

A Theoretical Investigation of the Structural, Spectroscopic and Optical Properties of Adenine

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(Received : 3 September 2015; Accepted: 12 January 2016)

Abstract

The structural, spectroscopic (IR, NMR and UV-Vis) and optical properties of adenine (6-aminopurine, C₅H₅N₅) are investigated theoretically using HF/DFT hybrid approach B3LYP. The calculated results are compared with available experimental data. The optimized bond distances and bond angles are converged within ± 0.01 Å and $\pm 0.8^\circ$ with respect to the experimental values. The investigation of ¹H NMR chemical shift spectra of the aromatic C-H protons shows that the maximum deviation of the calculated chemical shift is ~ 0.53 ppm compared to the experimental data. The calculated vibrational spectra analysis shows four distinct IR active mode of vibrations which are assigned as scissoring vibration of –NH₂, symmetric stretching vibration of –NH₂, free –NH vibration and anti-symmetric stretching vibration of –NH₂, respectively. The electronic and optical properties are calculated by Time Dependent Density Functional Theory (TD-DFT) approach. A reasonable agreement is obtained for the calculated optical absorption energy with the experimental value.

Keywords: Adenine, TD-DFT, IR, NMR, Electronic properties, Optical absorption

I. Introduction

It is well known that adenine is one of the four nucleic acid bases (adenine, guanine, cytosine and thymine) that constitutes the building blocks of life. Adenine encodes the genetic information of all organisms in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).¹⁻³ It helps stabilize the nucleic acid portion of these molecules. Additionally, adenine is found in adenosine triphosphate (ATP), a molecule that carries the energy needed for work in cells. Adenine also occurs as a component of a number of coenzymes, such as coenzyme I (nicotinamide adenine dinucleotide (NAD⁺) or diphosphopyridine nucleotide (DPN⁺)) and coenzyme II (nicotinamide adenine dinucleotide phosphate (NADP⁺) or triphosphopyridine nucleotide (TPN⁺)). These coenzymes are often involved in oxidation-reduction processes in biological reactions together with the appropriated enzyme. These nucleobases absorb UV light strongly and act as a primary chromophores of DNA.⁴⁻⁶ Photostability of DNA bases is the essential criteria for the preservation of genetic information of DNA bases. As nucleobases absorb UV light strongly, therefore the knowledge of the electronic properties and excited state lifetimes are of paramount importance for understanding the UV radiation induced DNA damage.⁷⁻¹² Numerous experimental and theoretical studies on DNA and DNA bases have been performed to understand structural, electronic properties and excited state lifetimes.¹³⁻¹⁶ All the calculations have been focused on the ground state to the higher electronic singlet and triplet states of the neutral molecules.

In this paper, we have performed a theoretical investigation of structural, spectroscopic, electronic and optical properties of adenine with HF-DFT hybrid approach and compared with the available experimental data. The optical properties have been calculated at the excited states using TD-DFT method.

II. Computational Details

The total quantum chemical calculations have been performed using hybrid approach B3LYP¹⁷ as implemented in the quantum chemistry package G09.¹⁸ We have used 6-311+G(d,p) basis set in order to calculate the structure, IR, ¹H NMR and UV-Vis spectra of adenine in the ground state at the B3LYP level of theory. The optimized structure of adenine in the ground state was verified by calculating vibrational frequencies to confirm that there were no imaginary frequencies. Excited state calculations have been done by TD-DFT method employing B3LYP functional and 6-311+G(d,p) basis set to study electronic and optical properties of adenine and we have calculated six excited states of adenine.

III. Results and Discussion

Molecular geometry and thermodynamics parameters

The most optimized DFT geometry by B3LYP of adenine is shown in Fig. 1 with leveling. For optimizing minimum energy structure of adenine, first we have done intrinsic reaction coordinate (IRC) calculation with HF/6-31G and have taken minimum energy structure and reoptimized using DFT/B3LYP/6-311+G(d,p) level of theory.

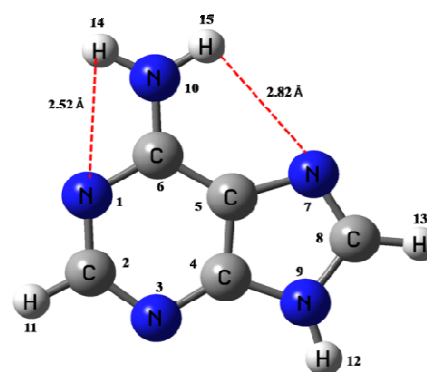


Fig. 1. Optimized structure of adenine

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The final geometry corresponds to true energy minima as revealed by the lack of imaginary frequencies in the vibrational mode calculation. Due to the lone pair of electron on the nitrogen atom in the amino group of adenine, amino group exist as bent shape. However, the optimized structure of adenine is planer which is due to the delocalization of electrons through the whole molecule. The

optimized bond distances and bond angles are compared with available experimental data in Table 1.

It is observed that the bond distances converged within ± 0.01 Å and the largest deviation of bond angle is 0.8° with respect to the experimental values.¹⁹

Table 1. Comparison of calculated bond lengths (Å) and bond angles (°) with available experimental data.

