DFT supported investigations on molecular geometry and electronic structure of Mannich Base N-(Morpholinomethyl) pyrrolidine-2,5-dione

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Abstract: The N-(Morpholinomethyl) pyrrolidine-2,5-dione (SMF) is a synthesized mannich base which has significant application for optical properties. The optimized structural parameters obtaining through B3LYP method with 6-31G (d,p) basis set were indicatively concurrence with available experimental crystal structure. The electronic structure of the molecular system and the optical properties were also studied from quantum chemical calculations with the help of Density Functional Theory (DFT). The dipole moment, Mulliken charge population and molecular electrostatic potential were employed at the same basic set of theory. The second harmonic generation (SHG) of SMF molecule was estimated to be 14.45 times greater than the standard urea material.

Keywords: DFT, SMF, SHG, Mannich reaction, electron density, Mulliken analysis

1. INTRODUCTION

The Mannich-type reactions indicate the significant strategy in the field of organic compounds. The Mannich base reaction is one of the most vital results in the formation of carbon-carbon-carbon bond bridge. As a resultant of these types of reactions, the organic chemist can develop several outstanding structures for molecules containing nitrogen which act as the "architectural" blocks for designing pharmaceutical products and many biologically active compounds like alkaloids, peptides, nucleotides, antibiotics, steroid hormones and vitamins [1,2]. The Mannich reactions have been designed by several research teams utilizing the variety of catalysts i.e. amino acids and their derivatives and also the organometallic complexes [3,4]. Nowadays, the most significant synthesized of Mannich base compounds are used for corrosion protection by adding of organic inhibitors which apply on the brass. Most of the inhibitors consist of organic compounds containing aromatic rings, nitrogen, sulphur, oxygen, and phosphorous that enhances the adsorption on the metal surface [5]. The Mannich base molecule containing C=N group, increases the adsorption capacity and efficient of inhibition activity. The morpholine derivatives are broadly used in synthesis of organic compounds. It is a construction block in the synthesis of the anticancer agent gefitinib [6] and antibiotic linezolid [7]. The derivatives of morpholine molecule are widely used as agricultural fungicides. Cyclic imides like maleimides, succinimides, phthalimides, glutarimides and interrelated compounds own their structural features. Their molecule consists of imide ring having the general molecular formula CO-N(R)-CO-, so that they are neutral and hydrophobic which can diffuse through biological membranes [8]. Bundgaard and coworkers have formerly discovered the significance of N-Mannich bases like prodrug forms for antibiotics containing amine compounds [9]. For design, the N-Mannich type bases of amines with succinimide are represented as the prodrug of pharmaceutical importance.

To the best of our knowledge, the ab-initio studies of the molecular geometry and correlation diagram based on DFT studies of our synthesized molecule in the gas phase have not been made. In this work, the B3LYP levels of the 6-31G (d,p) basis set were used to make the Ab-initio studies of the complete molecular geometry of the SMF molecule. The molecular characters such as molecular geometry, UV-DRS, band gap energy, Mulliken charge analysis, dipole moment and NLO activity of these molecules are described via DFT studies.

2. Experimental Details

2.1. SYNTHESIS OF 1-(MORPHOLINOMETHYL)SUCCINIMIDE (SMF)

N-(Morpholinomethyl) Succinimide (SMF) was synthesized by Mannich condensation reaction [10] among succinimide, morpholine and formaldehyde in 1:1:1 molar ratio. Succinimide (5.00g, 0.05M) a n d morpholine (4.5 ml, 0.05M) mixed with the less amount of e t h a n o l was stirred until the content becomes homogenous. To this mixture 40 % formaldehyde solution (3.8ml, 0.05M) was poured slowly in drops, as the stirring action continued. Once the adding process was over, stirring continued for 2 h at 60°C and then it was made to cool in refrigerator. The obtained solid mass was washed with distilled water, desiccated and the final product was recrystallized from acetonitrile to get a white crystalline powder (Yield: 88 %). The synthesized scheme of SMF molecule was earlier reported [10].

