. These authors have employed B3LYP method on basis set 6-31++G(d,p). We have done the theoretical study using by second order Moller-Plesset (MP2) and density functional theory (DFT) B3LYP with the higher basis set 6-311++G(d,p), all these calculations shows the more stable structure than studied by Schlucker et al. We study the structures and spectra of some possible hydrogen bonded pyrimidine-water complexes, such as PdW, PdW₂₍₂₊₀₎, PdW₂₍₁₊₁₎, PdW₃₍₃₊₀₎, PdW₃₍₂₊₁₎, PdW₄₍₃₊₁₎, PdW₄₍₂₊₂₎, PdW₅₍₃₊₂₎, PdW₆₍₃₊₃₎. In this paper the ab-initio and

DFT derived optimized geometries and vibrational spectra of the nine pyrimidine-water complexes are presented and the change in the structures and spectral features within this group has been discussed. The optimized geometry, interaction energies and ring breathing vibration ν_1 of the pyrimidine-water complexes has been characterized theoretically for the first time using comparative study of ab-initio (MP2) and DFT calculations (B3LYP) with 6-311++G(d, p) basic set.

1. Computational Methodology:

The ground state geometries and vibrational spectra for free Pyrimidine (Pd) and its hydrogen-bonded complexes with molecules of water have been optimized and corresponding ring breathing vibration ν_1 were calculated using ab initio method:-(i) MP2 and hybrid density functional theory (DFT) methods- (ii) B3LYP which uses Becke's three-parameter functional with nonlocal correlation provided by Lee-Young-Parr expression with 6-311++G(d, p) basic set. The optimized structure at MP2/6-311++G(d, p) has been taken as the input structure for the calculations at the B3LYP/6-311++G(d, p) All calculations have been performed using the GAUSSIAN 09 (revision D.01) package of programs without any constraint on the geometry. It has already been shown that this level of theory is sufficient to reliably predict molecular geometries as well as vibrational spectra of hydrogen bonded systems. Geometries have been first optimized with full relaxation on the potential energy surfaces.

2. DFT Calculations on Pyrimidine-Water Complexes

In the binary system Pd/W, many different hydrogen-bonded complexes can be simultaneously present. The two nitrogen atoms of Pd are potential hydrogen-acceptor sites. We therefore calculated the structures and the vibrational spectra of various small PdMy clusters with stoichiometric ratios ranging from 1 : 1 to 1: 6. Our calculations are restricted to species with a maximum of three water molecules (W_3 subcluster) attached to one N atom of Pd having overall a maximum of six water molecules.

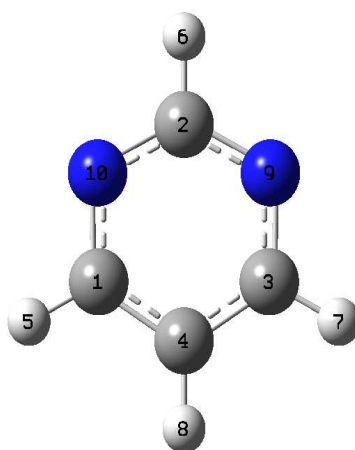


figure 1(a) : Optimized structure of Pyrimidine (Pd) at B3LYP/6-311++G(d,p)



Fig. 1(b) & 1(c): Optimized structure of Pyrimidine-Water complex PdW and PdW₂₍₂₊₀₎ at B3LYP/6-311++G(d,p)

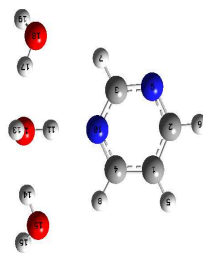


figure 1(d) & 1(e) : Optimized structure of Pyrimidine-Water complex PdW₂₍₁₊₁₎ and at B3LYP/6-311++G(d,p)

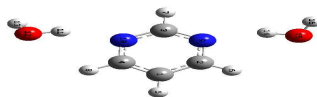


figure 1(e) : Optimized structure of Pyrimidine-Water complex PdW₃₍₃₊₀₎

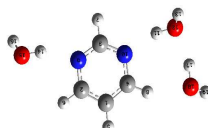


figure 1(f) : Optimized structure of Pyrimidine-Water complex PdW₃₍₂₊₁₎ at B3LYP/6-311++G(d,p)

