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DFT Studies on Excited State Geometry, Vibrational Modes, NMR, Molecular Orbital and Mulliken Charges of Laser Dye

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Abstract

The laser dye 2, 5-diphenyl-1, 3, 4-oxadiazole (PPD), which has many uses in science and technology, has been the topic of DFT investigation using the Gaussian 16. Laser dye geometry has been optimised at the 6-311++G(d, p)/B3LYP basis set using the DFT approach. A graphic representation of the overall energy variation as a function of optimisation phases is shown. The DFT approach yielded a ground state dipole moment of 3.61 Debye. A computational technique called TD-DFT at 6-311++G (d, p)/B3LYP basis set has been utilised to analyse the UV-visible spectra of laser dye in ethanol. The eccentric state geometry yielded parameters such as absorption maxima, oscillator strength, and excited-state energy. The dipole moment in the excited state is about 5.11 Debye. The excited state's dipole moment is larger than the ground state's. The DFT and TD-DFT techniques were used to determine the Mulliken atomic charges. Chemical shifts and vibrational modes have been studied using NMR and IR spectroscopy, respectively. Atomic charges and electron densities can be used to determine a molecule's dipole moment and charge distribution. Given the small HOMO-LUMO energy gap, the molecule should be soft. The electrostatic potential map is used to identify the molecule's electrophilic and nucleophilic locations.

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According to these investigations, the molecule might be used in optoelectronics.

Keywords: DFT, TD-DFT, Laser dye, HOMO-LUMO, ESP

1. Introduction

Calculations of electronic structure are commonly performed by Gaussian software. Studying ever-larger molecular systems is made possible by Gaussian 16's new computational techniques and features [1]. It uses simple computer techniques to predict a wide range of molecular properties. Physicists, chemists, chemical engineers, biochemists, and other scientists can use Gaussian software to conduct research in both well-established and newly emerging chemical fields. It saves a significant amount of laboratory experiment time and enables us to execute virtual chemistry at a fair price [2]. By comparing structures with and without the bond, the hydrogen bond was studied using Density functional theory (DFT), which forecasts the probe's lowest energy in the solvent and gas phase and its structural characteristics. In this present work, we have investigated the electronic structure properties of laser dye using theoretical computation methods.

In addition to being used as fluorescence indicators and anticoagulants, laser dyes have anthelmintic and optical brightness qualities [3]. Using computational techniques, we present the ground and excited state dipole moments of a few laser dyes in this study. The excited state geometries are associated with UV-visible spectra. Gaussian offers a number of techniques, including TD-DFT (Time-Dependent Density Functional Theory), ZINDO (Zerner's Intermediate Neglect of Differential Overlap), and CIS (Configuration Interaction Singles), for studying excited state systems. One of the most used tools for studying excited state geometries is TD-DFT. Rich details about the electrical and geometrical structure of the molecule in the short-lived state can be obtained by examining the excited state dipole moments of PPD. In certain photochemical reactions, this information would be useful for determining the site of attack by electrophilic and nucleophilic reagents, for designing nonlinear optical materials, and for clarifying the nature of the excited states. It would also reflect the charge distribution in the molecule.

Each organic and inorganic molecule's optical parameters are simulated using DFT and TDDFT. DFT is used to study the molecule's ground state parameters, while TD-DFT is used to model the energies, systems, and properties of electronically excited states. DFT provides a theoretical prediction for molecular drug design and enables us to comprehend the chemical processes in organic structures. The title molecule has generated interest due to its several applications in 2, 5-diphenyl-1,3,4-oxadiazole laser dye, as previously indicated. Therefore, using quantum chemical calculations, an effort has been made to conduct systematic research of geometrical qualities, structural properties, frontier molecular orbital analysis, total electron density (TED), and electrostatic potential (ESP).

2. Computational Methods

Theoretical computations have been performed using DFT with B3LYP level theory utilising the 6-311++G(d,p)/B3LYP basis set in Gaussian-16. Using computational methods in solution, such as TD-DFT evaluated with IEFPCM (Integral Equation Formalism Polarizable Continuum Model), the UV-visible spectra of laser dyes have been obtained for the optimum shape. Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO), electron density, Mulliken charges, and ESP map are all calculated at the same basis level using the DFT and TD-DFT methods [4].

3. Results and Discussion

The findings of computational investigations utilising Gaussian 16 software are represented in this paper. To optimise the shape of the chosen laser dye PPD, many molecular characteristics have been investigated. Using the necessary basis sets, TD-DFT computational methods have been used to study spectroscopic analysis, including UV-visible spectra. Mulliken atomic charges have been examined in conjunction with the HOMO-LUMO, and ESP maps 3D molecular orbital plots.

