International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 17 No. 1 Jul. 2016, pp. 13-32
© 2016 Innovative Space of Scientific Research Journals
http://www.ijias.issr-journals.org/

Density functional theory investigation on the conformational analysis, molecular structure and FT-IR spectra of Tryptophan methyl-ester molecule

***Nabil Omri*[1]*, Mohammed Yahyaoui*[1]*, Seifeddine Bennia*[1]*, Sabri Messaoudi*[1]*, Fathi Moussa*[2]*, and Manef Abderrabba*[1]**

[1]Laboratoire Matériaux, molécules et Applications,
IPEST, Université de Carthage,
BP51, 2070 La Marsa, Tunisia

[2]LETIAM, Groupe de Chimie Analytique de Paris Sud, EA 4041,
IUT d'Orsay, Université Paris Sud 11, Plateau de Moulon,
91400 Orsay, France

ABSTRACT: Tryptophan methyl-ester (TrpME) is derived from a natural amino acid, which contains an indole heterocycle. This gives tryptophan its absorption and fluorescence spectroscopic properties. TrpME has become a commonly tool used in many fields namely medicine which is considered as the most important one. In front of his major importance, we found interesting to make a theoretical study on the conformational analysis by DFT/B3LYP method with 6-31G(d,p) basis set to find the most stable form of TrpME. Seven staggered stable conformers were observed on the torsional potential energy surfaces, it is shown that TrpME_1 conformer (D1= 178.62°, D2= -69.77°, D3= -67.33° and D4= -140°). is the most stable form. The optimized geometrical parameters and vibrational frequencies of the most stable conformation of this molecule were calculated by HF and DFT methods with 6-31G(d,p) standard basis. The electronic and orbital properties like HOMO and LUMO energies of this molecule were also calculated by DFT/B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets. This study is expanded to determine the gap energy, polarizability, Mulliken charges and thermodynamic properties of the TrpME. The correlation of certain thermodynamic functions with temperature has been determined in the form of quadratic equations. The UV spectrum is also recorded by TDDFT. It shows good conformity with the experimentally found spectrum and confirms that TDDFT is a powerful tool to study the electronic properties of molecules.

KEYWORDS: Tryptophan methyl ester; DFT; absorption spectra; molecular structure.

1 INTRODUCTION

Despite the fact that amino acids have different origins [1], they form one of the most important classes of molecules with several biological applications the most important of which is to form proteins by their incorporation into polypeptides [2].

In aquatic environment [3,4], the amino acid has two ionisable groups; the carboxyl group that gives its proton to the amine group forming than a zwitterion structure.

The amino acids participate in the regulation of numerous intracellular biochemical pathways. Their signal role has been studied at the muscular level, where some amino acids like leucine have been found to perform a signaling role in the promotion of protein synthesis of muscle [5].

Tryptophan is an aromatic, apolar and hydrophobic amino acid, containing an indole heterocycle that confers absorption and fluorescence properties. Widely used to describe the structural deformation of proteins [6], tryptophan is considered among the most studied of the amino acids in the literature [7-11].

Here we set out to study the optimized molecular structure of TrpME and its electronic and orbital properties using the density functional theory (DFT). To describe the molecular electronegativity process we need determined the Mulliken charges of the most stable structure of this molecule by DFT/B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets, the study of the molecular polarizability and dipole moment allows us to understand the intramolecular charge transfer of this molecule. On the bases of the vibrational analysis the evolution of certain thermodynamic functions likes entropy, heat capacity and enthalpy, calculated by HF and DFT with 6-31G(d,p) standard basis at different temperatures, has a great effect on the behaviour and the movement of this molecule.

2 COMPUTATIONAL APPROACH

The optimized geometric parameters, UV spectra wavelengths, electronic polarizabilities, atomic charges, dipole moments and other parameters investigated in the present work, were calculated by two methods of calculations, at the level of the Hartree-Fock (HF), and the density functional theory (DFT) [12], that is included in the Gaussian 09W program [13], with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets, and three functional, the first is B3LYP [12,14], the other is the GGA like BPW91 [15], and the LDA like SVWN5 [16], these results are combined by the GAUSSVIEW program [17,18].

The geometric structures of the labeled TrpME, and both cationic and zwitterionic forms, are shown in Fig. 4 (a, b and c). The values of these two forms which are found with X-ray [11] are compared with the optimization geometry of the TrpME molecule that is theoretically found in the gaseous state.

3 RESULTS AND DISCUSSION

3.1 CONFORMATIONAL STABILITY

The TrpME molecule has same groups of side chains which may influence its geometric structure and its different properties. Whose purpose for determining the most stable conformation and optimized geometry of this molecule, we have chosen to work on four dihedral angles **D1**(C27-O26-C6-C3), **D2**(O26-C6-C3-C5), **D3**(N1-C3-C5-C9) and **D4**(C3-C5-C9-C12).

For this conformational study we have chosen to take the D1, D2, D3 and D4 dihedral angles, to forecast the influence of their variations (from 0 to 360°) on the chains of groups linked O26-C6 to D1, C6-C3 to D2, C3-C5 to D3 and C5-C9 to D4.

The conformations of the TrpME molecule essentially depend on the orientation of the -OCH_3 group attached to the O26-C6 bond to D1, the -$COOCH_3$ group linked to C6-C3 bond to D2, the –$NH_2CHCOOCH_3$ group to the C3-C5 to D3 and –$CNH_2CHCOOCH_3$ group linked to the C5-C9 bond to D4.

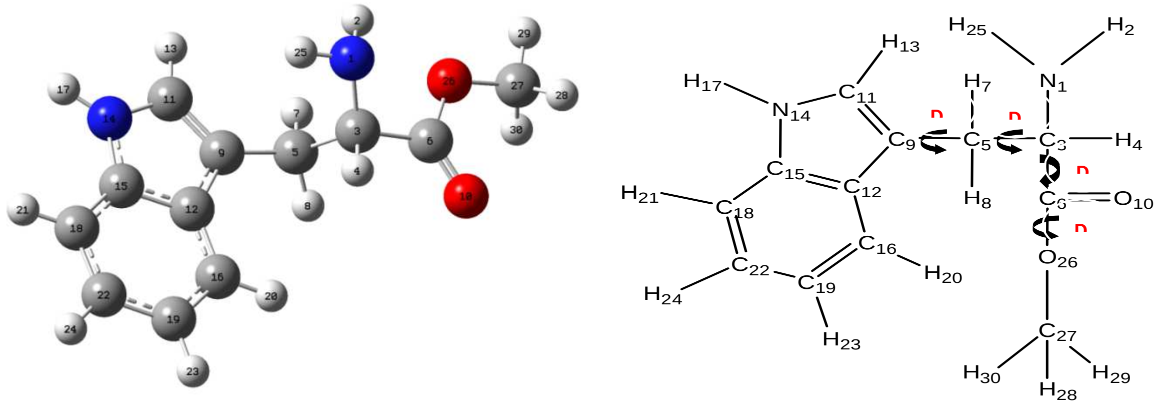


Fig. 1. The B3LYP/6-311+G(d,p) optimized structure, rotational bond names and atomic numbering scheme of TrpME molecule

The energy profiles of potential internal rotations of O26-C6, C6-C3, C3-C5 and C5-C9 bonds calculated at B3LYP/6-31G(d,p), by varying torsion coordinates D1, D2, D3 and D4 from 0° to 360°, are grouped in Fig. 1.

All recovered conformations are obtained after scanning procedure of the dihedral angles at each fixed values of D1-4.

If we carefully study the results obtained at B3LYP/6-31G(d,p) level and presented in Fig. 2, we can mention that the internal rotation of the O26-C6 bond gives three energy minimums, the lowest energy was recorded for a 180° (-725.688801

Hartree) while the two others angles which are respectively 170° and 190° have relatively higher setting values (725.688443 Hartree).

The variation of the dihedral angle (O26-C6-C3-C5) and through definition by D2 also gives four values with a relatively higher energy, for the three angles 80°, 90°, 270° and 280°, while the lowest energy (-725.690725 Hartree) was recorded for a 280°.

Integrally for the dihedral angle D3, the internal rotation of C3-C5 bond gives two minimums, the first was recorded for a 170° (-725.689422 Hartree), while the lowest energy value was stored for a 300° (-725.690744 Hartree).

The potential profile of internal rotation of the C5-C9 bond for D4 gives two minimums; the first was recorded for two dihedral angles 70° (-725.689523 Hartree) and 80° (-725.689427 Hartree), while the second was recorded for a 350° (-725.891241 Hartree).

