ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ЭЛЕКТРОННОЙ СТРУКТУРЫ И СПЕКТРАЛЬНЫХ СВОЙСТВ МОЛЕКУЛЫ 2,5-ДИФЕНИЛОКСАЗОЛА (PPO) С ИСПОЛЬЗОВАНИЕМ КВАНТОВО-ХИМИЧЕСКИХ МЕТОДОВ

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Аннотация: в данном теоретическое исследование направлено на изучение геометрических, электронных и спектральных свойств молекулы 2,5-дифенилоксазола (PPO), которая широко используется в качестве первичного органического сцинтиллятора в детекторах высокоэнергетического излучения. В данном исследовании были использованы квантово-химические методы, в частности, теория функционала плотности (DFT) с использованием гибридного функционала B3LYP и базиса 3-21+G*. Расчеты были выполнены с помощью программного пакета Gaussian 09, в результате чего была определена оптимальная геометрия молекулы и глобальная минимальная энергия (-704,379679 Хартри или -19167,1473 эВ). Результаты показывают, что молекула PPO обладает высокой стабильностью, что подтверждается энергетической щелью HOMO-LUMO 4,18 эВ (или 0,15362 Хартри).

Ключевые слова: PPO, DFT, Gaussian 09, HOMO-LUMO, инфракрасный спектр, спектр Рамана.

THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE AND SPECTRAL PROPERTIES OF THE 2,5-DIPHENYLOXAZOLE (PPO) MOLECULE USING QUANTUM CHEMICAL METHODS

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Abstract: this theoretical study is aimed at investigating the geometrical, electronic, and spectral properties of the 2,5-diphenyloxazole (PPO) molecule, which is widely used as a primary organic scintillator in high-energy radiation detectors. Quantum-chemical methods, specifically the Density Functional Theory (DFT) framework utilizing the B3LYP hybrid functional and the 3-21+G basis set*, were employed in this research. The calculations were performed using the Gaussian 09 software package, resulting in the determination of the molecule's optimal geometry and the global minimum energy (-704.379679 Hartree or -19167.1473 eV). The results indicate that the PPO molecule possesses high stability, which is confirmed by the HOMO-LUMO energy gap of 4.18 eV (or 0.15362 Hartree).

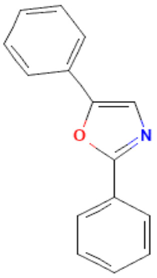
Keywords: PPO, DFT, Gaussian 09, HOMO-LUMO, infrared spectrum, Raman spectrum.

INTRODUCTION

2,5-Diphenyloxazole (PPO) is a primary organic scintillator widely utilized in modern nuclear physics and medicine. Its main function is to absorb high-energy radiation and re-emit it in a range detectable by photomultiplier tubes [1,3,4]. The efficiency of PPO is directly dependent on its electronic structure and molecular vibrations. Alongside experimental methods, quantum-chemical calculations provide a deeper understanding of the molecule's energy levels and stability. The objective of this work is to determine the optimal geometry of the PPO molecule using the Gaussian 09 software package and theoretically predict its physicochemical properties [2,5,6,7].

To strengthen the theoretical basis of this research, fundamental works on modern quantum-chemical calculations and spectral analysis were studied. Specifically, unique studies on the photostability and synthesis of scintillation materials, including compounds based on PPO, as well as research into creating highly efficient liquid scintillators by hybridizing organic molecules with perovskite nanocrystals, were analyzed. Furthermore, works conducted on two-photon excited luminescence in polycyclic aromatic compounds and methods for recording the Raman spectra of various organic/inorganic powders provided a theoretical foundation for deeply understanding the optical properties of the PPO molecule [8,9,10]. This analysis serves to evaluate the electronic structure of PPO and its role in synergistic materials. Table 1 shows the molecular weight, chemical and structural formulas of the PPO molecule.

Table 1. Molecular weight, structural and chemical formulas of PPO molecule

Chemical formula	$C_{15}H_{11}NO$
Chemical structure	
Molar mass	221.15 u.a.