4. Geometry Optimization

Using DFT, the geometry optimisation of PPD has been done in a vacuum. Fig. 1 (a) displays the three molecules' optimised geometry. The dipole moment's direction is indicated by the arrow mark [5]. Fig. 1 (b) displays the change in total energy as a function of PPD optimisation phases. For PPD, there are nine optimisation phases. As optimisation steps rise and reach a fixed amount, energy declines. At the lowest optimisation stage, the energy is at its maximum, and at the highest optimisation level, it is at its minimum. Polarizability is approximately 167 Debye, while the ground state dipole moment is approximately 3.61 Debye.

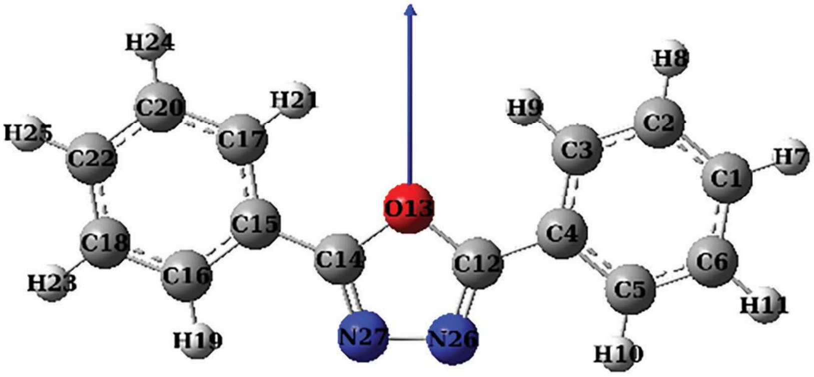

Fig. 1 a) Optimized geometry of PPD by DFT method in the gas phase.

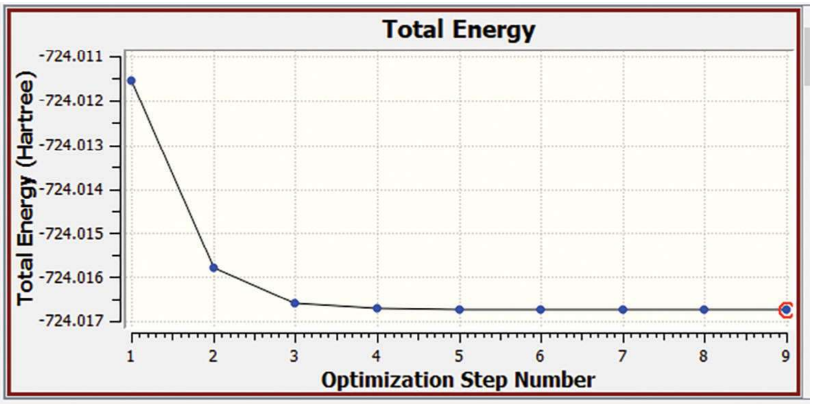

Fig. 1 b) Variation of optimisation steps as a function of energy.

UV-Visible Spectra

With absorption maximums at 322, 276, and 273 nm in ethanol, respectively, Fig. 2 displays UV–Vis absorption values derived from the TD-DFT method at 6-311++G(d,p)/B3LYP basis set displayed in

Table 1. Only the first transition will be visible in the UV-Vis spectrum, the second is completely impossible, and the third will have a very low absorption coefficient, according to the oscillator strengths for the corresponding transitions, which are 0.936, 0.0000 and 0.024 [6]. When the absorption coefficient is less, the excited state energies are larger. The absorption coefficient of UV-visible spectra depends on Oscillator Strength. If the oscillator strength is maximum, there is a high absorption coefficient, if it is minimum, there is less absorption coefficient. If it is zero, the absorption coefficient is not at all possible. The ground state dipole moment derived from the DFT approach is 3.16 Debye, while the excited state dipole moment derived from TD-DFT is 5.11 Debye. It is evident that the dipole moment of the excited state is greater than that of the ground state.