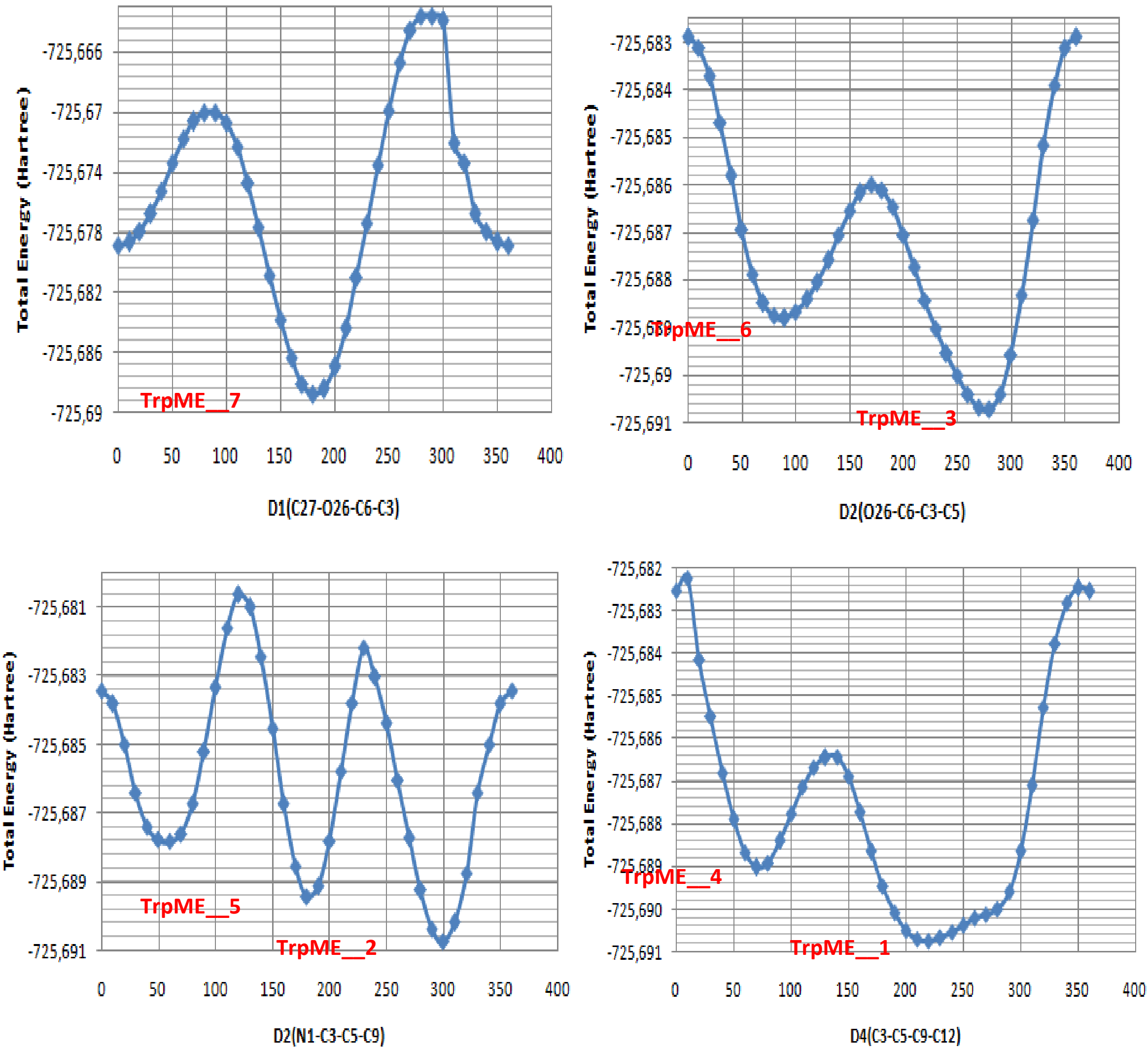
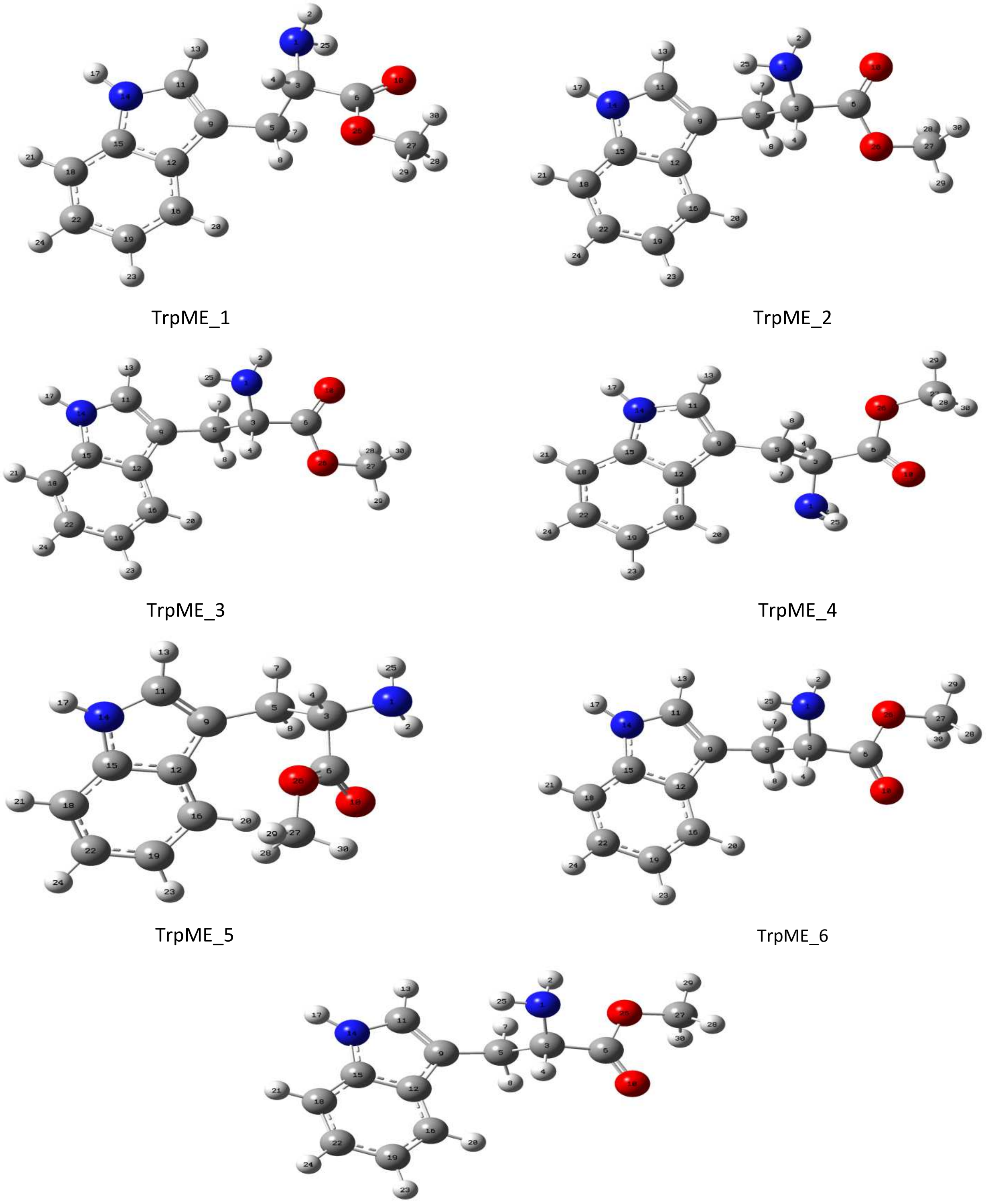


Fig. 2. Rotational energy curves computed at B3LYP/6-31G(d,p) level of TrpME molecule along D1, D2, D3 and D4 dihedral angles

Thus the comparison of minimums energy values given by internal rotation of the four trihedral angles D1, D2, D3 and D4 of the TrpME molecule after a conformational analysis leads us to point out that the TrpME molecule has seven conformations (Fig. 3) where TrpME_1 presents the most stable form.

Based on collected data we studied carefully the most stable form of TrpME for determining its various properties using HF and DFT/B3LYP methods with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets.



TrpME_1

TrpME_2

TrpME_3

TrpME_4

TrpME_5

TrpME_6

TrpME_7

Fig. 3. The B3LYP/6-31G(d,p) optimized geometric structures for the 7 conformers of TrpME molecule

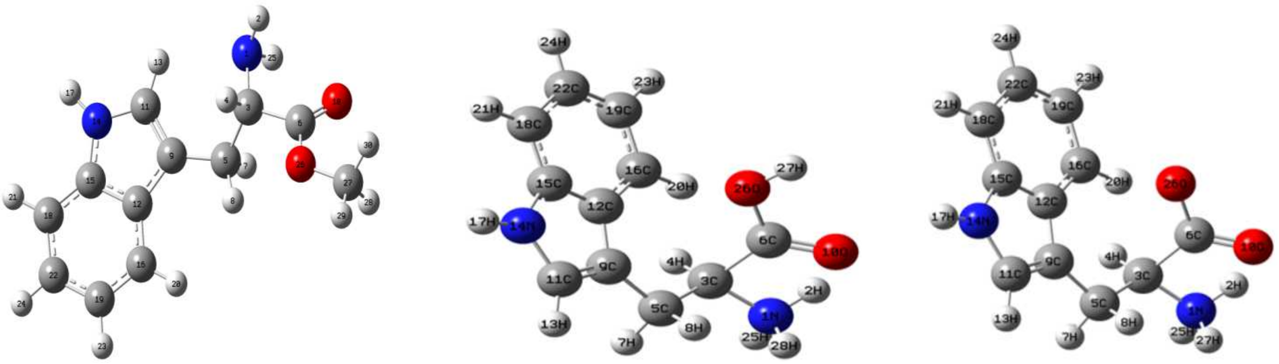
3.2 MOLECULAR GEOMETRY

The purpose of molecular geometry is to study the molecule of the TrpME and determine its different optimized parameters. We started by calculating the energies using both methods of calculations HF and DFT, using the functional B3LYP, BPW91 and SVWN5 and the same basis standard 6-31G(d,p), the energies are summarized in Table 1.