Bond Length (Å)		Calc.	Expt.
	N(1)-C(2)	1.341	1.338
	C(2)-N(3)	1.334	1.332
	N(3)-C(4)	1.340	1.342
	C(4)-C(5)	1.397	1.382
	C(5)-C(6)	1.410	1.409
	C(6)-N(1)	1.348	1.349
	C(4)-N(9)	1.373	1.376
	C(5)-N(7)	1.385	1.385
	N(7)-C(8)	1.312	1.312
	C(8)-N(9)	1.374	1.367
	C(6)-N(10)	1.348	1.337
Bond Angle (°)			
	N(1)-C(2)-N(3)	128.5	129.0
	C(2)-N(3)-C(4)	111.6	110.8
	N(3)-C(4)-C(5)	126.3	126.9
	C(4)-C(5)-C(6)	116.4	116.9
	C(5)-C(6)-N(1)	118.3	117.6
	C(6)-N(1)-C(2)	118.7	118.8
	C(5)-C(4)-N(9)	104.8	105.7
	N(1)-C(6)-N(10)	119.0	119.0

The total energy (SCF), zero point vibrational energy (ZPVE), rotational constants, specific heat capacity (C_v) at

constant volume, entropy (S) and dipole moment of adenine are provided in the Table 2.

Table 2. Calculated thermodynamic parameters of adenine

SCF energy /Hartree	Z PV energy /kcal mole ⁻¹	Rotational constant /GHz	Specific heat Capacity (C_v) /cal mol ⁻¹ K ⁻¹	Entropy (S) /cal mol ⁻¹ K ⁻¹	Dipole moment, μ /Debye
-467.4661	69.9800	2.3775 1.5639 0.9433	28.866	84.494	3.4109

¹H NMR spectral analysis

The NMR spectroscopy is one of the most powerful techniques for the structural analysis of organic compounds. It is well-established that the combined use of experimental NMR spectroscopic technique and computational simulation methods give a powerful gadget to interpret and predict the

structure of organic compound, even for the structures of large biomolecules. To get theoretical ¹H NMR results of adenine, first the full geometry optimization is carried out with the B3LYP/6-311G+(d,p) in gas phase. After optimization, ¹H NMR calculations are calculated by using the gauge-including atomic orbital (GIAO) method. The chemical shifts of the compounds are reported in ppm

relative to tetramethylsilane (TMS) for ^1H NMR spectrum presented in Table 3. The chemical shift of H(11), H(12), H(13), H(15) and H(14) protons are observed at 8.42, 8.15, 7.58, 5.15 and 4.74 ppm, respectively.

Table 3. Calculated ^1H NMR data of adenine

Protons with number	Chemical Shift (This work) /ppm	Chemical Shift (Experimental) /ppm
H(11)	8.42	8.14
H(12)	8.15	
H(13)	7.58	8.11
H(15)	5.15	
H(14)	4.74	

As we know that electron donating atom increases the shielding and moves the resonance towards lower frequency and electron-withdrawing atom can decrease the shielding and moves the resonance of attached proton towards higher frequency.

Table 4. IR calculated and experimental frequencies of adenine

IR calculated frequencies/cm $^{-1}$	IR experimental frequencies/cm $^{-1}$	IR active mode of vibration
1542	-	Scissoring of $-\text{NH}_2$
3420	3400	Symmetric $-\text{NH}_2$ stretching vibration
3445	3441	Free $-\text{NH}$ stretching vibration
3540	3495	Anti-symmetric $-\text{NH}_2$ stretching vibration

Calculated values were corrected by multiplying the frequency factor, $f = 0.950$

Table 5. Calculated wavelengths λ (nm), excitation energies E(eV) and oscillator strength (f) and major electronic transitions of adenine

λ /nm	E/eV	f	Major transitions
251	4.93	0.273	H \rightarrow L (90%) & H \rightarrow L+1 (4%) H-1 \rightarrow L (98%)
243	5.10	0.0007	

H = HOMO & L = LUMO

The computed electronic values such as absorption wavelength (λ), excitation energies (E) and oscillator strengths (f) are tabulated in Table 5. The major transition with highest oscillator strength for adenine molecule is at 251 nm (4.93 eV). This transition occurs from HOMO to LUMO (90%) ($\pi\rightarrow\pi^*$) with a minor transition at 243 nm

We have also found similar results for adenine. As amino protons, H(15) and H(14) are de-shielded compared to the other protons, chemical shift moves to the lower frequency region. H(15) shows chemical shift at 5.15 ppm whereas H(14) shows at 4.74 ppm. This difference in chemical shift is due to the interaction with nearest nitrogen atoms. Theoretically we measured the distance between H(15) and N(7) is 2.82 Å and H(14) and N(1) is 2.52 Å. Experimental ^1H NMR spectrum of adenine shows exactly similar results depending upon solvents.²⁰

Vibrational spectral analysis

The assignments of the vibrational frequencies (calculated and observed) are shown in Table 4. In the calculated spectrum of adenine, four IR active mode of vibrations were found at 1542, 3420, 3445 and 3540 cm^{-1} which are assigned as scissoring vibration of $-\text{NH}_2$, symmetric stretching vibration of $-\text{NH}_2$, free $-\text{NH}$ vibration and anti-symmetric stretching vibration of $-\text{NH}_2$ respectively. Three IR absorption bands at 3400, 3441 and 3495 cm^{-1} were observed experimentally which are assigned asymmetric stretching vibration of $-\text{NH}_2$, free $-\text{NH}$ vibration and anti-symmetric stretching vibration of $-\text{NH}_2$, respectively.²¹

(5.10 eV) from HOMO-1 to LUMO. Experimental²² and theoretical UV-Visible absorption spectrum of adenine is shown in Fig. 2. From the figure it is very clear that adenine is a colorless compound as it does not absorb any visible light.