2.2. Experimental Method

The SMF molecule was synthesized and reported earlier [10]. UV-Vis spectrum was recorded in DMSO solvent by employing the Lambda-35 Perkin Elmer spectrophotometer as a part of the spectral locale of 1100-190 nm as display in Fig.1.
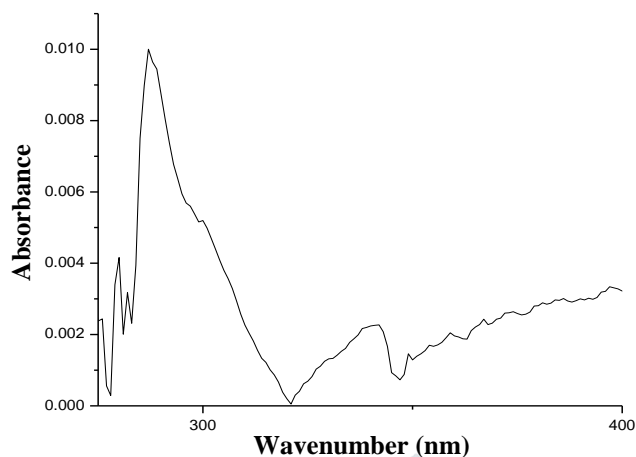
Fig.1 UV- Visible spectrum of SMF molecule

2.3. Computational Details

Density Functional Theory (DFT) predictions were obtained in the Gaussian-09 program [11] package used in SMF molecule. The Becke three parameter hybrids functional process has been available in this work. It consists of non-local exchange functional of Becke style three parameter sets and the non-local correlation functional of Lee, Yang and Parr [12,13]. The triple-split valence Gaussian function commonly with polarization functional, for both heavier atoms and lightest atom like hydrogen, 6-31G (d, p) basis levels have been concerned in the calculations. The UV-Vis spectra and electronic properties of molecular orbital energies were simulated by Time-Dependent DFT (TD-DFT).

3. Result and Discussion

3.1. Molecular geometry

Generally, the complete molecular properties are always correlated with the structural parameters of a molecule. Therefore, an accurate inquiry has been available on structural characterization of SMF molecule order to archive this complicated task and the structural parameters of bond length (BL) was computed under B3LYP/6-31G (d,p) theoretical models and compared with available experimental crystal structure. The optimized molecular geometry of SMF molecule is shown in Fig.2. which contain 26 individual atoms and their connectivity resulted in the assembly of 27 BL. The predicted and observed results about the relative plot of bond length are shown in Fig.3a and the resultant values are given in Table 1. The agreement within the estimated experimental uncertainty has been evaluated by means of correlation coefficient (R2). The graphical imprint of R2 is given in Fig.3b for bond length. All the 27 BL shows agreement with the computed and crystal geometrical data. The BL of C-C, C-N, and C=O show the least difference from observed value, but the major difference was observed in C-H BL. This could be due to the physical state of the material, when the structural parameters of the molecule are calibrated by DFT studies (gas phase) and the experiment (solid phase) [14]. The experimental results are linked by simulated results and quadratic equations for model chemistry are given as follows,
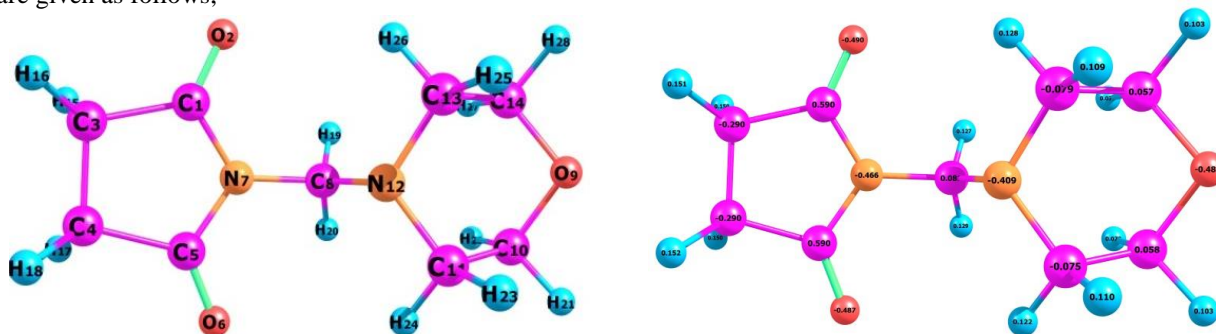