Table 1. Energies of the TrpME calculated in the gaseous state, by HF/6-31G(d,p), B3LYP/6-31G(d,p), BPW91/6-31G(d,p) and SVWN5/6-31G(d,p).

	Energies (Hartree)	**Energies (Kcal/mol)**
HF/6-31G(d,p)	-720.953	-437981.394
B3LYP/6-31G(d,p)	-725.428	-455208.586
BPW91/6-31G(d,p)	-725.349	-455159.105
SVWN5/6-31G(d,p)	-719.242	-451326.673

The analysis of the results shows that with the B3LYP functional, we could obtain the lowest energy, and consequently, the most stable thermodynamically geometric structure. For the rest of this study, we used the functional DFT/B3LYP with three different basis to find the best basis to be adequate to describe and predict the experimental studies.



(a) (b) (c)

Fig. 4. The molecular structure and atomic numbering: (a) TrpME, (b) the cationic form and (c) the zwitterionic form

The optimized bond lengths and angles of the TrpME molecule, found by DFT/B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets, are listed in the Table 2. These values are well correlated to the atomic number given in the Fig. 4 (a, b and c).

Table 2. The geometric parameters of the optimized TrpME (a) calculated by B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p), in addition to the experimental values found in X-ray of the two forms (b) and (c), bond lengths (A°), tertiary angles (°)

Bond length(Å) and Bond angle (°)	Value (b)	Value (c)	Value (a)		
			B3LYP/6-31G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-311+G(d,p)
C_6-O_{26}	1.31	1.24	1.34	1.34	1.34
O_{10}-C_6	1.20	1.24	1.21	1.21	1.21
C_3-C_6	1.51	1.52	1.53	1.52	1.53
C_3-N_1	1.48	1.48	1.46	1.46	1.46
C_3-C_5	1.53	1.52	1.54	1.54	1.54
C_5-C_9	1.49	1.48	1.50	1.50	1.50
C_9-C_{11}	1.37	1.36	1.37	1.37	1.37
C_9-C_{12}	1.43	1.43	1.44	1.44	1.44
C_{11}-N_{14}	1.37	1.36	1.38	1.38	1.38
N_{14}-C_{15}	1.36	1.36	1.38	1.36	1.38
C_{15}-C_{12}	1.41	1.41	1.42	1.42	1.42
C_{12}-C_{16}	1.40	1.40	1.40	1.39	1.40
C_{16}-C_{19}	1.38	1.37	1.38	1.39	1.35
C_{19}-C_{22}	1.40	1.40	1.41	1.40	1.41
C_{22}-C_{18}	1.37	1.37	1.36	1.37	1.39
C_{18}-C_{15}	1.40	1.39	1.49	1.39	1.39
O_{10}-C_6- O_{26}	124.74	126.28	123.52	123.51	123.40
O_{26}-C_6-C_3	111.90	117.25	112.39	112.42	112.35
O_{10}-C_6-C_3	123.34	116.45	124.02	124.01	124.21
C_6-C_3-N_1	107.76	109.87	111.33	111.34	111.79
C_6-C_3-C_5	113.70	107.22	109.50	109.39	109.77
C_5-C_9-C_{11}	127.28	126.16	126.55	126.56	126.71
C_9-C_{11}-N_{14}	110.03	110.51	110.08	110.08	110.06
C_5-C_9-C_{12}	126.60	127.78	127.14	127.12	127.01
C_{12}-C_9-C_{11}	106.08	105.84	106.28	106.28	106.27
C_{11}-N_{14}-C_{15}	109.39	109.29	107.75	109.20	109.19
N_{14}-C_{15}-C_{12}	107.47	107.28	110.13	107.12	107.13
N_{14}-C_{15}-C_{18}	130.43	130.69	129.10	130.54	130.49
C_{15}-C_{18}-C_{22}	117.54	117.92	115.81	117.49	117.50
C_{18}-C_{22}-C_{19}	121.25	121.15	122.88	121.20	121.16
C_{22}-C_{19}-C_{16}	121.54	121.07	121.07	121.08	121.06
C_{19}-C_{16}-C_{12}	118.72	119.20	119.15	119.13	119.13
C_{16}-C_{12}-C_{15}	118.85	118.61	120.31	118.75	118.75
C_{16}-C_{12}-C_9	134.13	134.33	133.95	133.95	133.91
C_9-C_{15}-C_{12}	107.02	107.06	105.73	107.29	107.32
C_{18}-C_{15}-C_{12}	122.10	122.03	120.75	122.32	122.37
C_9-C_5-C_3	115.32	117.43	113.96	114.02	114.50
N_1-C_3-C_5	111.35	111.37	109.27	109.29	109.24

The geometric parameters of the optimized compound were compared with the values given by the X-ray [11] of both similar structures (b) and (c).

Based on these results, we could conclude that the values of the bond lengths and angles are well correlated with the experimental values, and being located within the margin of the measurement error.

The graphical comparisons of the bond lengths and bond angles in this molecule (Fig. 5 and Fig. 6) confirm that the variation of angles depends primarily on the electronegativity of the central atom, and the conjugation of double bonds, in other words, when the electronegativity of the atom decreases the value of the bond angle decreases. We also note that, the values of the optimized lengths, as well as the angles of the TrpME, found by the functional B3LYP/6-31G(d,p), are similar to the experimental values of the cationic form than the zwitterionic form.

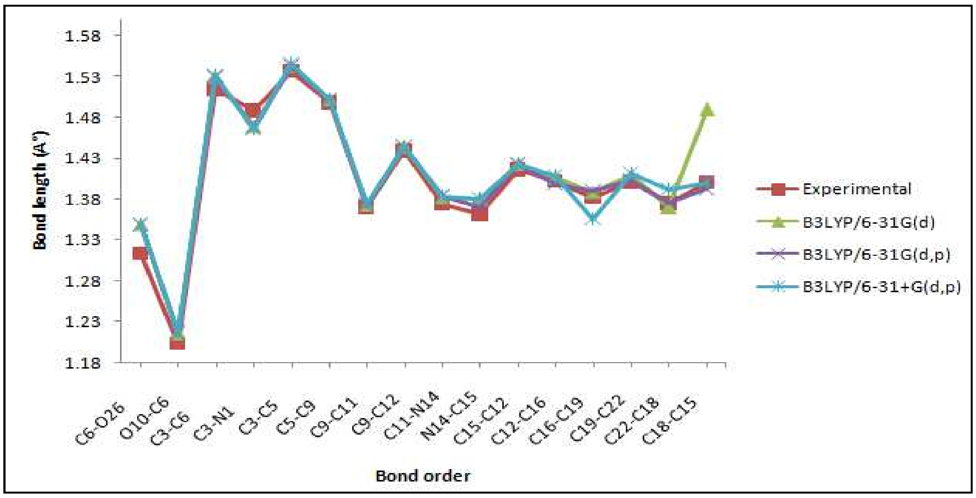


Fig. 5. The difference between the bond length of the molecule of TrpME obtained by B3LYP functional and 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets.

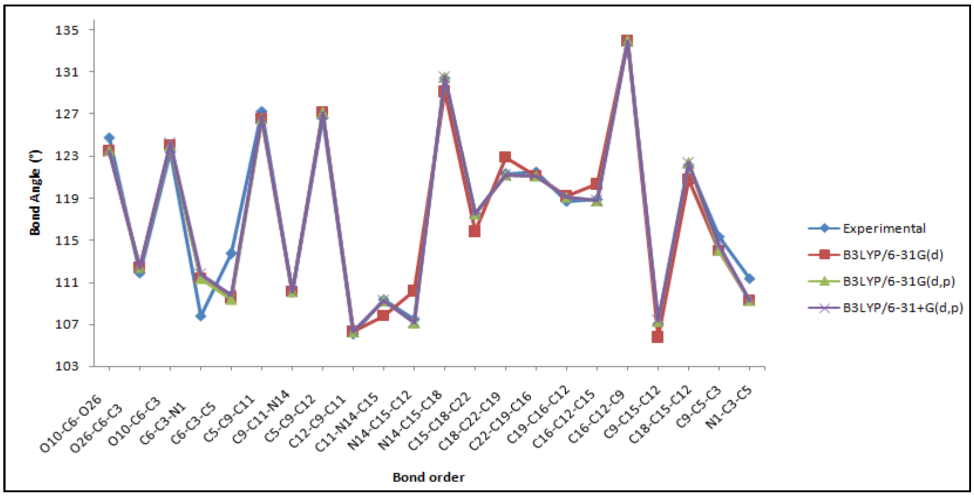


Fig. 6. The difference between the bond angle of the molecule of TrpME obtained by B3LYP functional and 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets.

3.3 MOLECULAR PROPERTIES AND THE ENERGY GAP

The spatial distribution of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) is considered as one of the indicators of electrons transport inside the molecular system.

The energy gap between the HOMO and LUMO, the chemical hardness, electrophilicity and the chemical potential of this molecule can be determined.

LUMO and HOMO energies of the TrpME (Fig. 7) were calculated as well as the energy gap (HOMO-LUMO) which is shown in Table 3. The energy gap generally reflects the nature of the chemical activity of the molecule, in other words, the atom that has the most important density of the HOMO should have the possibility to easily release an electron, whereas the atom which has the occupation of the higher LUMO owns a strong probability to earn an electron [19].

