Quantum Chemical Studies on Structure and Electronic Properties of the 2,7-Bis(4-Methoxyphenyl) 9,9-Dipropyl-9H-Flurene

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Abstract. 2,7-Bis(4-Methoxyphenyl) 9,9-Dipropyl-9H-Flurene (2,7-BMDF) compound used as, biomedical inhibitor, fluorescent tag and a laser dye in other applied applications. Even though this laser dye is usually used in liquid phase, this is promoting to result in more optoelectronic material properties are testified in the literature. The energy levels of HOMO and LUMO of laser grade dyes has vast e□ects on the performance of OLED, DSSCs, and these methods of structured modification will a way to progress in many more advanced organic dyes in the forthcoming. In this paper we have calculated thermodynamic properties, HOMO, LUMO, energy band gap and molecular potential maps using Gaussian o9 with density functional theory of 6-311G basis set. These outcomes provide a deep understanding of structure of the molecule and electronic properties in different mediums characteristics for optoelectronic applications.

INTRODUCTION

The exalite laser grade dye series are identified as unique popular dye laser fields and impacted significant attention in applied fields starting from molecular spectroscopy to dermatology. In particular, the titled compound, 2,7-BMDF is extensively used for laser grade fluorescent dyes in solutions and shows efficient properties of photophysical absorption, fluorescence (λ_{max}) and high quantum yields. Because of high absorption coefficients and high quantum yield of laser dyes make them as latent application for pumping source for the third harmonic generation of a solid state lasers[1].These exalite laser dyes are derivatives of para-quaterphenylenes and their configurations of molecules were augmented to make best production of the compounds as fluorescent laser grade dyes. The spectroscopic investigations are attended by theoretical calculations to know a deeper understanding into photophysical processes arising in the studied molecule. The purpose of our investigation is to explain how the rigidity of the linker influences the structure and electronic properties of a molecular system[2-3].

COMPUTATIONAL METHODS

Compound 2,7-Bis(4-Methoxyphenyl) 9,9-Dipropyl-9H-Flurene (2,7-BMDF) was supplied by Sigma-Aldrich. Quantum chemical DFT and TD-DFT calculations were executed by using Gaussian 09[4] to study the electronic structures of 2,7-BMDF molecule in ethanol, n-heptane acetonitrile solvents and in vacuum by using the B3LYP/6-311G(d) basis set. From this study, we report, theoretical analysed the absorptions, emissions, homo, lumo, bandgap and other structural characteristics of the 2,4-BMDF[5-6].

RESULTS AND DISCUSSION

Absorptions and emissions studies

The optimized structure of 2,7-BMDF (ground state) in various polarities of solvents were performed to Time Dependent (TD) first 06 states calculations in direction to get vertical excitations by means of the B3LYP/6-311G(d) basis set. These directed to additional knowledge of the absorption parameters of the studied dye and observed results are tabulated in Table 1. The outcomes of DFT and TD-DFT also suggests directly influence on the absorption of the 2,7-BMDF molecule when expose to the change in solvent polarities (Table 1). The maximum absorption in all di□erent solvents are 606-654 nm and in vacuum 691 nm which is highest compare to solvents media.

The minimum energy required to S1, in order to get further optimized emissions structures were subjected to the time dependent (TD) 06 states energy calculations (B3LYP/6-311G(d)) 10, and the calculated emission wavelengths are noted in Table 1. From the calculated (Table 1) emissions like vertical excitations, it clearly understands that, there is small amount wavelength changes because, the solvent polarity influence on the emission wavelengths. By TD-DFT the calculated emission wavelength maxima for the 2,7-BMDF in different polarity solvents are correlated with the transition of HOMO to LUMO around 617−721 nm and 0.0027−0.0034 order of an oscillator strength also summarized in Table 1.

Table 1: Theoretically computed energy, UV-Vis excitation energy and oscillator strength and dipole moment by B3LYP method.

Solvents	***E_{so-s1} (eV)**	**Absorption λ_{max} (nm)**	**Emission λ_{max} (nm)**	**Oscillator strength 'f'**	**Dipole moment 'μ' (Debye)**			
					X	Y	Z	Total
Vacuum	0.9418	691.10	721.10	0.0027	0.6460	0.4100	-1.7309	1.8925
Ethanol	1.3386	609.41	620.23	0.0031	0.9174	1.1158	-2.6394	3.0089
n-Heptane	1.1151	654.33	680.03	0.0034	0.7571	0.6815	-2.1007	2.3346
Acetonitrile	1.3451	608.15	617.58	0.0030	0.9223	1.1299	-2.6561	3.0302