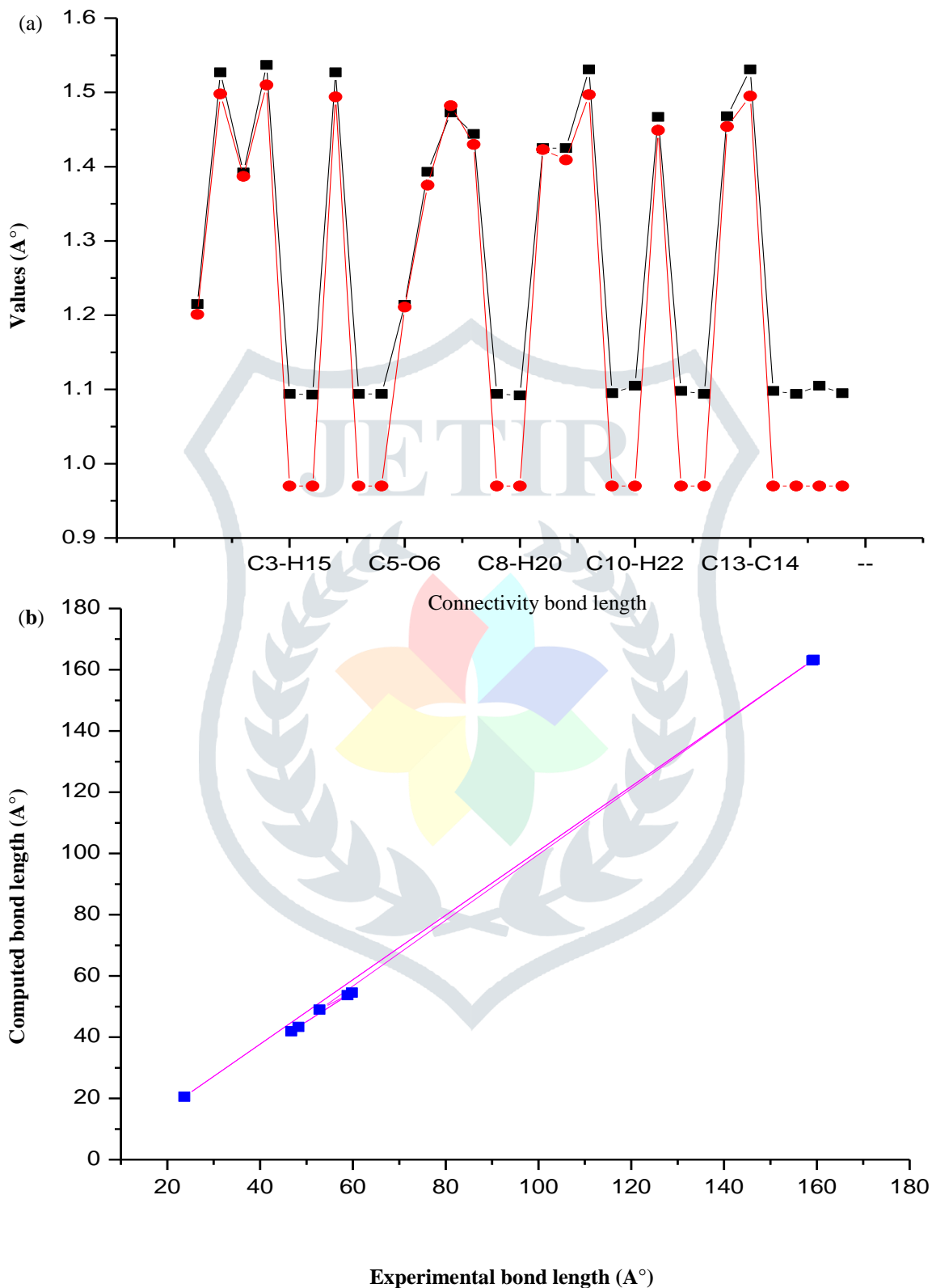**Fig. 2. Optimized geometry of SMF molecule**

Fig. 3: Comparative plot of experimental and calculated
bond length of SMF by B3lyp method