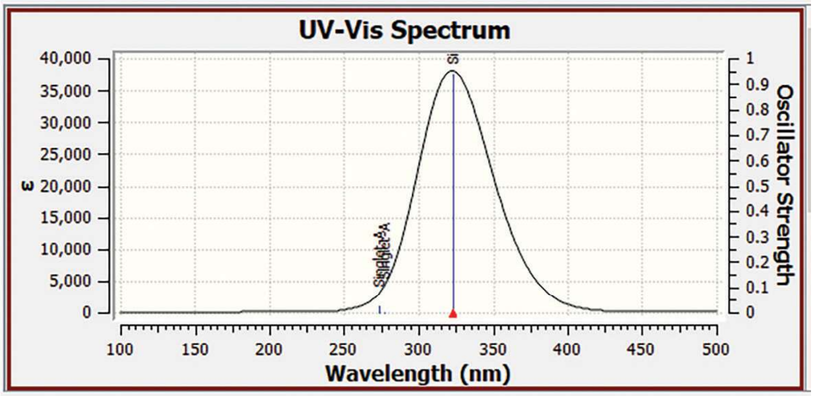

Fig. 2 UV-Visible spectra of PPD using TD-DFT method in ethanol.

Table 1: Data of PPD from UV-Visible Spectra by TD-DFT method in ethanol

	Values of the Parameter		
Absorption maxima (nm)	λ_1 =322	λ_2 =276	λ_3 =273
Oscillator strength	f_1 =0.936	f_2 =0.000	f_3 =0.024
Excited state energy (eV)	E_1 =3.84	E_2 =4.47	E_3 =4.53

IR Spectra

In organic chemistry, where identifying functional groups is crucial, vibrational spectroscopy is frequently used. It is also employed in the research of kinetics and molecular confirmations. When light from vibrating molecules is absorbed, infrared spectra are produced. Stretching and bending vibrations are the two fundamental kinds. The molecule exhibits the C=C, C-O-C, C-H, N-C, and N-N bond vibrations listed in Table 2. Stretching and bending are the two main categories of vibrations. The region of 1000 cm^{-1} to 1700 cm^{-1} is where the largest peak of various vibration types is observed. Typically, C-H vibrations are seen above 3000 cm^{-1}.

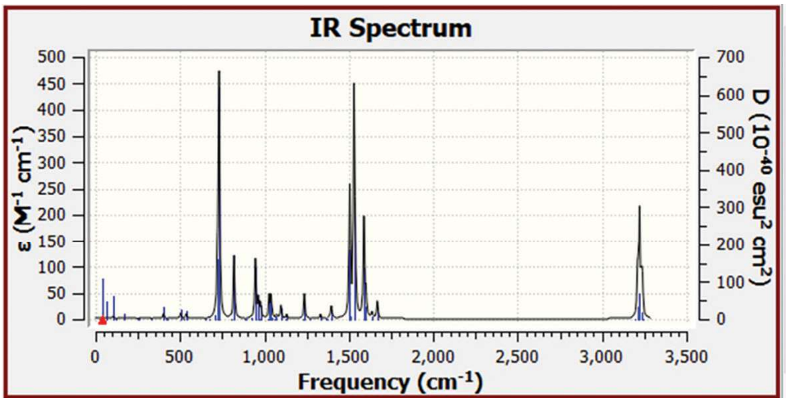

Fig. 3 IR spectra of PPD using DFT method in vacuum.

Table 2 Vibrational modes of laser dye.

v (cm^{-1})	Vibrational modes
946	C-O-C stretching
1097	C-O-C Stretching, C-C C=C C-H bending
1236	C-H bending
1507	C-O C-C C=C C-H bending
1536,	N=C Stretching, C-H Bending,
1600	C-H stretching

NMR Spectra

Using the DFT 6-311++G (d, p) basis set in a vacuum, the laser dye PPD for the ^{1}H & ^{13}C NMR shielding values was calculated in conjunction with the GIAO theory. Figure 4 shows the calculated isotropic shifts. The shielding values for ^{13}C NMR are greater than those for ^{1}H NMR. ^{13}C NMR values range from 61 to 66 ppm, with a maximum of roughly 66.98 ppm for C-5. ^{1}H NMR shielding values fall between 24 and 25 ppm. One of the most crucial methods for the structural investigation of organic compounds is chemical shift analysis. (Table 3)

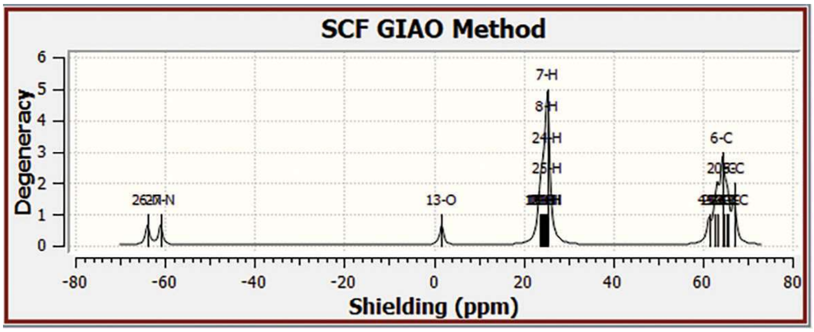

Fig. 4 NMR spectra of PPD using GIAO method in a vacuum.