*Abbreviations: E, energy required for S_o-S_1 state

Frontier molecular orbitals

Frontier molecular orbitals, HOMO, LUMO of the Energy levels and their three-dimensional distributions have the information about behavior of the organic molecules in terms of lasing parameters, photo-stabilities and photophysical properties. Figure 1. Shows the frontier molecular orbitals (used by the B3LYP/6-311G(d) basis set) of the dye 2,7-BMDF in vacuum and one of selected solvent acetonitrile. In Table 2 contains the HOMO, LUMO (energies in eV) and the energy band gaps of the 2,7-BMDF in vacuum, ethanol, n-heptane and acetonitrile solvents of various polarities. From Figure 1, it clear picture of the HOMO in the 2,7-BMDF the electron density is distributed on the 2,7-bis(4-methoxyphenyl) -9H-flurene core but completely away from 9,9-dipropyl and but in the LUMO of the 2,7-BMDF, the electron cloud density is localized nearly uniformly entire the complete molecule in vacuum. These results may be confirmed that, the 2,7-BMDF dye in the HOMO may easily interact with the in position generated singlet oxygen upon excitation, for the reason that all the double bond has a maximum electron density distribution in the HOMO (Figure 1.) compared to the LUMO[4].

In the case of the 2,7-BMDF in acetonitrile, the distribution of electron density in HOMO and LUMO orbitals shows opposite trend observations when compared to in vacuum, this confirms again the participation of the 2,7-BMDF in HOMO has photochemical reaction with oxygen. Table 2 reveal that, 2,7-BMDF, the energy band gap (HOMO-LUMO) is the order of 4.10 eV in vacuum and in solvent media the energy band gap is decreasing with the various solvent polarity.

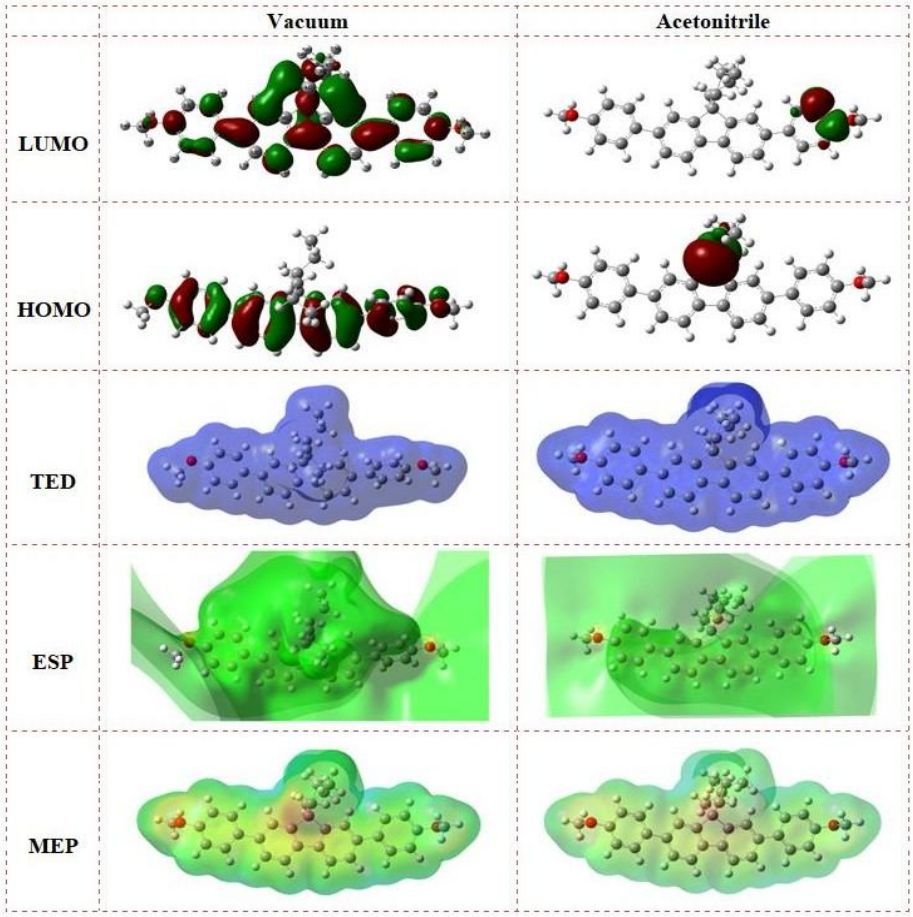

FIGURE 1. 3D Plot of HOMO-LUMO, Total electron density, Electrostatic potential and Molecular electrostatic potential in vacuum and solvent using DFT/B3LYP/6-311G.