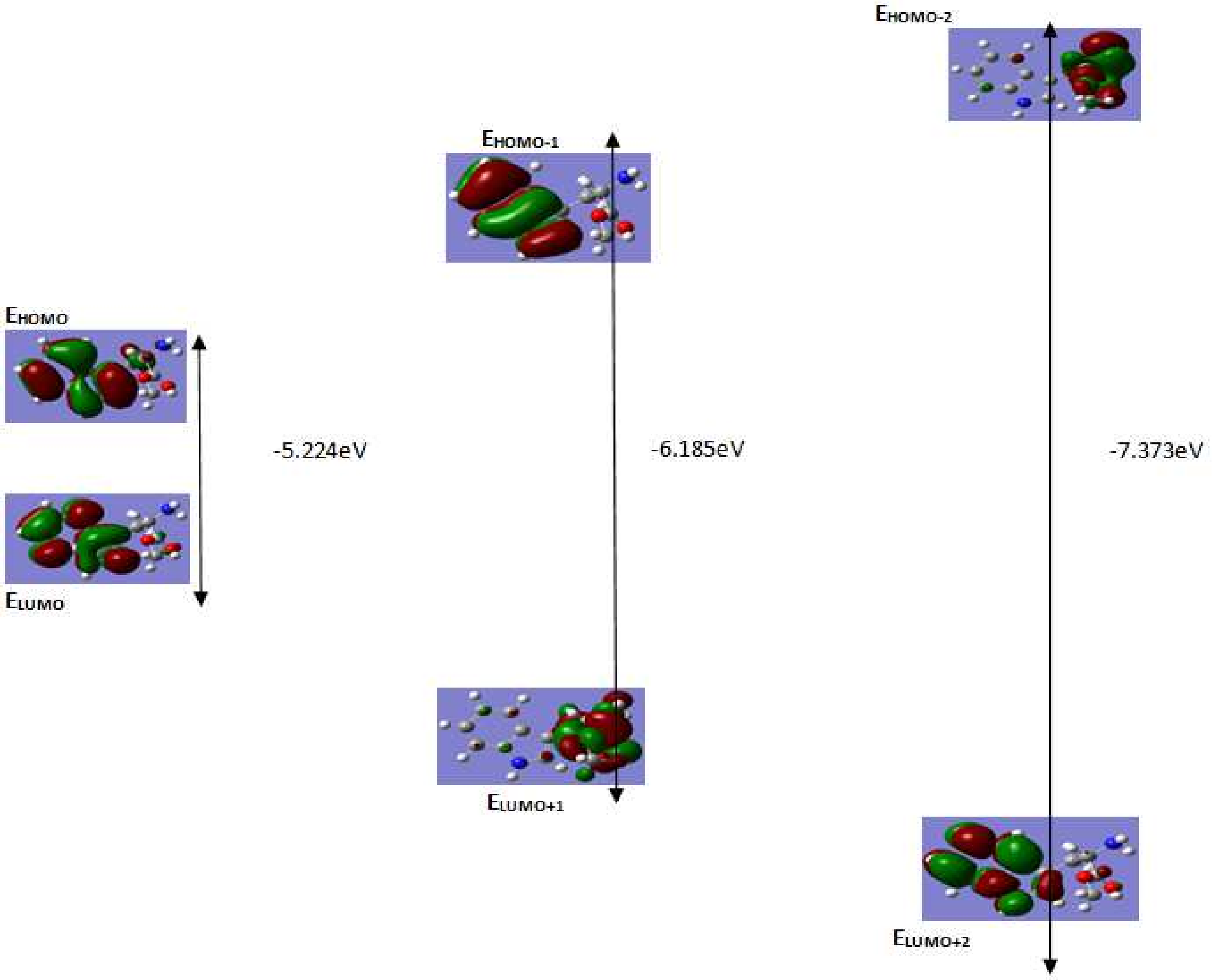


Fig. 7. The energies of the frontier orbital of TrpME calculated by B3LYP/6-31G(d,p).

The TrpME molecule is characterized by a small variation of the energy gap (5.224159 eV), which is the result of a significant change between the two donating and electron acceptors of intramolecular groups.

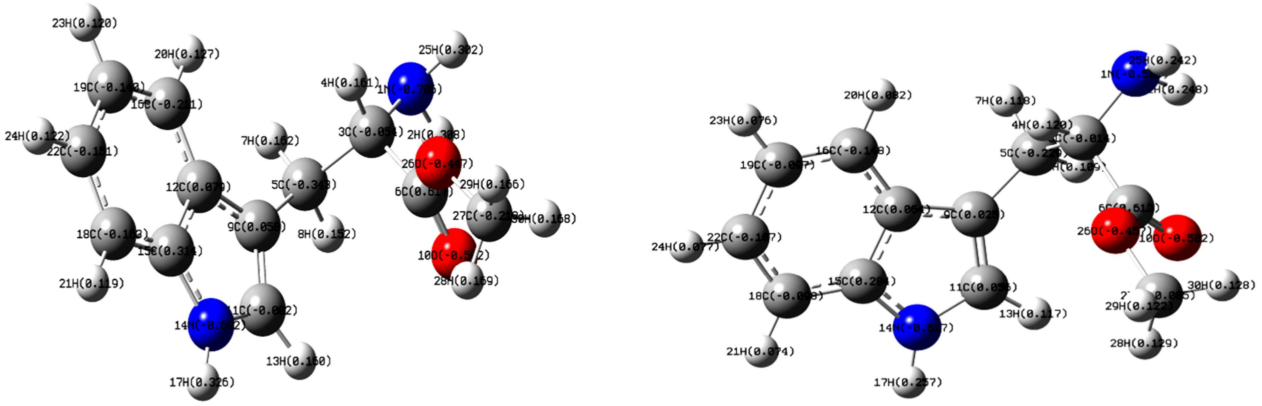
We also determined, with the same function, the electron affinity and the ionization potential of this molecule that have been expressed in terms of HOMO and LUMO orbital energies, according to the following equations $A= -E_{LUMO}$ and $I= - E_{HOMO}$. The global electrophilicity of this molecule is given by the following equation: $\omega=\mu^2/(2\eta)$, to calculate this value we need to determine the values of the chemical potential $\mu=(E_{HOMO}+E_{LUMO})/2$, and chemical hardness $\eta=(E_{LUMO}-E_{HOMO})$. All these values are summarized in the Table 3.

Table 3. The HOMO and LUMO energy, the energy gap, and the molecular properties of the TrpME molecule.

	B3LYP/6-31G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-311+G(d,p)
E_{HOMO} (u.a)	-0.196	-0.196	-0.208
E_{LUMO} (u.a)	-0.003	-0.004	-0.022
E_{HOMO} - E_{LUMO} (u.a)	-0.192	-0.191	-0.185
E_{HOMO-1} (u.a)	-0.215	-0.216	-0.228
E_{LUMO+1} (u.a)	0.011	0.011	-0.008
E_{HOMO-1} - E_{LUMO+1} (u.a)	-0.226	-0.227	-0.219
E_{HOMO-2} (u.a)	-0.238	-0.238	-0.251
E_{LUMO+2} (u.a)	0.032	0.032	-0.005
E_{HOMO-2} - E_{LUMO+2} (u.a)	-0.271	-0.270	-0.245
Ionisation potential (I)	0.196	0.196	0.208
Electron affinity (A)	0.003	0.004	0.022
Chemicalhardness (η)	0.192	0.191	0.185
Chemicalpotential (μ)	-0.100	-0.100	-0.115
Global electrophilicity(ω)	0.026	0.026	0.036

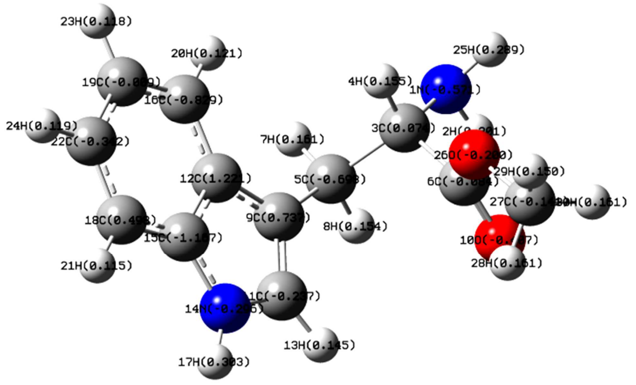
3.4 MULLIKEN CHARGES

The methods of quantum chemistry allow us to estimate the partial atomic charges of the studied molecule. Mulliken charges have a great effect on the dipole moment, the electronic structure and molecular polarizability [20]. The atomic charges can also be used to describe the molecular electronegativity process.



(a) B3LYP/6-31G(d,p)

(b) B3LYP/6-31+G(d,p)



(c) B3LYP/6-311+G(d,p)

Fig. 8. The Mulliken atomic charges of TrpME

The Mulliken charges values of the TrpME molecule, calculated by the functional DFT/B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets, are displayed on the molecular structures presented in the Fig. 8(a, b and c), and summarized in Table 4. These results could be illustrated in graphical forms, shown in Fig. 9.