Table 1: Bond length of SMF molecule

Bond length	B3LYP/613-G (d, p)	XRD[a]
C1-O2	1.215	1.201
C1-C3	1.527	1.498
C1-N7	1.392	1.387
C3-C4	1.537	1.510
C3-H15	1.094	0.970
C3H-16	1.093	0.970
C4-C5	1.527	1.494
C4-H17	1.094	0.970
C4-H18	1.094	0.970
C5-O6	1.214	1.211
C5-N7	1.393	1.375
N7-C8	1.473	1.482
C8-N12	1.444	1.430
C8-H19	1.094	0.970
C8-H20	1.092	0.970
O9-C10	1.425	1.423
O9-C14	1.425	1.409
C10-C11	1.531	1.497
C10- H21	1.095	0.970
C10-H22	1.105	0.970
C11-N12	1.467	1.449
C11-H23	1.098	0.970
C11-H24	1.094	0.970
N12-C13	1.468	1.454
C13-C14	1.531	1.495
C13-H25	1.098	0.970
C13-H26	1.094	0.970
C14-H27	1.105	0.970
C14-H28	1.095	0.970

$$BL\ (B3LYP/6\text{-}31G(d,p)) = -3.111 + 5.531(BL_{EXP}) - 1.648\ (BL_{EXP})^2$$

The R2 value of bond length for all the predicted model is found to be greater than 0.99. Apart from covalent bond, the molecule stability is found mainly related to inter and intra molecular hydrogen bonding. The bond length of intra molecular hydrogen consists of nature of the bond strength, pressure and temperature of a molecule per unit cell.

3.2 UV-Vis spectral analysis

The experimental and predicted UV-Visible concurrent spectrum of SMF molecule is shown in Fig.1 and 4. The maximum (λ_{max}) absorption value of SMF molecule is calculated by TD-DFT/B3LYP method with 6-31G (d,p) basis level. The computation of molecular orbital structure shows the absorption maximum of the SMF molecule which resembles the electronic excitation from HOMO to LUMO. The observed UV-Vis spectra of SMF molecule were carried out to DMSO solvent and simulated calculations were used in the DMSO and gas phase.
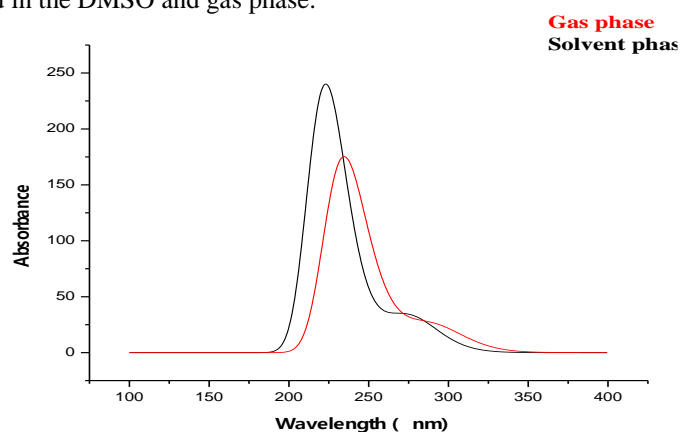

Fig. 4: Theoretical UV – Vis spectrum of SMF molecule

The electronic excitation amid frontier molecular orbitals such as electron transformation from HOMO to LUMO as can be seen from the UV-Vis spectra absorption values 287 (Experimental), 275 (DMSO) and 276 nm (gas phase) are listed in Table 2. The band gap diagram of SMF molecule as shown in Fig. 5
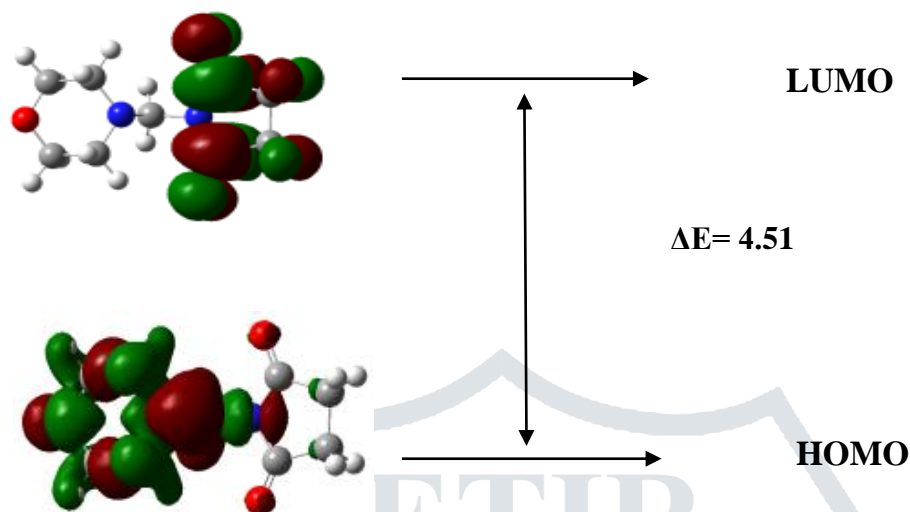