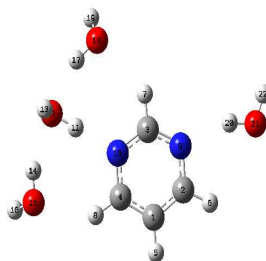


figure 1(g): Optimized structure of Pyrimidine-Water complex PdW₄₍₃₊₁₎ at B3LYP/6-311++G(d,p)

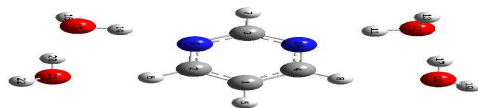


figure 1(h): Optimized structure of Pyrimidine-Water complex PdW₄₍₂₊₂₎ at B3LYP/6-311++G(d,p)

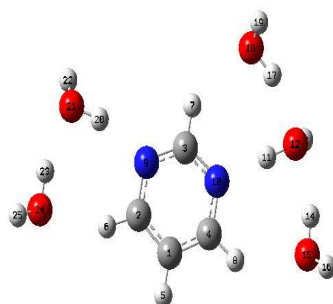


figure 1(i): Optimized structure of Pyrimidine-Water complex PdW₅₍₃₊₂₎ at B3LYP/6-311++G(d,p)

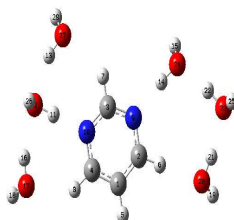


figure 1(j): Optimized structure of Pyrimidine-Water complex PdW₆₍₃₊₃₎ at B3LYP/6-311++G(d,p)

RESULTS AND DISCUSSION

Calculated total energies (Hartree) for Pyrimidine-Water Complexes

Complex	B3LYP/6-31++G(d,p)	B3LYP/6-311++G(d,p)	Mp2/6-311++G(d,p)
PdW	-340.78491399	-340.86209604	-339.92202677
PdW ₂₍₂₊₀₎	-417.23548583	-417.33649308	-416.21371511
PdW ₂₍₁₊₁₎	-417.22837484	-417.32974154	-416.20745684
PdW ₃₍₃₊₀₎	-493.67975036	-493.80443467	-492.49934734
PdW ₃₍₂₊₁₎	-493.67902712	-493.80422210	-492.49911176
PdW ₄₍₃₊₁₎	-570.12385146	-570.27290655	-568.78531584
PdW ₄₍₂₊₂₎	-570.12954870	-570.27853304	-568.79072512
PdW ₅₍₃₊₂₎	-646.57453684	-646.74744449	-645.07716539
PdW ₆₍₃₊₃₎	-723.02535302	-723.22210343	-721.36890457

The pyrimidine-water complexes are found to be most stable at B3LYP/6-311++G(d,p) level. We also see that as number of water molecule increases the stability of complexes also increases.

Calculated N-H Distance and ring breathing mode Frequencies for pure pyrimidine and various Pd-W Complexes for most stable structure (B3LYP/6-311++G(d,p))

Complex	d (N1-H) (Å)	d (N2-H) (Å)	ν_1 (cm ⁻¹)
Pd			993.715
PdW	1.96516		1011.37
PdW ₂₍₂₊₀₎	1.87130		1013.7
PdW ₂₍₁₊₁₎	1.98311	1.98311	1018.13
PdW ₃₍₃₊₀₎	1.73482		1017.22
PdW ₃₍₂₊₁₎	1.88766	1.97351	1020.33
PdW ₄₍₃₊₁₎	1.76910	1.97715	1032.14
PdW ₄₍₂₊₂₎	1.88160	1.88160	1022.18
PdW ₅₍₃₊₂₎	1.76362	1.89163	1033.61
PdW ₆₍₃₊₃₎	1.76181	1.85149	1034.83

CONCLUSION

1. Quantum Chemical studies of hydrogen bonded Pyrimidine –water complexes show that as the number of water molecules increases stability of the complexes increases. The variations in bond length depend on the side of the Pyrimidine ring in which water molecule is attached.

2. The ring-breathing mode ν_1 of the reference system Pd has changed with the addition of water molecule and shows blue shift.

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