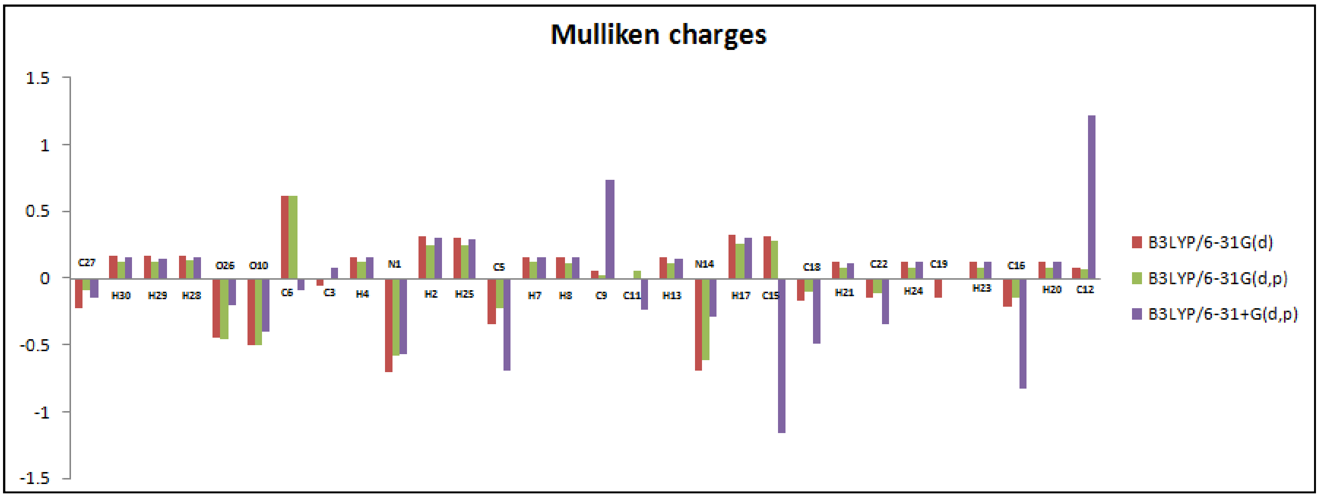


Fig. 9. Comparison of the atomic charges calculated by B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p) of the TrpME

Table. 4. Mulliken charges of the optimized geometry of TrpME obtained by B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p)

Atomic num	**Mulliken charges**		
	B3LYP/6-31G(d,p)	**B3LYP/6-31+G(d,p)**	**B3LYP/6-311+G(d,p)**
C_{27}	-0.219	-0.085	-0.141
H_{30}	0.168	0.128	0.161
H_{29}	0.166	0.122	0.150
H_{28}	0.169	0.129	0.161
O_{26}	-0.447	-0.457	-0.2
O_{10}	-0.502	-0.502	-0.407
C_6	0.617	0.613	-0.084
C_3	-0.054	-0.014	0.074
H_4	0.161	0.120	0.155
N_1	-0.706	-0.586	-0.571
H_2	0.308	0.248	0.301
H_{25}	0.302	0.242	0.289
C_5	-0.343	-0.343	-0.698
H_7	0.162	0.162	0.161
H_8	0.152	0.152	0.154
C_9	0.058	0.058	0.737
C_{11}	-0.002	-0.002	-0.237
H_{13}	0.160	0.160	0.145
N_{14}	-0.692	-0.692	-0.296
H_{17}	0.326	0.326	0.303
C_{15}	0.314	0.314	-1.167
C_{18}	-0.163	-0.163	-0.498
H_{21}	0.119	0.119	0.115
C_{22}	-0.151	-0.151	-0.342
H_{24}	0.122	0.122	0.119
C_{19}	-0.140	-0.140	-0.009
H_{23}	0.120	0.120	0.118
C_{16}	-0.211	-0.211	-0.829
H_{20}	0.127	0.127	0.121
C_{12}	0.079	0.079	1.221

It is important to point out that all the hydrogen atoms of the TrpME have positive charges, and the charge carried by the H_{17} atom, has the maximum value, since it is linked to the N_{14} nitrogen atom. It is interesting to note also that the C_6 atom has the highest positive charge, which is obviously due to the presence of two oxygen atoms which are more electronegative than the carbon atom.

However both O_{10} and O_{26} oxygen atoms, have a negative charges, and whether we compare its values, we will find that the O_{10} atom has a maximum value of the negative charge, which explains its position in the molecular structure (carbonyl group), while the O_{26} atom has a smaller value, since it is linked between two carbon atoms C_6 and C_{27} that are less electronegative. Both O and N atoms present the lowest negative charge values, while the hydrogen atom have the most important positive charge value, these results give us an idea about the intramolecular interaction in TrpME molecule.

3.5 THE MOLECULAR POLARIZABILITY

In order to understand the electronic distribution and the intramolecular transfer charges of TrpME, we tried to determine the molecular polarizability and the dipole moment, by the functional B3LYP and 6-31G(d), 6-31G(d,p) and 6-31+G(d,p) basis sets. This dipole moment reflects the distribution of the molecular charges and the three-dimensional vector that represents the movement of atomic charges of the TrpME molecule.

The dipole momentμ (Debye), static polarizability α(u.a), the average or linear polarizability α_0(0.1482*10^{-24}esu) and the anisotropy of polarizability $\Delta\alpha$(0.1482*10^{-24}esu) of this molecule, are given in Table 5, and calculated by the following equations [21].

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

$$\Delta_\alpha = {}^{1}\!/_{\sqrt{2}}\,[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2 + 6\alpha_{xx}^{2}]^{1/2}$$

Table 5. The dipole moment μ (Debye), the average polarizabilityα_0 (0.1482*10^{-24}esu) and the anisotropy of the polarizabilityΔ_α (0.1482*10^{-24}esu) of TrpME calculated by B3LYP/6-31G(d,p) , B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p).

	B3LYP/6-31G(d,p)		**B3LYP/6-31+G(d,p)**		**B3LYP/6-311+G(d,p)**	
	a.u.	**e.s.a*10^{-23}**	**a.u.**	**e.s.a*10^{-23}**	**a.u.**	**e.s.a*10^{-23}**
α_{xx}	164.099	2.431	165.380	2.450	185.787	2.753
α_{xy}	6.624	0.098	6.663	0.098	4.363	0.064
α_{yy}	139.561	2.072	140.697	2.085	160.544	2.379
α_{xz}	-30.972	-0.459	-30.944	-0.458	-27.637	-0.409
α_{yz}	17.506	0.259	17.543	0.259	14.228	0.210
α_{zz}	109.293	1.619	110.146	1.632	138.532	2.053
α_0	137.651	2.039	138.741	2.056	161.621	2.395
Δ_α	286.361	4.243	288.599	4.277	323.038	4.787
μ_x	0.284		0.2589		-0.0268	
μ_y	-2.700		-2.6640		-2.641	
μ_z	0.687		-2.6640		0.726	
μ_0	2.801		2.7590		2.739	

The highest value of the dipole momentμ (2.8010 Debye) is calculated by B3LYP/6-31G(d).We note that the functional B3LYP/6-31+G(d,p) gives the highest value of the dipole moment for the compoundμ_z (0.7266), while the lowest value was noted for μ_y (-2.7006) and given by B3LYP/6-31G(d).

The linear polarizability and the anisotropy of the polarizability data by functional B3LYP/6-31+G(d,p) are respectively 2.395223*10^{-23} and 4.787423*10^{-23}esu.

3.6 THERMODYNAMIC PROPERTIES

The different movements of the TrpME molecule are associated with different energies, and if we provide enough energy via temperature, this molecule will be agitated increasingly by rotation and vibration.

To describe these vibratory movements and the reactions of the molecule, we have to determine its various thermodynamic properties.

We calculated these thermodynamic properties by DFT/B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets, such as the vibration energy (ZPVE), entropy, heat capacity and rotational constants which are summarized in Table 6.

Table 6. The vibration energy (ZPVE), the rotational constants, entropy and heat capacity of the TrpME molecule determined by DFT/B3LYP

Parameters	B3LYP/ 6-31G(d,p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311+G(d,p)
Zero-point vibrational energy (kcal mol^{-1})	155.439	155.125	154.725
Rotational constant (GHz)	0.909 0.325 0.300	0.909 0.326 0.300	0.893 0.327 0.304
Rotationaltemperature (K)	0.043 0.015 0.014	0.043 0.015 0.014	0.042 0.015 0.014
Energy (kcal mol^{-1})			
Total	164.809	164.508	164.142
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	163.031	162.730	162.364
Molecular capacity at constant volume (cal mol^{-1}K^{-1})			
Total	56.269	56.368	56.637
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	50.308	50.406	50.675
Entropy (cal mol^{-1} K^{-1})			
Total	127.005	127.434	126.588
Translational	42.043	42.043	42.043
Rotational	32.558	32.554	32.557
Vibrational	52.405	52.838	51.988

The most important value of ZPVE (155.439 kcal mol^{-1}) is obtained by B3LYP/6-31G(d,p), whereas B3LYP/6-311+G(d,p) gives the lowest value (154.725 kcal mol^{-1}). On the bases of the vibrational analysis, we followed the evolution of certain thermodynamic functions for instance the entropy (S), the thermal capacity (C) and the enthalpy (H) of the TrpME molecule, that depend on the temperature (Table 7). The results obtained show that these thermodynamic functions increase with the increasing of the temperature from 100 to 500K, since the vibrational intensity of the molecule is proportional to the temperature [22].

