Structural and Electronic Properties of Adenine-Thymine Basepair :
A Computational Study

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Abstract

It is well known that stability of deoxyribo-nucleic acid (DNA) double helix depends on hydrogen bonding (HB) between adenine-thymine and guanine-cytosine. HB plays an important role in molecular systems, particularly in biological systems because all lives on the earth may be viewed as a matter of hydrogen-bonding supramolecular systems. Since HBs have a central role on the mechanism of life phenomena including the structure and functions, it is essential to understand the molecular-level aspects of HB systems. Therefore, we studied the structural properties of adenine-thymine (A-T) basepair theoretically using DFT/B3LYP/6-31G level of theory. Theoretically we found four isomers of A-T basepair and the most stable isomer is one in which adenine and thymine are connected via two hydrogen bonding. The electronic properties were calculated by Time Dependent Density Functional Theory (TD-DFT) approach.

Keywords: A-T basepair, TD-DFT, Electronic properties, DFT/B3LYP/6-31G and Hydrogen bonding

I. Introduction

It is well known that deoxyribonucleic acid (DNA) is the hereditary material in humans and almost all other organisms. DNA consists of four nucleic acid bases (adenine, guanine, cytosine and thymine) that constitutes the building blocks of life and encodes the genetic information of all organisms in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).[1-3] The two intertwined strands of DNA are held together through base pairing-the formation of hydrogen bonds between bases located opposite each other on the strands. But the stability of DNA and base pair depends on the cooperative hydrogen bonding between DNA bases (two hydrogen bonds between adenine-thymine, three hydrogen bonds between guanine-cytosine) and solvation of DNA. Without cooperative hydrogen bonding between DNA bases, the molecular recognition and unique helical structure of DNA will be disrupted.[4]

These nucleobases absorb UV light strongly and act as a primary chromophore of DNA.[5-7] Photostability of DNA bases is the essential criteria for the preservation of genetic information of DNA bases. As nucleobases absorb UV light strongly, the knowledge of the electronic properties and excited state lifetimes are of paramount importance for understanding the UV radiation induced DNA damage.[8-11] Numerous experimental and theoretical studies on DNA and DNA bases have been performed to understand structural, electronic properties and excited state lifetimes.[12-16] All the calculations have been focused on the ground state to the higher electronic singlet and triplet states of the neutral molecules.

In this report, we have performed a theoretical investigation of structural and electronic properties of adenine-thymine (AT) basepair with DFT/B3LYP hybrid approach.

II. Computational Details

All the quantum chemical calculations have been performed using the hybrid approach of B3LYP as implemented in the quantum chemistry package G09.[17] We have used 6-31G basis set in order to calculate the structure and UV–Vis spectra of AT basepair in the ground state at the B3LYP level of theory. The optimized structure of AT basepair in the ground state was verified by calculating vibrational frequencies. There are several methods to calculate singlet excited states such as symmetry adapted cluster method/configuration interaction (SAC/CI) method[18], configuration interaction singles (CIS) method[19] and time dependent density functional theory (TD-DFT)[14] calculations. Among them, the TD-DFT is new approach for studying electronic excitations which gives more accurate results. Therefore, excited state calculations have been done by TD-DFT method employing B3LYP function and 6-31G basis set to study electronic properties.

III. Results and Discussion
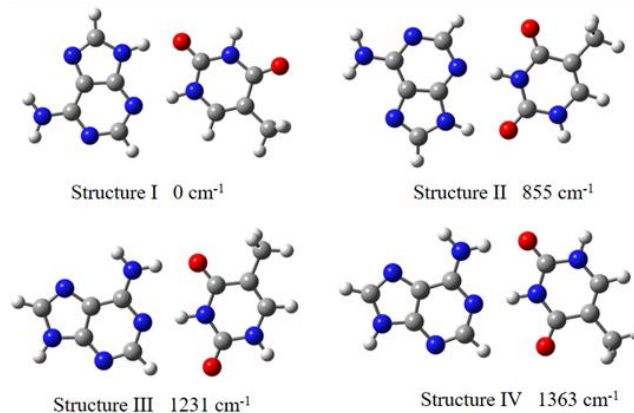
Structural properties analysis

Fig. 1. Four most stable isomers of adenine-thymine basepair

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Adenine and thymine can exist several ways via double or triple hydrogen bonding. Therefore, several minimum energy structures are possible. Among them, four minimum energy structures have been shown in Fig.1. For optimizing minimum energy structure of AT basepair, first we have done intrinsic reaction coordinate (IRC) calculation with HF/6-31G level of theory. These minimum energy structures were re-optimized using DFT/B3LYP/6-31G level of theory. The final geometry corresponds to true energy minima as revealed by the lack of imaginary frequencies in the vibrational mode calculation.

The calculated total energies of four isomers of AT basepair with absolute energy (E), relative energy of the most stable isomer (ΔE) and binding energy (E_{bind}) of adenine and thymine are summarized in Table 1.

