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Ab *initio*, DFT and TD-DFT electronic absorption spectra investigations on 3,5-diamino-1,2,4-triazole

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ABSTRACT

The electronic absorption spectra of 3,5-diamino-1,2,4-triazole was recorded in the region of 190-450 nm. Quantum chemical calculations of energies, geometrical structures and electronic absorption spectra of 3,5-diamino-1,2,4-triazole were carried out by ab initio HF/6-31+G*, DFT (B3LYP/6-31+G*) and TD-DFT /B3LYP/6-31+G* level of theory with complete relaxation in the potential energy surface. The Mulliken charge analysis indicates that the nitrogen atoms of the triazole ring and the amino group attached to the ring are the main reactive centers of 3,5-diamino-1,2,4-triazole. The calculated HOMO-LUMO energies show that the molecule has low energy gap which implies low kinetic stability and high chemical reactivity. The study is extended to the analysis of dipole moment, E_{HOMO}, E_{LUMO} both in the gas phase and in the presence of solvent for comparison. Thermodynamic properties were also calculated and discussed. The calculated values of absorption wavelengths are compared with the experimental data for this molecule as a means of validation of the theoretical model used. The predicted results are in excellent agreement with the experimental ones.

Introduction

A good number of five membered aromatic systems having three heteroatoms at symmetrical positions have been studied because of their interesting physiological properties. The presence of three nitrogens in triazole provides an interesting class of compounds. Triazole and its derivatives exhibits broad spectrum of pharmacological properties such as antibacterial and antifungal activities [1] and also there are a lot of reports on the interaction between triazole and metal in preventing corrosion of metals [2-5]. Although triazole and its derivatives show a wide spectrum of activity, literature search revealed that not much has been reported about the structure/activity relationship of this class of compounds. The electronic properties in particular the HOMO-LUMO gap of a compound gives information about the stability and chemical reactivity of the compound [6-8].

In order to gain an insight into the relationship between structure and reactivity, a derivative of triazole (3,5-diamino-1,2,4-triazole), a molecule with two symmetrical positioned NH_2 groups has been chosen for this study. The vibrational frequencies of parent triazole compound have been reported [9, 10] based on classical or low level quantum chemical calculations. Kumar et.al., [11] also reported on the influence of hydrogen bonding on the vibrational spectroscopic properties of triazole and 3,5-diamino-1,2,4-triazole using DFT at B3LYP/6-31G* level of theory. To the best of our knowledge, the electronic absorption spectra of 3,5-diamino-1,2,4-triazole in DMSO using TD-DFT at B3LYP/6-31+G* level of theory has not been reported.

Therefore using classical ab *initio* methods based on self-consistent field molecular orbital Hartree-Fock theory (HF), density functional theory (DFT) and time dependent density functional theory (TD-DFT) with the 6-31+G* basis set, we investigate the optimized structure, Mulliken charge distributions, HOMO-LUMO gap, thermodynamic and electronic transition of 3,5-diamino-1,2,4-triazole. The electronic absorption spectra obtained theoretically have been compared with the experimental absorption bands.

Experimental and Computational methods

3,5-diamino-1,2,4-triazole of analytical grade, was obtained commercially from Molekula (USA) and was used without further purification.

The electronic absorption spectra of 3,5-diamino-1,2,4-triazole was obtained in DMSO in the UV-Visible region on a Shimadzu UV3100 spectrophotometer.

The ground state geometries of 3,5-diamino-1,2,4-triazole were optimized by using the Gaussian-03 series of programs [12]. For this purpose the B3LYP/DFT approach, which includes the interchange hybrid functional from Becke [13] in combination with the three–parameter correlation functional by Lee-Yang-Parr [14] and Hatree Fock calculation [15] was employed in combination with the basis set 6-31+G* which include diffuse functions which are required to get more reliable results [16].

Vibrational frequencies calculated showed that there was no imaginary frequencies (the compound is a minimum on the potential energy surface).