Table 7. The thermodynamic properties of TrpME measured at different temperatures by HF and DFT/B3LYP

	HF/6-31G(d,p)			DFT/B3LYP/6-31G(d,p)		
	S (cal/mol K)	C (cal/mol K)	H (kcal/mol)	S (cal/mol K)	C (cal/mol K)	H (kcal/mol)
100	80.301	22.089	168.042	85.118	23.528	156.847
200	101.657	37.120	171.209	107.732	39.608	160.202
300	120.408	52.615	175.886	127.796	56.688	165.208
400	138.283	68.294	182.136	146.999	73.370	171.923
500	155.524	82.450	189.889	165.414	87.804	180.203

The correlation equations of the heat capacity, enthalpy and entropy with temperature are given in the form of quadratic equations. These equations as well as its adjustment factors calculated by HF/6-31G(d,p) and DFT/B3LYP/6-31G(d,p), are the following:

For HF/6-31G(d,p)

$C= 6.161 + 15.86T - 0.111T^2 \quad R^2 = 0.999$
$H= 166.4 + 0.857T + 0.767T^2 \quad R^2 = 1.000$
$S= 58.56 + 22.61T - 0.650T^2 \quad R^2 = 0.999$

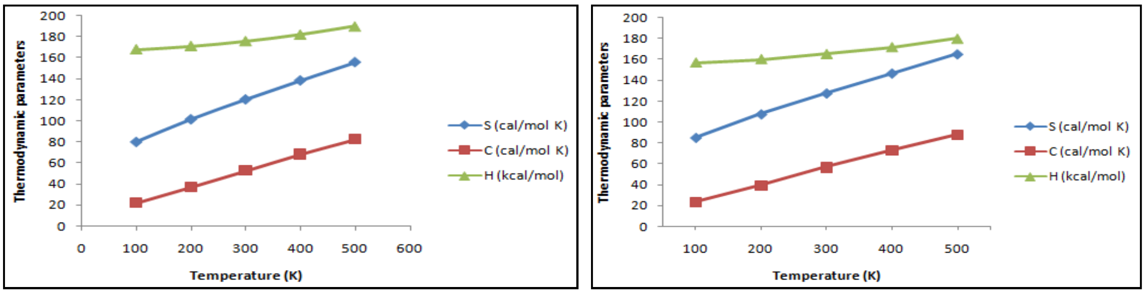
For DFT/B3LYP/6-31G(d,p)

$C= 5.660 + 17.81\,T - 0.263\,T^2 \quad R^2 = 0.999$

$H= 155.1 + 0.889\,T + 0.825\,T^2 \quad R^2 = 1.000$

$S= 62.02 + 23.95\,T - 0.661\,T^2 \quad R^2 = 0.999$

The graphic correlations of these parameters with temperature have been given in Fig. 10 (a and b).



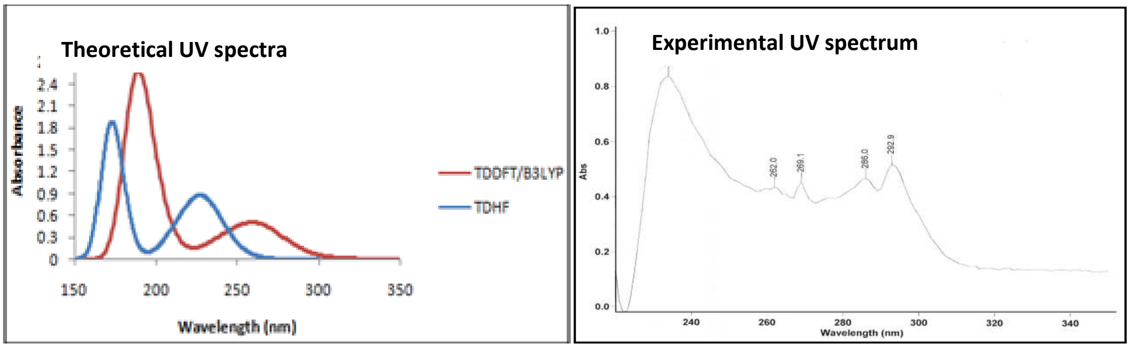
(a) (b)

Fig. 10. The graphic correlation of the thermodynamic properties of TrpME at different temperatures calculated by (a): HF/6-31G(d,p) and (b): DFT/B3LYP/6-31G(d,p).

3.7 ANALYSIS OF UV SPECTRA

The analysis of Ultraviolet spectra was studied by theoretical and experimental calculation in addition the functional theory of density independent of time TD-DFT [23] is widely used as a powerful tool to determine the static and dynamic properties of molecules.

Through using this method, we studied the excited states of the TrpME in its optimized geometry, and we compared the values of the wavelengths, as well as the shape of the spectrum found in its gas state with the results obtained in methanol solution. These spectra are shown in Fig. 11.



(a) (b)

Fig. 11. (a) Experimental and (b) theoretical UV spectra of TrpME

The results for the excitation energy, absorption wavelengths and the oscillation strengths (f) of this molecule are summarized in Table 8.

Table 8. The wavelengths Λ(nm), the excitation energy and the vibration strengths (f) of TrpME calculated by TD-HF and TD-DFT.

Experimental		**Theoretical**							
		TDHF				**TDDFT**			
Methanol		**Gaz phase**							
Λ (nm)	**Abs**	**Λ (nm)**	**E(ev)**	**f**	**contribution**	**Λ (nm)**	**E(ev)**	**f**	**contribution**
292.9	0.5	229.31	5.406	0.1930	H -> L+1	390.03	3.178	0.0016	H-1 -> L
286	0.45	215.46	5.754	0.0005	H-4 -> L H-5 -> L	383.09	3.236	0.0014	H -> L
269.1	0.43	211.93	5.850	0.0683	H-1 -> L+1 H -> L+2	303.97	4.078	0.0013	H-2 -> L
262	0.42	184.93	6.704	0.0007	H-2 -> L	266.31	4.655	0.0005	H-4 -> L H-3 -> L
234	0.82	180.80	6.857	0.0127	H -> L	262.93	4.715	0.1092	H -> L+1
		172.58	7.018	0.4577	H -> L+2 H-3 -> L+1	254.56	4.870	0.0004	H-1 -> L+1
						242.35	5.116	0.0018	H-3 -> L H-4 -> L
						238.57	5.197	0.0488	H-2 -> L+1 H -> L+2

HOMO (H) ; LUMO (L)

The UV spectrum of this compound has two interesting experimentally absorption bands, one at a wavelength Λ = 234 nm and the other at a wavelength Λ = 292 num. Theoretically with TDDFT method and with 6-31G(d,p) basis set, we found the following absorption bands; Λ = 238.57nm, Λ = 262.93nm, Λ = 266.31nm and Λ = 303.97nm, this difference in values is due to the state of TrpME. In fact, we studied this molecule in two completely different states and we found the following interesting results: The energies of the HOMO and LUMO frontier orbitals, calculated in Table 3, have a great importance that enable to explain the electrical and optical properties of the molecules and to explain the UV spectra [24].

The absorption band at 238nm (theoretical value) due to the π-π* transition (from the ground state to the first excited state), is mainly attributed to the HOMO-2 -> LUMO+1 (56%) or HOMO -> LUMO+2 (36%) transitions. Whereas the 266nm band corresponds to the HOMO-4 -> LUMO (65%) transition.

3.8 INFRARED SPECTROSCOPY

The observed vibrational assignments [11] and analysis of TrpME are discussed in terms of fundamental bands and combination IR bands. The harmonic vibrational frequencies calculated for this molecule using ab-initio HF/6-31G(d,p), and DFT B3LYP/6-31G(d,p), BPW91/6-31G(d,p) and SVWN5/6-31G(d,p) methods along with their absolute and relative intensities have been summarized in table 9. The observed and calculated FT-IR spectrum of TrpME molecule is shown in Fig. 12.