Table 1. DFT calculated total energy (E), absolute energy (E_{zpve}), relative energy to the most stable isomers (ΔE), and binding energy (E_{bind}).

Molecule	E/ hartree	*E_{ZPVE}/ hartree	ΔE/cm^{-1}	E_{bind} /cm^{-1}
A	-467.1588	-467.0452		
T	-453.9955	-453.8792		
A -T (I)	-921.1945	-920.9629	0	8446
A -T (II)	-921.1906	-920.9593	791	7654
A-T (III)	-921.1889	-920.9573	1220	7226
A -T (IV)	-921.1883	-920.9568	1331	7115

A= adenine, T= thymine, * E_{ZPVE} = Corrected with zero point vibrational energy

The most stable structure is the isomer I where adenine and thymine are connected via two hydrogen bonding. Second, third and fourth stable isomers are II, III and IV where adenine and thymine are connected via three hydrogen bonding. Isomer II, III and IV are less stable by 791 cm^{-1},1220 cm^{-1} and 1331 cm^{-1} than isomer I, respectively. Binding energy between adenine and thymine is found 8446 cm^{-1} in case of the most stable isomer I. On the other hand, 7654 cm^{-1}, 7226 cm^{-1} and 7115 cm^{-1} are found for isomers II, III and IV.

Electronic absorption properties

To understand the electronic properties of adenine-thymine basepair, we have used TD-DFT to calculate excited state properties for excitation from the ground state to the higher electronic states. For this purpose, we have calculated six lowest singlet electronic states from the ground state of AT basepair.

Table 2. Calculated wavelengths λ (nm), excitation energies E(eV), oscillator strength (f) and major electronic transitions of adenine-thymine basepair

λ/nm	E/eV	f	Major transitions
262	4.73	0.0139	HOMO→LUMO (99%)
248	5.00	0.2133	H-1→LUMO (37%), H-1→L+1 (18%), HOMO→L+1 (34%)
245	5.06	0.0698	H-1→LUMO (53%), H-1→L+1 (11%), HOMO→L+1 (20%)
243	5.10	0.0804	H-1→L+1 (70%), HOMO→L+1 (18%), H-4→L+1 (3%), HOMO→L+2 (6%)

H = HOMO & L = LUMO

The computed electronic values such as absorption wavelength (λ), excitation energies (E) and oscillator strengths (f) are tabulated in Table 2. The major transition with highest oscillator strength (f = 0.2133) for AT basepair is at 248 nm (5.00 eV). This is a mixture transition occurs at H-1→LUMO (37%), H-1→L+1 (18%) and HOMO→L+1 (34%). HOMO to LUMO (99%) ($\pi \rightarrow \pi^*$) transition occurs at 262 nm (4.73 eV) with an oscillator strength of 0.0139.

As we know that the frontier molecular orbitals (FMO) play an important role in the electronic properties. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy were calculated by TD-DFT/B3LYP/6-31G method and the HOMO-LUMO energy gap of adenine-thymine basepair is as follows:

$HOMO_{energy}$ = -6.33 eV, $LUMO_{energy}$ = -1.17 eV, HOMO - LUMO energy gap = 5.16 eV.

Therefore, the energy gap of FMO of AT basepair is 5.16 eV. The HOMO and LUMO that participate in lowest electronic transitions of AT basepair are presented in Fig. 2 as a Jablonski diagram.
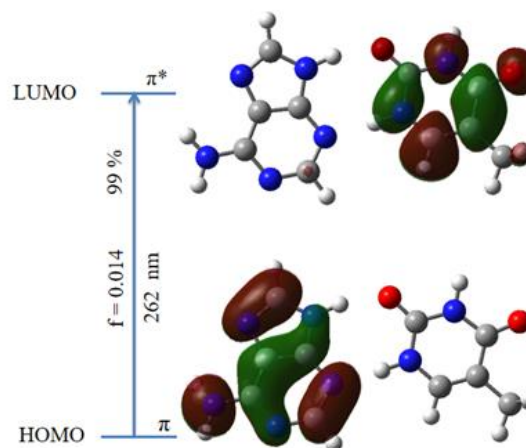

Fig. 2. Banlonski Diagram and Singlet excited-state transition from HOMO→LUMO of adenine-thymine basepair

Conclusion

The structural and electronic properties of adenine-thymine (AT) basepair were studied theoretically. Four isomers of AT basepair were found. The most stable isomer is one where adenine and thymine are connected via two hydrogen bonding. The investigation of electronic properties shows that the HOMO-LUMO energy band gap of AT basepair at B3LYP level is 5.16 eV. The major transition with highest oscillator strength (f = 0.2133) for AT basepair is at 248 nm (5.00 eV) occurs at H-1→LUMO (37%), H-1→L+1 (18%) and HOMO→L+1 (34%) whereas HOMO to LUMO (99%) (π→π*) transition occurs at 262 nm (4.73 eV) with an oscillator strength of 0.0139.

Acknowledgement

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