The experimental UV-Visible absorption spectrum of adenine is at 261 nm which shows that our calculated spectrum is in very good agreement with experiment. Little red shift from 251 nm is due to the solvent used to measure UV-Visible absorption spectrum of adenine. As we know that the frontier molecular orbitals (FMO) play an important role in the optical and electronic properties. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy were calculated by TD-DFT/B3LYP/6-311+G(d,p) method and the HOMO-LUMO energy gap of adenine is as follows:

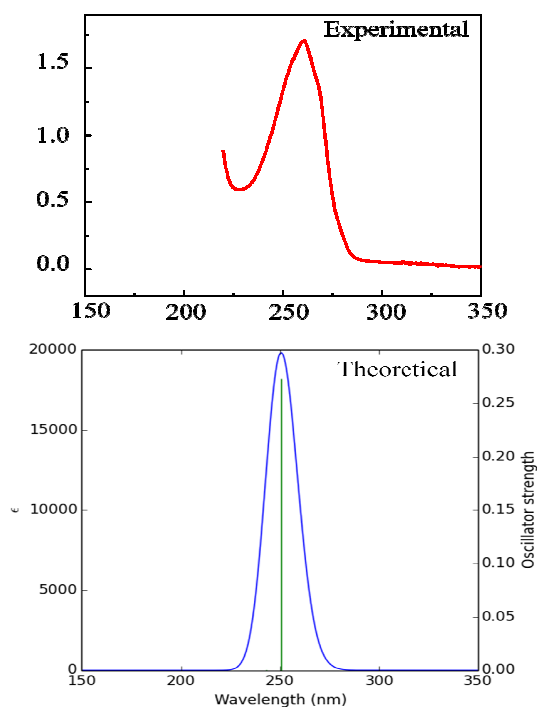


Fig. 2. Experimental (upper panel) and calculated (lower panel) UV-Vis absorption spectrum of adenine

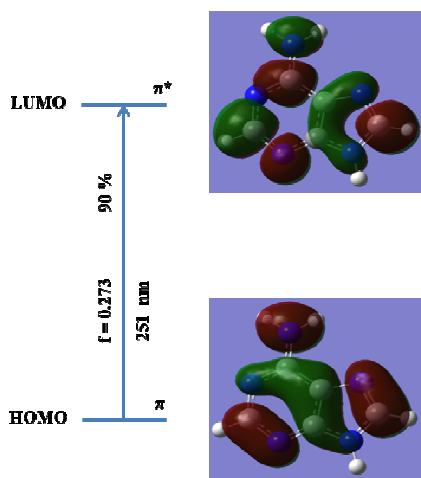


Fig. 3. Jablonski diagram and singlet excited-state transition from HOMO \rightarrow LUMO of adenine.

$\text{HOMO}_{\text{energy}} (\text{B3LYP}) = -6.45 \text{ eV}$,

$\text{LUMO}_{\text{energy}} (\text{B3LYP}) = -1.10 \text{ eV}$

$\text{HOMO} - \text{LUMO energy gap (B3LYP)} = 5.35 \text{ eV}$

Therefore the energy gap of FMO of adenine is 5.35 eV. The HOMO and LUMO that participate in lowest electronic transitions of adenine are presented in Fig. 3 as a Jablonski diagram.

IV. Conclusion

The molecular geometry optimization, thermodynamic properties, vibration frequency assignments, electronic and

optical properties of adenine molecule were studied theoretically. The optimized geometrical parameters such as bond distances and bond angles are well converged with respect to the experimental values. The calculated ^1H NMR chemical shift spectra of the aromatic C-H protons range between 8.0 to 8.15 ppm which are in well accord with the experimental data. The calculated IR active mode of vibrations and their assignments are in reasonable agreement with the available experimental data. The investigation of electronic properties shows that the HOMO-LUMO energy band gap of adenine at B3LYP level is 5.35 eV. The calculation of optical properties at excited states shows that the major transition (from HOMO to LUMO (90%) ($\pi \rightarrow \pi^*$)) occurs at 251 nm (4.93 eV) with a minor transition at 243 nm (5.10 eV). Our theoretical UV-Visible absorption spectrum clearly suggests that adenine is a colorless compound as it does not absorb any visible light which is in good agreement with experiment.

Acknowledgement

This work was supported by Dean Office, Faculty of Science, University of Dhaka, Dhaka-1000, Bangladesh.

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