After the ground state geometry optimization, the excitation spectrum of the title compound was computed with TD-DFT, using the 6-31+G* basis set. During the TD-DFT calculations, the bulk solvent effects are considered by means of the polarizable continuum model (PCM) [17,18]. In PCM, one divides the problem into a solute part (3,5-diamino-1,2,4-triazole) lying inside a cavity, and a solvent part (in this work, Dimethylsulphoxide (DMSO)) represented as a structureless material, characterized by its dielectric constant as well as other macroscopic parameters.

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Results and discussion

Optimized geometry

The optimized geometrical parameters, namely, bond lengths and angles calculated by B3LYP/6-31+G* and HF/6-31+G* levels listed in Table 1 are in accordance with atom numbering scheme given in Fig. 1. To the best of our knowledge, experimental data on the geometric structure of 3,5-diamino-1,2,4-triazole are not available in the literature.

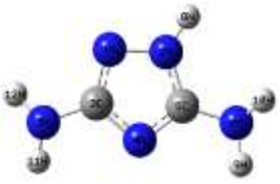

Fig. 1. The optimized structure of of 3,5-diamino-1,2,4-triazole

From Table 1, it is noted that the bond lengths calculated by B3LYP method are bigger than those calculated by HF method. Similar observations have been documented [19]. Optimized structure yields different bond lengths for the C=N bonds (C3-N1, C3-N4, C5-N2 and C5-N4) on the triazole ring at the two levels of calculations B3LYP/6-31+G* and HF/6-31+G*. The B3LYP/6-31+G* gave values of the C-N bonds on the triazole ring closer to the normal C=N bond length of 1.38 Å [20]. Furthermore the C-N bonds of the two amino groups gave values for both B3LYP/6-31+G* and HF/6-31+G* methods which are shorter than the experimental C-N single bond length value of 1.47 Å [21].

The bond angles calculated by B3LYP method are nearly equal to those calculated by HF method. The bond angles N1-N2-H8, N4-C3-N7, N2-C5-N6 and N4-C5-N6 are about 120^o at both level of theory, indicating that they are of sp^2 hybridization type. In addition, similar analysis are made for the other bond angles which are less than 120^o showing marked deviations from planarity.

Atomic charges

Table 2 gives the Mulliken atomic charges of 3,5-diamino-1,2,4-triazole calculated at B3LYP/6-31+G* and HF/6-31+G* levels, respectively. All the nitrogen atoms of the triazole ring carries considerable negative charge. However, the highest negative charges were carried by the two amino nitrogens (N6 and N7). It has been reported that the more negative the atomic charges that an atom carries, the more easily the atom donates its electron to the unoccupied orbital of a metal [21]. Thus, 3,5-diamino-1,2,4-triazole have reactive sites which can both undergo protonation and coordination with metallic ions. This feature makes the title compound very effective as a ligand. Another important feature of the atomic charge distribution is that C3 and C5 have net positive charges. which can accept electrons from orbital of metal atoms to form feedback bond. This makes 3,5-diamino-1,2,4-triazole to form strong coordination bond to metal because excellent ligands can not only offer electrons to unoccupied d- orbital of the metal, but also accept free electrons from the metal.

Electronic absorption spectra

The electronic absorption spectra of 3,5-diamino-1,2,4-triazole in a solution of DMSO exhibit an intense band near 208 nm (Fig. 2). We have also calculated electronic absorption spectra of 3,5-diamino-1,2,4-triazole in DMSO using TD-DFT at B3LYP/6-31+G* level by adding the polarizable continuum model (PCM). The theoretical and experimental absorption wavelengths are compared in Table 3. The absorption band maximum corresponding to HOMO-LUMO transition takes place at 208 nm for both approach. This wavength also gives the highest excitation energy of 5.9575 eV fot the title compound. It is clear from the study that the experimental and theoretically obtained absorption spectra are in excellent agreement. As the HOMO-LUMO transition takes place in the ultraviolet region, it can be predicted that this molecule will be colourless.