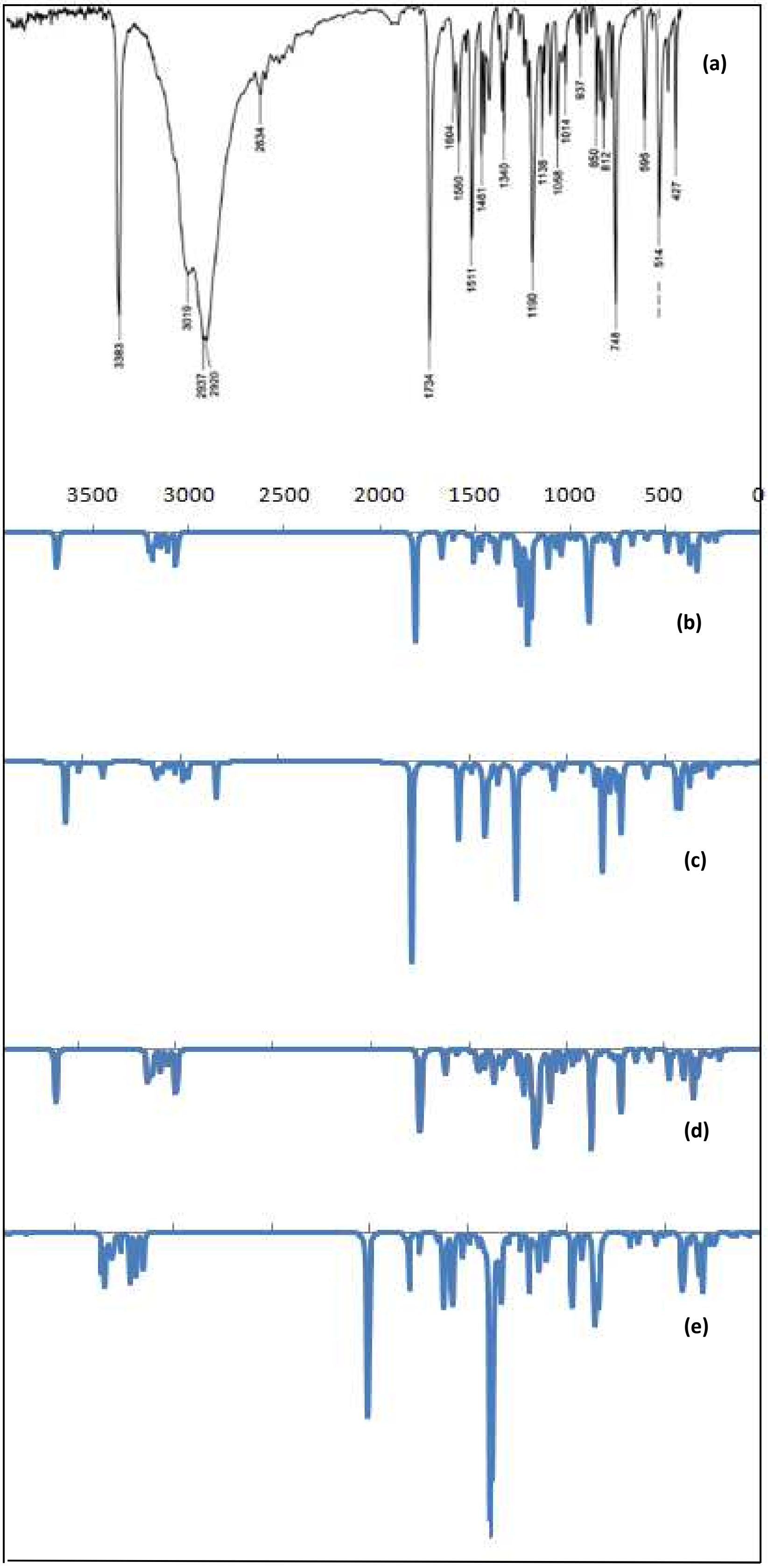


Fig. 12. Observed and theoretical FT-IR spectrum of TrpME (a) observed, (b) B3LYP/6-31G(d,p), (c) SVWN5/6-31G(d,p), (d) BPW91/6-31G(d,p) et (e) HF/6-31G(d,p).

The heteroaromatic structure shows the presence of C-H stretching vibrations in the region 3100-2900 cm^{-1}, which is characteristic region for the ready identification of C-H stretching vibrations and particularly the regions 3200-3100 cm^{-1} for asymmetric stretching and 3100-2950 cm^{-1} for symmetric stretching modes of vibration [25]. In the FT-IR spectrum of TrpME, two medium bands at 3076 and 3055 cm^{-1} are assigned to C-H stretching vibrations. The first band belongs to symmetric and the other asymmetric C-H stretching bands. The most discrepancy between the calculated and experimental C-H stretching mode for the first band is about 26 cm^{-1} at B3LYP/6-31G(d,p), while it is about 45 cm^{-1} at HF/6-31G(d,p) for the second band.

The C–H methyl group stretching vibrations are highly localized and generally observed in the range 3000–2800 cm^{-1} [26,27]. In the present investigation, the bands found at 2980 cm^{-1} in BPW91/6-31G(d,p) and 2990 cm^{-1} in SVWN5/6-31G(d,p) are assigned CH_3 stretching vibrations.

In the present study for the TrpME was found the experimental C=O stretching vibration at 1734 cm^{-1} which is closer than the calculated frequencies obtained for HF/6-31G(d,p) method, presenting the value of 1750 cm^{-1}

The C-N stretching vibrations occur in the region 1382–1266 cm^{-1} [28] for aromatic amines. In benzamide, the band observed at 1368 cm^{-1} is assigned to the C-N stretching vibration [29]. In the present study, the C-N stretching vibration is assigned at 1100 cm^{-1} of the title molecule at B3LYP/6-31G(d,p) level.

Table 9. Comparison of the calculated and experimental FT-IR vibrational spectra of TrpME by B3LYP/6-31G(d,p), BPW91/6-31G(d,p), SVWN5/6-31G(d,p) and HF/6-31G(d,p) methods.

Modes	**FT-IR**	**HF**	**B3LYP**	**SVWN5**	**BPW91**	**Assignments**
ν 1	3380	3400	3700	3500	3600	ν(NH) Indole
ν 2	3159	3250	3180	3150	3140	ν(NH), NH_2
ν 3	3117	3150	3110	3120	3100	ν(CH) pyrrole
ν 4	3076;3055	3100	3050	3030	3050	ν(CH) benzene
ν 5	3014;2965;2935	-	-	2980	2990	ν(CH), CH_2
ν 6	2882	-	-	2830	-	ν(NH), NH_2
ν 7	1734	1750	1800	1800	1750	ν(C=O)
ν 9	1606	1610	1620	1610	1615	BR str
ν 10	1567	1580	1530	1570	1550	$^{\delta}$as(NH2), BR str
ν 11	1496	1480	1500	1460	1450	$^{\delta}$s(NH_2)
ν 12	1422	1430	1450	1420	1420	$^{\delta}$(CH_2)
ν 13	1411	1400	1420	1400	1410	νs(COO^-)
ν 14	1306	1320	1350	1360	1320	$^{\delta}$(CH)
ν 15	1146;1130;1115;1095	1150	1170	1090	1150	$_{\rho}$(NH_2), $^{\delta}$(NH), Indole
ν 16	1072;1058;1050	1090	1100	1030	1040	ν(C-N)
ν 17	1016	-	1030	990	1010	β(CH), Indole
ν 18	877	850	900	840	890	$_{\rho}$(CH_2)
ν 19	748	720	750	720	740	$^{\gamma}$(CH), Indole
ν 20	521	540	550	590	570	$^{\gamma}$(NH), Indole

s – symmetric, as – asymmetric, ν – stretching, $^{\delta}$ – deformation, β – in-plane, $^{\gamma}$ – out of plane, $_{\rho}$–rocking, BR – benzene ring.

3.9 MOLECULAR ELECTROSTATIC POTENTIAL

To determine the sites and the reactivity for electrophilic attack, we calculated the molecular electrostatic potential (MEP) of TrpME with the method DFT/B3LYP and 6-31G(d,p) and 6-311+G(d,p) basis sets.

The values of the electrostatic potential of the molecule are represented by different colors, in which the negative region is marked by red color, and the positive region is identified by the blue color. These two regions are respectively linked to nucleophilic and electrophilic reactivities, and presented in Fig. 13.

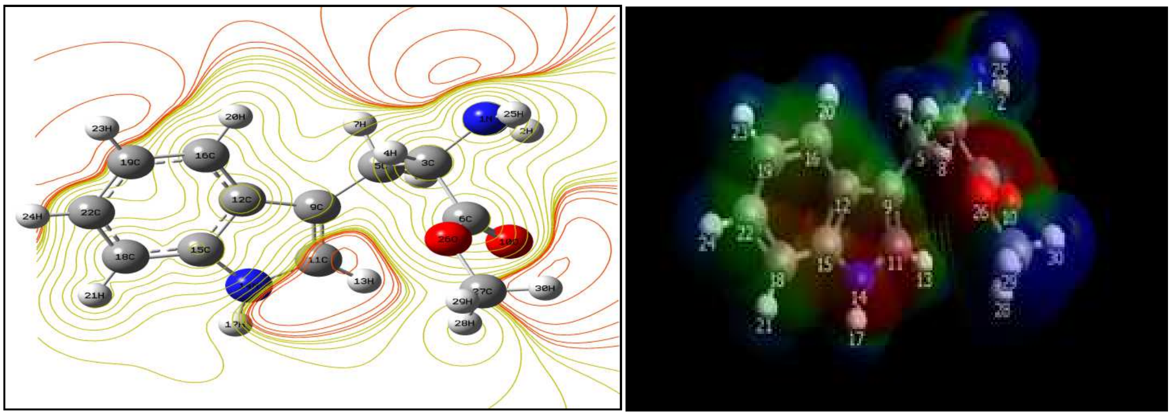


Fig. 13. The surface mapped with electrostatic potential of TrpME

We can readily observe, the region shown by the red color that is concentrated on the two oxygen atoms, while the blue region surrounds the hydrogen atoms. The most negative region is given by the functional B3LYP/6-311+G(d,p), and mainly localized on the nitrogen atom N_1 (-1.558 u.a) of the amino group, and on the carbonyl oxygen atom (Table 10).