Fig. 5: HOMO – LUMO diagram of SMF molecule

Table 2: Experimental and calculated absorption wavelength, bond gap value and oscillator strength of SMF molecule

Expt.		B3LYP/6-31G(d,p) method						Assignment
λ_{max} (nm)	Band gap (eV)	Gas phase			DMSO			
		λ_{cal} (nm)	Band gap (eV)	Energy	λ_{cal} (nm)	Band gap (eV)	Energy	
287	4.32	276	4.3014	0.70340	275	4.5068	0.70382	H →L(99%)
		240	4.9651	0.68682	237	5.2385	0.68818	H-1 →L (95%)
		226	5.3545	0.69898	221	5.5993	0.68818	H→L+1 (98%)

The theoretical data concerned with the wavelength and oscillating strength and band gap energy were carried out to compare with the experimental data. The energy gap was calculated with the formula, $E = hc/\lambda$. Here h and c are constant; λ is the cut off wavelength.

The energy difference among with HOMO and LUMO orbits is known as the band gap explains the stability of the molecular structure [15].

Table 3: Mulliken population analysis of SMF molecule

Atoms	Mulliken charge (e)	Atoms	Mulliken charge (e)
1 C	0.5898	15 H	0.1504
2 O	-0.4899	16 H	0.1515
3 C	-0.2897	17 H	0.1497
4 C	-0.2904	18 H	0.1523
5 C	0.5898	19 H	0.1267
6 O	-0.4874	20 H	0.1290
7 N	-0.4656	21 H	0.1028
8 C	0.0805	22 H	0.0777
9 O	-0.4823	23 H	0.1103
10 C	0.0584	24 H	0.1221
11 C	-0.0747	25 H	0.1089
12 N	-0.4086	26 H	0.1277
13 C	-0.0791	27 H	0.0789