Fig.2. Experimental UV-Visible spectra of 3,5-diamino-1,2,4-triazole

Frontier molecular orbital (FMOs)

The highest occupied molecular orbital (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are named as frontier molecular orbitals. The FMOs play an important role in the electrical and optical properties, as well as in UV-Vis spectra and chemical reactions [22]. According to the description of frontier orbital theory, HOMO is often associated with the electron donating ability of an inhibitor molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons. E_{LUMO} indicates the ability of the molecules to accept electrons [23]. The lower value of E_{LUMO} is the easier acceptance of electrons [24]. The gap between the LUMO and HOMO energy levels of molecules is another important stability index. The low absolute values of the energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) implies low kinetic stability and high chemical reactivity [25].

Fig. 3. Shows the HOMO and LUMO frontier orbitals of 3,5-diamino-1,2,4-triazole with B3LYP/631+G* basis set. The HOMO and LUMO are localized on the entire molecule. Both the HOMOs and the LUMOs are mostly π-antibonding type orbitals and thus, the electronic transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) are mainly derived from the contribution of π-π^* bands. It was confirmed experimentally [1] that the high antibacterial activity of 3,5-diamino-1,2,4-triazole was due to the presence of the triazole moiety. The HOMO and LUMO structures support this. The concentration of electron densities in the triazole moiety and in the two amino substituent makes 3,5-diamino-1,2,4-triazole a very active antibacterial compound.

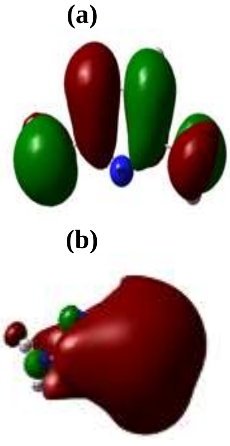

Fig. 3. (a) HOMO and (b) LUMO frontier orbitals of 3,5-diamino-1,2,4-triazole with B3LYP/631+G* basis set.

Table 4 shows the calculated values for E_{HOMO}, E_{LUMO}, energy of the gap (ΔE) and dipole moment (D) in the gas phase and in the presence of DMSO and methanol. It is evident from this table there is a difference in the values of the parameters calculated in the gas phase and in the presence of solvents in one hand and among the two solvents on the other hand. For example high values of dipole moment were obtained in the solvents as compared to the gas phase. Futhermore, higher dipole moment were obtained in DMSO than in methanol. This may be as a result of the high polarity of DMSO. Thus the title compound is expected to interact more with DMSO. It has been reported that with the rising polarity of the solvent, the total molecular energy of title molecule should diminish and so the stability of the structure should increase [15]. Due to the inductive solvent polarization effects in the polar solvents, the dipole moment increases with the polarity of the solvent. Since the HOMO-LUMO energy seperation has been used as a simple indicator of kinetic stability, it can be said that the title molecule which has a small HOMO-LUMO gap (0.1965 eV, calculated at the B3LYP/631+G^* level in the gas phase) implies low kinetic stability and high chemical reactivity.

Thermodynamics properties

Several thermodynamic properties like heat capacity, zero point energy, entropy along with the global minimum energy of ,5-diamino-1,2,4-triazole have been obtained by ab initio HF and density functional methods using 6-31+G^* basis set and the calculations are presented in Table 5. The difference in the values calculated by both the methods is only marginal. Scale factors have been recommended [26] for an accurate prediction in determining the zero-point vibration energy (ZPVE), and the entropy (Svib). The variation in the ZPVE seems to be insignificant. The total energy and the change in the total entropy of 3,5-diamino-1,2,4-triazole at room temperature at B3LYP/6-31+G^* and HF/6-31+G^* level of theory are only marginal.

Conclusions

The results of the study lead to the following conclusions.

1. Ab initio and DFT calculations on the equilibrium geometries of 3,5-diamino-1,2,4-triazole using HF/6-31+G^* and DFT/B3LYP/6-31+G^* has been performed for the first time.
2. The experimental UV-Vis absorption spectra were compared with the theoretical calculations for the molecule using TD-DFT/ B3LYP/6-31+G^*. The results obtained indicates that the two approaches are in agreement.
3. The TD-DFT calculations are powerful approach for calculating the electronic absorption spectra of organic compounds.
4. Atomic charge distribution analyses show that 3,5-diamino-1,2,4-triazole can use its four nitrogen atoms as reactive centers.
5. The HOMOLUMO energy gap and other related molecular and thermodynamic properties were discussed and reported.