Table 3 Shielding values (ppm) of laser dye.

Atoms	Shielding values	Atoms	Shielding values
12-C	23.52	8-H	25.44
14-C	23.88	7-H	25.45
19-H	24.19	4-C	61.37
10-H	24.58	15-C	62.65
9-H	24.89	22-C	63.20
21-H	25.04	1-C	63.33
23-H	25.35	3-C	64.29
11-H	25.42	20-C	64.34
25-H	25.43	6-C	64.37
24-H	25.43	18-C	64.77
16-C	65.34	17-C	66.97
2-C	65.62	5-C	66.98

Mulliken charges

DFT and TD-DFT calculations of the Mulliken atomic charge at the 6-311++G (d, p)/B3LYP basis set are shown in Table 4. In Figure 5, the atomic charges of the atom are represented graphically. Their function in defining electronic structure, dipole moment, molecule polarizability, and many other relevant aspects of molecular systems is significant [7]. While nitrogen and oxygen atoms are negatively charged, hydrogen atoms are positively charged. Atoms of carbon can have either a positive or negative charge. Among the donor atoms are 1C, 2C, 3C, 5C, 6C, 13O, 16C, 17C, 18C, 20C, 21C, 22C, 26N, and 27N. Acting as acceptor atoms are 4C, 12C, 14C, and 15C.

Table 4: Mulliken charges of PPD from DFT and TD-DFT method

Atoms	Ethanol	Gas phase	Atoms	Ethanol	Gas phase
1C	-0.1159	-0.1066	15C	0.0763	0.0905
2C	-0.1501	-0.1393	16C	-0.1208	-0.1160
3C	-0.1323	-0.1256	17C	-0.1323	-0.1256
4C	0.0763	0.0905	18C	-0.1553	-0.1424
5C	-0.1208	-0.1160	19H	0.1713	0.1760
6C	-0.1553	-0.1424	20C	-0.1501	-0.1393
7H	0.1564	0.1350	21H	0.1755	0.1574
8H	0.1566	0.1345	22C	-0.1159	-0.1066
9H	0.1755	0.1574	23H	0.1567	0.1373
10H	0.1713	0.1760	24H	0.1567	0.1345
11H	0.1567	0.1373	25H	0.1564	0.1350
12C	0.3532	0.3399	26N	-0.3149	-0.2851
13O	-0.5135	-0.5112	27N	-0.3149	-0.2851
14C	0.3532	0.3399			

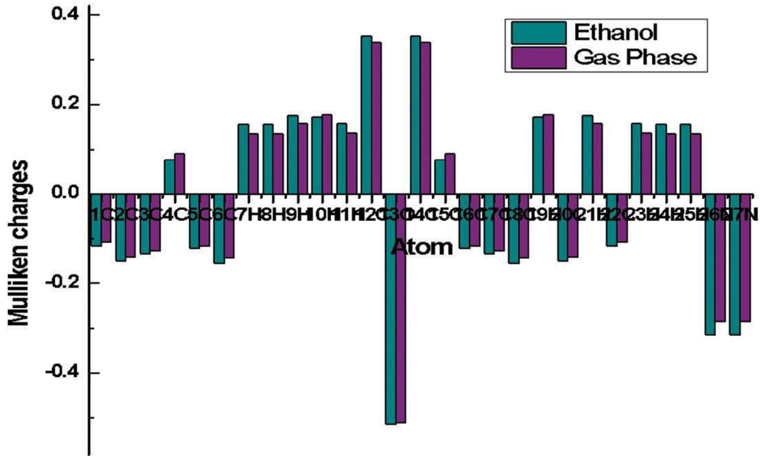

Fig. 5 3D-Plots of Mulliken charges of PPD from DFT and TD-DFT method.

HOMO-LUMO and ESP maps

The electrical, optical, and UV-Vis spectral research regards the frontier molecular orbit (FMO) as a crucial function. Numerous significant electron donors are represented by the HOMO orbital, while numerous significant electron acceptors are represented by the LUMO orbital [8, 9]. The sample's stability, hardness, softness, and chemical reactivity are all described by the gap between the HOMO and LUMO. The DFT approach performs HOMO-LUMO analysis, which is shown in Fig. 6 (a). The HOMO, LUMO, and energy gap of the title molecule are -0.233 eV, -0.067 eV, and 0.167 eV, respectively, in the gas phase. The energy gap in ethanol is -0.157 eV, the HOMO energy is -0.234 eV, and the LUMO energy is -0.077 eV. This small energy gap shows that the present molecule acts as a chemically stable and soft molecule [7].