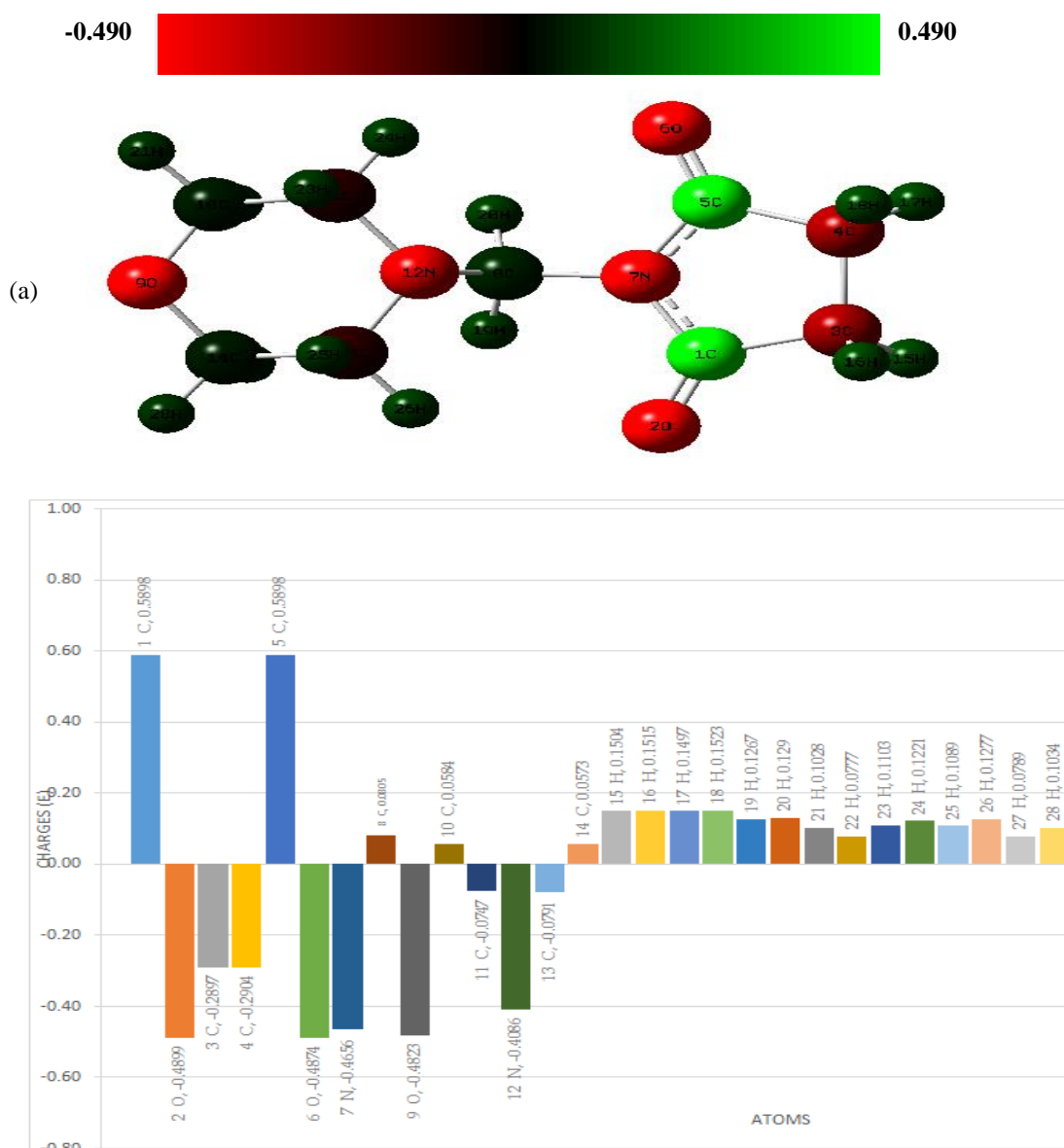| 14 C	0.0573	28 H	0.1034

Fig. 6: Mulliken population analysis of SMF molecule

The whole atomic charges of SMF molecule were obtained from Mulliken charge population analysis by using DFT method. The atomic charges contribute a significant role in theoretical chemistry and most of the research works continue to carry out the process for theory of an atomic charge. The Mulliken population analysis provides one of the simplest diagrams of atomic charge distribution and simulates the net atomic charges in the molecule [16]. The separated charge distribution of the entire atoms in the SMF molecule is shown in Fig. 6a. The atomic charges of the molecule are displayed in the ranging from -0.4591 and 0.4591 as shown in Fig. 6b. The Mulliken atomic charge of SMF molecule is summarized in Table. 3. Almost maximum numbers of hydrogen atoms have exhibited positive charge, whereas the maximum numbers of carbon and nitrogen atoms possessed the negative charge. The carbon atoms like C1 and C5 are electropositive while the other carbon atoms such as C3, C4, C8, C10, C11, C13, C14 are electronegative are obtained by these methods. As a result of electronegative character of C3, C4, C8, C10, C11, C13 and C14 we found that the atoms as capable of causing electrophilic substitution at these centers and therefore referred as –I effect. The hydrogen atom (H15 and H28) has the highest positively compared to all other atoms and this is so because of the influence of the attached neighboring carbonyl group and oxygen atom. The carbon C1 and C5 are electropositive in nature acting as the nucleophilic substitution centers i.e., +I effect, which indicates the attached electron withdrawing atom like nitrogen and electron deficient group carbonyl group.

3.3 Molecular electrostatic potential

The molecular electrostatic potential at a certain point circulates a molecule which can be described in terms of whole charge distribution of a molecule which correlates with dipole moments. It is a method to recognize the electron density which is

applicable for determining the nucleophilic reactivity and electrophilic reactivity sites and also hydrogen-bonding interactions [17,18]. Therefore, the above-mentioned map allocates the information concerning the electronic density distribution of a molecule [19]. The MEP diagram of the SMF molecule obtained by the B3LYP/6-31G (d, p) method as shown in Fig. 7 shows the positive (blue) and negative zones (red) in the plot indicating the nucleophilic and electrophilic attack respectively in a reaction for the SMF molecule.