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Table 1. Optimized geometrical parameters of the title compound with HF and B3LYP method with 6-31+G* basis set, Bond Lengths (Å) and Bond Angles (^{o}).

Bond lengths	HF	B3LYP	Bond angles	HF	B3LYP
N1-N2	1.3758	1.3870	N2-N1-C3	101.7	101.2
N1-C3	1.2930	1.3240	N1-N2-C5	109.5	109.8
N2-C5	1.3262	1.3502	N1-N2-H8	120.2	119.4
N2-H8	0.9927	1.0090	C5-N2-H8	129.3	129.5
C3-N4	1.3596	1.3721	N1-C3-N4	115.6	115.7
C3-N7	1.3726	1.3836	N1-C3-N7	123.5	123.0
N4-C5	1.3037	1.3243	N4-C3-N7	120.8	121.1
C5-N6	1.3690	1.3841	C3-N4-C5	102.5	102.6
N6-H9	0.9976	1.0141	N2-C5-N4	110.7	110.3
N6-H10	0.9976	1.0139	N2-C5-N6	123.9	124.1
N7-H11	0.9970	1.0127	N4-C5-N6	125.3	125.4
N7-H12	0.9973	1.0129	N5-N6-H9	112.6	111.6
			N5-N6-H10	115.8	115.5
			H9-N6-H10	112.4	111.6
			C3-N7-H11	113.6	113.5
			C3-N7-H12	114.1	114.0
			H11-N7-H12	113.2	113.1

Table 2. Mulliken atomic charges of the title compound

Atom	HF/6-31+G*	B3LYP/6-31+G*
N1	-0.275528	-0.234491
N2	-0.649321	-0.529273
C3	0.486278	0.372377
N4	-0.598936	-0.505336
C5	0.729521	0.570850
N6	-0.932947	-0.829964
N7	-0.906784	-0.807583
H8	0.470356	0.410141
H9	0.438269	0.404444
H10	0.408083	0.378404
H11	0.415127	0.384322
H12	0.415881	0.386110

Table 3. Theoretical and experimental adsorption wavelength for the title compounds using TD-DFT/631+G* in DMSO (ε =46.7).

Oscillator strength (f)	Theoretical wavelength, nm	Expt. wavelength, nm	Excitation energy, eV
0.0002	244.19	-	5.00773
0.0081	229.73	-	5.3970
0.1269	208.11	208.20	5.9575

Table 4. Calculated E_{HOMO}, E_{LUMO}, energy of the gap (ΔE) and dipole moment (D) in the gas phase and in the presence of DMSO and methanol.

	Gas phase (ε =1)		TD-DFT/B3LYP /6-31+G*	
Parameters	HF/6-31+G*	B3LYP/6-31+G*	DMSO(ε =46.7)	Methanol (ε =33)
E_{HOMO} (eV)	-0.32495	-0.21216	-0.21566	-0.21555
E_{LUMO} (eV)	0.05583	-0.01565	0.00335	0.00329
ΔE (eV)	0.26912	0.19651	0.21231	0.21226
μ (D)	2.8855	2.5936	3.5852	3.5716

Table 5. Theoretically computed energies (au) , zero-point vibrational energies(ZPVE) (kcal/mol), rotational constants (GHz) and entropies (cal/mol/K) for the title compound at 298.15 K and 1 atm. with 631+G* basis set.

Parameters	HF	B3LYP
Total Energy	-350.8944	-352.9876
Zero-point energy	63.44895	58.62435
Rotational constants	7.57339	7.32556
	0.10793	0.10549
	0.08351	0.08146
Entropy		
Total	76.594	78.312
Translational	39.690	39.690
Rotational	26.786	26.690
Vibrational	10.118	11.755