Table 10. The electrostatic potential and the charge atomic of TrpME calculated by DFT/B3LYP with 6-31G(d,p) and 6-311+G(d,p) basis sets

Atom	DFT/B3LYP/6-31G(d,p)		DFT/B3LYP/6-311+G(d,p)	
	Charge	Electrostaticpotential (a.u.)	Charge	Electrostaticpotential (a.u.)
N_1	-1.379	-18.412	-1.558	-18.396
H_2	0.574	-1.056	0.639	-1.052
C_3	0.589	-14.681	0.746	-14.670
H_4	0.006	-1.101	-0.016	-1.092
C_5	-0.247	-14.730	-0.235	-14.721
C_6	0.546	-14.586	0.533	-14.577
H_7	0.107	-1.111	0.104	-1.104
H_8	0.085	-1.117	0.079	-1.111
C_9	-0.083	-14.763	-0.146	-14.751
O_{10}	-0.497	-22.309	-0.533	-22.294
C_{11}	-0.131	-14.720	-0.097	-14.711
C_{12}	-0.078	-14.781	-0.059	-14.770
H_{13}	0.159	-1.084	0.166	-1.078
N_{14}	-0.477	-18.312	-0.599	-18.301
C_{15}	0.376	-14.739	0.522	-14.728
C_{16}	-0.049	-14.761	-0.110	-14.750
H_{17}	0.364	-1.004	0.393	-1.003
C_{18}	-0.379	-14.758	-0.463	-14.748
C_{19}	-0.227	-14.774	-0.233	-14.764
H_{20}	-0.009	-1.121	0.001	-1.114
H_{21}	0.150	-1.115	0.169	-1.109
C_{22}	-0.059	-14.763	-0.049	-14.753
H_{23}	0.109	-1.135	0.113	-1.129
H_{24}	0.110	-1.128	0.115	-1.122
H_{25}	0.410	-1.092	0.443	-1.087
O_{26}	-0.026	-22.266	-0.030	-22.253
C_{27}	-0.236	-14.710	-0.225	-14.705
H_{28}	0.104	-1.119	0.101	-1.115
H_{29}	0.096	-1.118	0.082	-1.114
H_{30}	0.092	-1.123	0.083	-1.118

The maximum values of the positive region are at the level of the carbonyl carbon atom C_6 0.533 u.a (calculated by the same basis), and on the C_3 atom attached to the nitrogen atom of the amino group that indicate a possible site for nucleophilic attack.

The MEP map presented in Fig. 13, clearly shows that the sites of the negative potential are located on the most electronegative atoms, while the positive potential sites are located around the carbon of the carbonyl carbon atom.

4 CONCLUSION

Through this survey, we tried to study the molecule of TrpME in its gaseous state by the calculation of its thermodynamic, electronic and orbitals properties, using B3LYP with 6-31G(d,p), 6-31+G(d,p) and 6-311+G(d,p) basis sets.

The complete vibrational assignments and analysis of this molecule have been carried out from the FT-IR spectrum. The equilibrium geometries of the most stable conformers were found and analyzed at DFT/B3LYP/6-31G(d,p) level of theory. The electronic distribution and the intramolecular transfer charge of this molecule are also audited by the calculation of the polarizability and dipole moment.

The study of the molecular electrostatic potential shows that both amino and carbonyl groups of TrpME, which present the negative region, are the most favorable for nucleophilic attack, and that the negative potential sites are located on the most electronegative atoms.

The results of the excitation energy and the absorption wavelengths, obtained by the analysis of UV spectra, show that the electronic absorption corresponding to π-π* transition is attributed mainly to the transition HOMO-2 to LUMO+1, and confirm that the TDDFT method is a powerful tool to study the static and dynamic properties of molecules.

REFERENCES

[1] A. Brack and F. Raulin, L'évolution chimique et les origines de la vie, Masson, Paris, 1991.

[2] M. A. Scotto, S. Antonczac, J. H. Bredehöft, S. V. Hoffmann and U. J. “Meierhenrich, Chiroptical Properties of Amino Acids: A Density Functional Theory Study,” *Symmetry 2,* vol. 2, pp. 935-949, 2010.

[3] M. J. Friedman*,* “Chemistry nutrition and microbiology of D-amino acids,” *Journal of Agricultural and Food Chemistry,* vol. 47, pp. 3457-3479, 1999.

[4] R. Rosset, M. Caude, A. Jardy, Chromatographies en Phases liquide et Supercritique, Masson, Paris, 1991.

[5] S. Walrand, C. Guillet, J. Salles, N. Tardif, A. C. Maurin, P. Fafournoux, N. Cano and Y. Boirie, “Acides aminés et signalisation cellulaire*,*” *Nutrition* Clinique et *Métabolisme*, vol. 22, pp. 161-167, 2008.

[6] J. R. Lakowicz, Principales of Fluorescence Spectroscopy, Kluwer Academic/ Plenum Publishers, New York, 1999.

[7] E. Gindensperger, A. Haegy, C. Daniel and R. J. Marquardt*,* “Ab initio Study of the Electronic Singlet Excited-State Properties of Tryptophan in the Gas Phase: The Role of Alanyl Side-Chain Conformations,” *The Journal of* Chemical Physics*,* vol. 374, pp. 104-110, 2010.

[8] A. Ajdarzadeh, C. Consani, O. Bram, A. Tortschanoff, A. Cannizzo and M. Chergui, “Ultraviolet transient absorption, transient grating and photon echo studies of aqueous tryptophan,” *The Journal of* Chemical Physics*,* vol. 422, pp. 47-52, 2013.

[9] P. Leyton, J. Brunet, V. Silva, C. Paipa, M. V. Castillo and S. A. Brandan, “An experimental and theoretical study of l-tryptophan in an aqueous solution, combining two-layered ONIOM and SCRF calculations, *Spectrochimica Acta part A,* 2012, vol 88, pp. 162-170, 2012.

[10] C. J. Duarte, R. A. Cormanich, “H-1 NMR and theoretical studies on the conformational equilibrium of tryptophan methyl ester,” *Journal of Molecular Structure*, vol. 1050, pp. 174-179, 2013.

[11] V. V. Ghazaryan, M. Fleck and A. M. Petrosyan, “L-Tryptophan L-tryptophanium chloride,” *Spectrochimica Acta A.,* 2015, 136, 743-750.

[12] A. D. Becke, “Density functional thermochemistry. III. The role of exact exchange,” *The Journal of* Chemical Physics*,* vol. 98, pp. 5648-5652, 1993.

[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P.

Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 2009, Revision A. 02 Gaussian Inc, Wallingford CT, 2009.

[14] C. Lee, W. Yang and R. G Parr, “Development of the Colle-Salvetti conelation energy formula into a functional of the electron density,” *Physical Review B,* vol. 37, pp. 785-789, 1988.

[15] J. P. Perdew, K. Burke and Y. Wang, “Generalized gradient approximation for the exchange-correlation hole of a many-electron system,” *Physical Review B,* vol. 54, pp. 16533-16539, 1996.

[16] S. H. Vosko, L. Wilk and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis,” *The Canadian Journal of Physics,* vol. 58, pp. 1200-1211, 1980.

[17] A. Frisch, A. B. Nielson and A. J. Holder, GAUSSVIEW User Manual, Gaussian Inc, Pittsburgh PA, 2000.

[18] A. Frisch, A. B. Nielson and A. J. Holder, GAUSSVIEW User Manual, Gaussian Inc, Pittsburgh PA, 2009.

[19] P. Senthil Kumar, K. Vasudevan, A. Prakasam, M. Geetha and P. M. Anbarasan, “Quantum chemistry calculations of 3-Phenoxyphthalonitrile dye sensitizer for solar cells, *Spectrochimica Acta part A,* vol. 77, pp. 45-50, 2010.

[20] I. Sidir, Y. G. Sidir, M. Kumalar and E. Tasal, “Ab initio Hartree–Fock and density functional theory investigations on the conformational stability, molecular structure and vibrational spectra of 7-acetoxy-6-(2,3-dibromopropyl)-4,8-dimethylcoumarin molecule,” *Journal of Molecular Structure,* vol. 964, pp. 134-151, 2010.

[21] D. Sajan, J. Hubert, V. S. Jayakumar and J. Zaleski, “Structural and electronic contributions to hyperpolarizability in methyl p-hydroxy benzoate,” *Journal of Molecular Structure*, vol. *785*, pp. 43-53, 2006.

[22] J. Bevan Ott and J. Boerio-goates, Calculations from Statistical Thermodynamics, Academic Press, 2000.

[23] A. Dreuw and M. Head-Gordon, “Single-reference ab initio methods for the calculation of excited states of large molecules,” *Chemical Reviews*, vol. 105, pp. 4009-4037, 2005.

[24] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, John Wiley, London, 1976.

[25] G. Varsanyi, Assignments for Vibrational spectra of Seven Hundred Benzene derivatives, vol 1 and 2, Academic Kiaclo, Budapest, 1973.

[26] F. R. Dollish, W. G. Fateley and F. F. Bentely, Characteristic Raman Frequencies on Organic Compounds, John Wiley, New York, 1997.

[27] R. M. Silverstein, R. M. Clayton Bassler and T. C. Morril, Spectroscopic Identification of Organic Compounds, John Wiley, New York, 1991.

[28] N. Sundaraganesan, J. Karpagam, S. Sebastian and J. P. Cornard, “The spectroscopic (FTIR, FT-IR gas phase and FT-Raman), first order hyperpolarizabilities, NMR analysis of 2,4-dichloroaniline by ab initio HF and density functional methods,” *Spectrochimica Acta part A,* vol. 73, pp. 11-19, 2009.

[29] R. Shunmugam and D. N. Sathyanarayana, “Raman and polarized infrared spectra of pyridine-2-thione,” *Spectrochimica Acta part A*, vol. 40, pp. 757-761, 1984.