Total electron density, Electrostatic potential and Molecular electrostatic potential maps

All maps above said subtitle, are constructed with DFT theory with 6-311G level are shown in Fig.1. Total electron density plots show uniform distribution. A MEP is very influential tool describes, the molecular sites of hydrogen bonding interaction, nucleophilic reactions and electrophilic attack. By using 6-311G level theory we calculated the ρ(r) - molecular electrostatic potential surface is found 5×10^{-5} electrons/bohr^3 contour of the total self-consistent field (SCF) electron density for 2,7-BMDF dye. In Fig.1. the localized electron regions with electrostatic potential are red in colour as negative, and green in colour as positive distribution maps. The negative MEP (red colour) region of high electron density which are in the location of O1 (E = 1.414 eV & E = 1.635 eV) and O2 (E= - 2.480 eV and E= -2.224 eV) in vacuum and in acetonitrile respectively. The positive MEP (green colour) regions of highly depleted electron density, which are the location of H62 be bounded by C41 (E = 0.264 eV & E = -0.650 eV), H68 be bounded by C47 (E = 0.413 eV & E = 0.561 eV), H14 be bounded by C11 (E = 0.177 eV & E = -0.424 eV) and H7 bounded C1 (E = 0.154 eV & E = 0.081 eV) in vacuum and in acetonitrile respectively.

Dipole moments and Thermodynamic properties

Table 1 summarized the dipole moments of the 2,7-BMDF in vacuum and in various solvent polarities by using TD-DFT method. The results of this calculations revealed notifying changes in dipole moment values of the S_0 (ground state) and S_1 (excited state) states of the 2,7-BMDF in vacuum and solvents of different polarities,

supportive of the strong solvatochromism[6]. Table 3 presents the thermodynamic parameters calculated gives the direction of chemical reactions according to the thermodynamic law.

Table 2: The HOMO, LUMO and Energy bandgap computed by DFT/B3LYP/6-311G.

Solvents	HOMO (eV)	LUMO (eV)	Energy band gap E_g(eV)	Major contributions
Vacuum	-5.3738	-1.2719	4.1020	H→L (79.16%)
Ethanol	-4.5842	0.2471	4.8313	H→L (50.83%)
n-Heptane	-4.0909	-1.6961	2.3948	H→L (68.08%)
Acetonitrile	-4.3144	-1.7418	2.5726	H→L (50.34%)

Table 3: Calculated thermodynamic parameters with DFT theory using B3LYP/6-311G basis set.

Parameters	DFT/B3LYP/6-311G
Energy(kcal mol^{-1})	
Translational	0.889
Rotational	0.889
Vibrational	385.923
Total	387.700
Nuclear repulsion energy(Hartrees)	3359.263
Zero-point vibrational energy (kcal mol^{-1})	367.5032
Heat capacity, C_v(Cal/Mol-Kelvin)	124.931
Entropy, S(Cal/Mol-Kelvin)	207.914
Molecular capacity of constant volume (cal mol^{-1} k^{-1})	
Translational	2.981
Rotational	2.981
Vibrational	118.969
Total	124.931
Rotational constants (GHZ)	
A	0.33644
B	0.03784
C	0.03661
Rotational temperatures (Kelvin)	
A	0.01615
B	0.00182
C	0.00176

CONCLUSION

The electronic properties and structural studies by using the Time Dependent-DFT method are significantly calculated by the titled compound. From molecular orbital, it is confirmed that, the 2,7-BMDF dye in the HOMO may easily interact with the in position generated singlet oxygen upon excitation, for the reason that all the double bond has a maximum electron density distribution in the HOMO compared to the LUMO. The results notifying changes in dipole moment values of the S_0 (ground state) and S_1 (excited state) states of the 2,7-BMDF in vacuum and solvents of different polarities, supportive of the strong solvatochromism. The thermodynamic parameters give the direction of chemical reactions according to the thermodynamic law. These results will be useful for the forthcoming synthesis and designing of e□cient photophysical and laser properties of photostable2,7-BMDF laser dyes.

REFERENCES

1. W. F. Vaz, J. M. F. Custodio, N. M. N. Rodrigues, L. G. Santin et al. J. Mol. Mod. **23** 315 (2017).
2. G.H. Pujar, M.N. Wari, B. Steffi, H. Varsha, et al. J. Mol. Liq**244** 453 (2017).
3. C. G. Renuka, Y. F. Nadaf, G. Sriprakash, and S. Rajendra Prasad, J. Fluoro.**28** 839 (2018).
4. Carlo Adamo and Denis Jacquemin, ChemSoc Rev**42** 845 (2013).
5. YugalKhajuria, MeeraMahajan,Ujval Gupta1, Satishwer Singh, and Kamni1, Mat Focus**4** 385 (2015).
6. Shivraj, Anup Thomas, B. Siddlingeshwar and Sharanabasappa B. Patil,Lumine**32** 1328 (2017).