For the SMF molecule, as seen in Fig. 7, the red colour refers to the negative regions which are mainly located on oxygen and nitrogen around the electron deficient atom like carbonyl group and the positive regions are located on the hydrogen atoms. From these regions, the molecule can have non-covalent interactions.
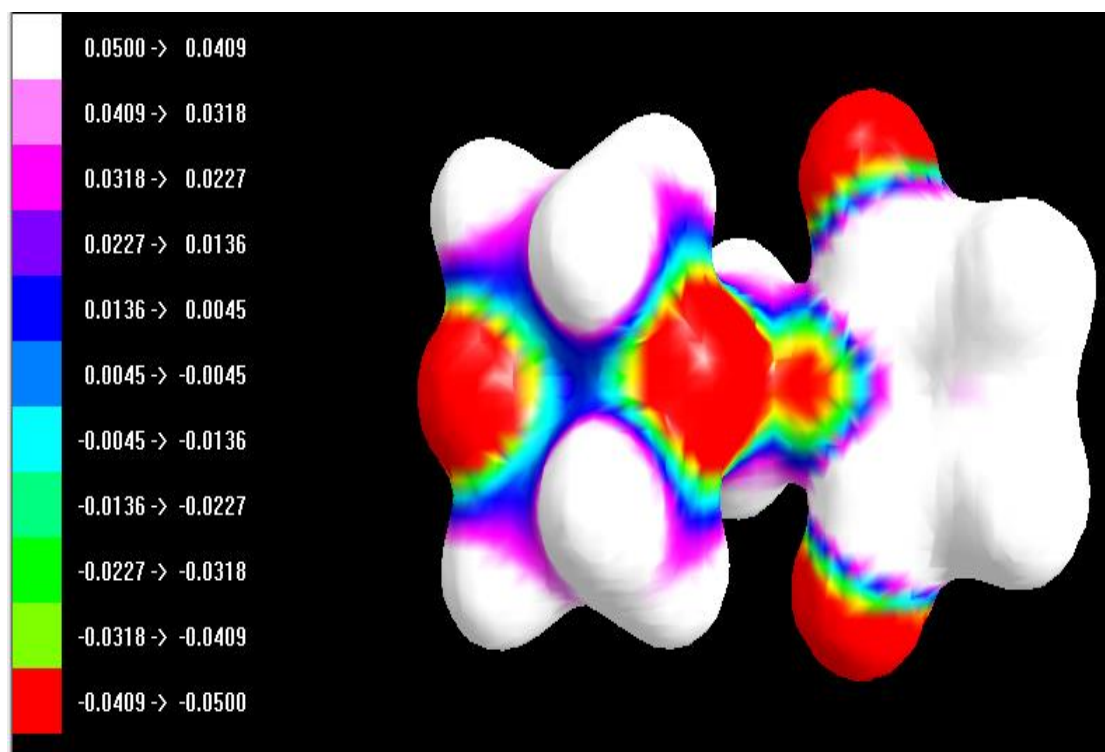

Fig. 7: Molecular electrostatic potential of SMF molecule

3.4 Nonlinear optical properties

The theoretical calculation of hyper polarizability results is the field of concentrated research, since it is correlated to invent the new NLO materials to describe the interaction among electromagnetic field and matter. The calculated SHG values of SMF molecule are listed in Table 4. The simulated first hyperpolarizability of the SMF molecule is 1.878×10^{-30} esu which is 14.45 times greater than the standard NLO reference material urea (0.13×10^{-30} esu) [20]. We conclude that the SMF molecule is a gorgeous object for further studies of nonlinear optical applications.

Table 4: Calculated all β components and tot ($\beta \times 10^{-30}$) value of SMF

Parameters	B3LYP/6-31G(d,p)
β_{xxx}	-18.097
β_{xxy}	-20.009
β_{xyy}	52.175
β_{yyy}	-30.007
β_{zxx}	51.505
β_{xyz}	4.302
β_{zyy}	-19.925
β_{xzz}	32.587
β_{yzz}	-5.973
β_{zzz}	-64.578

β_{tot}(esu)	1.878

4. Conclusions

In the present study, the molecular structure and UV-Vis of SMF molecule have been studied experimentally and theoretically. The electronic properties are also calculated and compared with the experimental UV-Vis spectrum. Comparative band gap energy is found to be 4.32 eV. Consequently, the title molecule has a greater stability. Band gap energy is clearly shown SMF molecule biologically active. The first order hyperpolarizability of the SMF molecule is fourteen times greater than the value of urea.

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