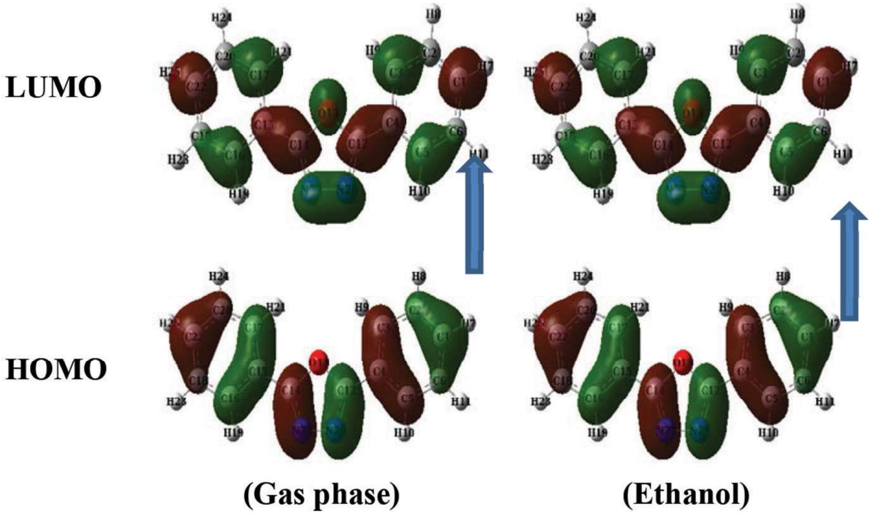

Fig. 6 (a) 3D Plots of HOMO-LUMO by DFT (in gas phase) and TD-DFT (in ethanol) method at B3LYP/6-311 (G) basis set.

Electron density is the foundation of ESP analysis. Studying molecular characteristics, including hydrogen bonding, electrophilic, and nucleophilic assaults on the molecule sit,e is made easier with the use of the ESP [10–12]. Using colour coding, this study helps determine the molecule’s size, structure, and charge areas. The colour blue indicates the largest positive charge on the molecule, whereas the colour red indicates the highest negative charge. Fig. 6 (b) displays the ESP surface plotted on the optimised molecule. The oxadiazole ring has a deep red nitrogen atom, the source of the most electrophilic assault.

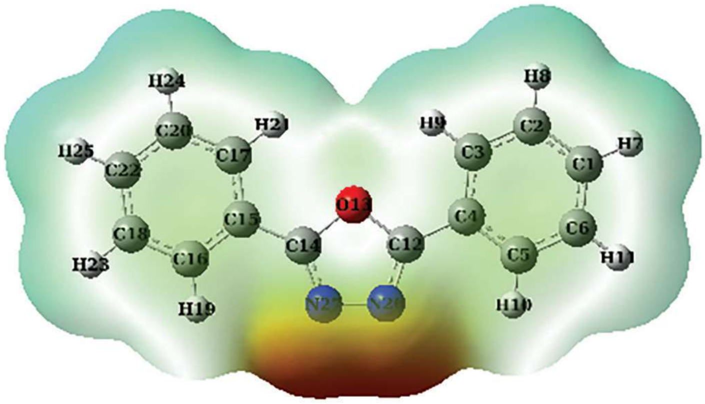

Fig. 6 (b) ESP map of PPD in ethanol from TD –DFT method.

5. Conclusion

In this paper, several molecular characteristics of laser dye PPD are theoretically studied using computational approaches. The geometry of PPD in the gas phase is optimised using the DFT approach at the 6-311++G(d,p) basis set. The highest absorption peak corresponding to the strongest oscillator is UV-visible absorption at 322 nm. DFT yielded a ground state dipole moment of 3.61 Debye, while the TD-DFT approach yielded an excited state dipole value of 5.11 Debye. The dipole moment of the excited state is greater than that of the ground state. The different molecular characteristics of the laser dye can be ascertained with the use of Mulliken atomic charges. The title molecule has an energy gap of 0.167 eV, indicating that it is soft. According to the ESP surface analysis, the nitrogen atoms in the oxadiazole ring exhibit a dark red region that predicts electrophilic assault, while the hydrogen atoms in the benzene ring have a bright sky blue region that is responsible for the nucleophilic attack.

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Conflict of Interest: Authors declare that they have no conflict of interest.

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