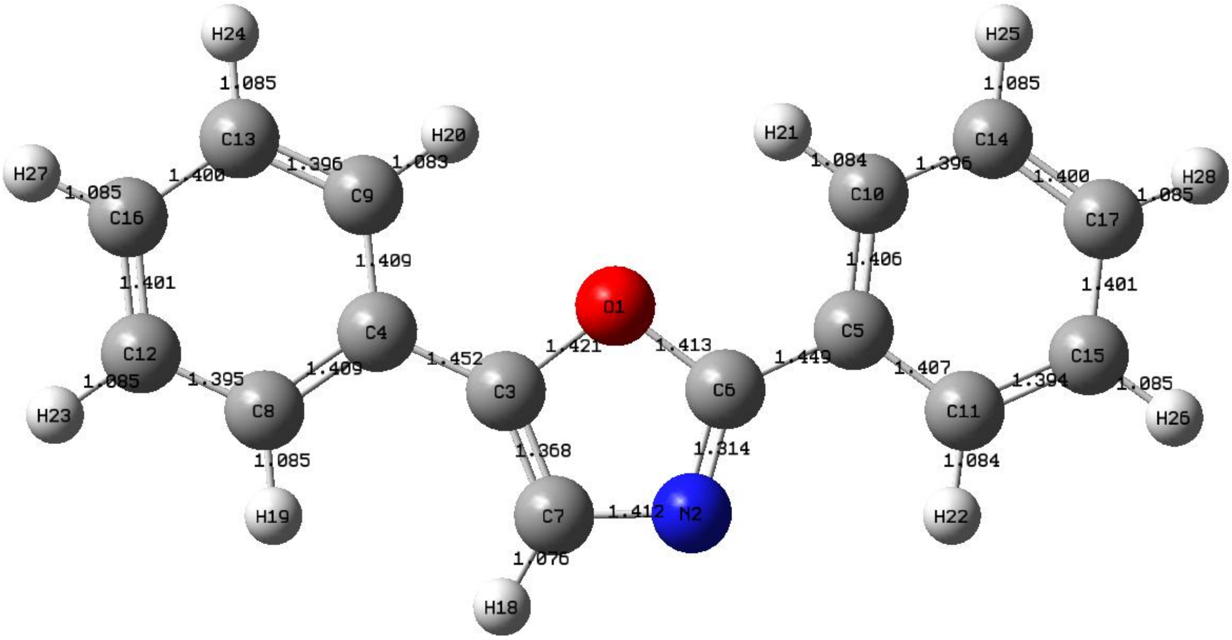


Figure 1. Bond lengths (Å) between atoms in the PPO molecule.

RESEARCH METHODOLOGY

All quantum-chemical calculations were performed using the Gaussian 09W (Revision A.02) software package. Density Functional Theory (DFT) was employed for the calculations. Functional and Basis Set: The B3LYP (Becke, 3-parameter, Lee-Yang-Parr) hybrid functional and the 3-21+G basis set* were selected. This basis set includes diffuse (+) and polarization (*) functions, which aids in a more accurate description of the molecule's electron cloud.

The geometry of the molecule was fully optimized using the Berny algorithm. After the stable point was found, harmonic vibrational frequencies and the Raman scattering spectrum were calculated.

RESULTS AND DISCUSSION

The optimal geometric and energetic parameters of the molecule were determined through quantum-chemical calculations. The optimization process was successfully completed, and a stationary point (global minimum) was found on the potential energy surface. The calculation results are presented in Table 2.

Table 2. Energetic parameters of the PPO molecule.

Electronic Energy	-19167.1473	eV
RMS Gradient Norm	8.2275×10^{-4}	eV/Å
Imaginary Frequency	-	-
Dipole Moment	1.595147	Debye
Polarizability (α)	198.850178	a.u.
Hyperpolarizability (β)	501.281519	a.u.

HOMO / LUMO. HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are core concepts of molecular orbital theory. HOMO determines the molecule's ability to donate electrons (donor capacity), while LUMO determines its ability to accept electrons (acceptor capacity).

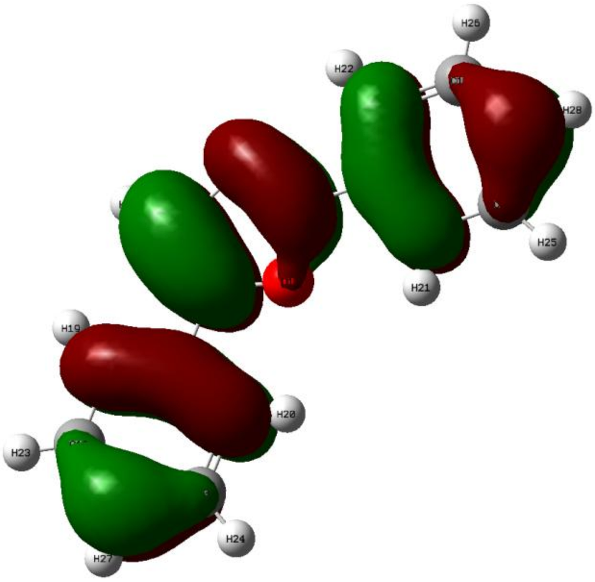


Figure 2. Visual analysis of the HOMO and LUMO of the PPO molecule.

The energies of the frontier orbitals, which determine the molecule's chemical activity and optical properties, are presented in the following Table 3

Table 3. HUMO and LUMO energies.

Orbital	Energy (Hatree)	Energy (eV)
LUMO	-0.07210	-1.96
HOMO	0.22572	-6.14
Energy gap	0.15362	4.18

The IR (Infrared) spectrum and Raman spectrum of the PPO molecule were calculated using quantum-chemical modeling. The analysis of the vibrational frequencies showed that all frequencies have positive values, which confirms the stability of the optimized structure.

Figure 3 and Figure 4 present a segment of the characteristic diagnostic infrared (IR) and Raman spectra of the PPO molecule. Spectral analysis makes it possible to determine the molecular structure, the stretching and deformation vibrations, and the symmetry properties of the molecule.

The main bands in the IR spectrum reflect the functional groups and types of bonds present in the molecule. For PPO, the spectrum was analyzed in the following key regions:

3600-3200 cm^{-1} Range: This range corresponds to the O–H or N–H stretching vibrations. The 2,5-diphenyloxazole molecule does not contain a defined O–H group, so small or insignificant bands in this range may only arise from electron cloud interactions or overtone vibrations.

3100-3000 cm^{-1} Range: This corresponds to the C–H stretching vibrations, particularly those of the hydrogen atoms in the aromatic phenyl groups. High-intensity bands are located in this range of the spectrum, indicating the symmetric and asymmetric stretching vibrations of the phenyl ring C–H bonds.

1600-1450 cm^{-1} Range: The C=C stretching vibrations in the aromatic rings are typically observed in this region. Two or three noticeable bands in the spectrum reflect the symmetric and asymmetric stretching vibrations of the aromatic phenyl groups.

1300-1000 cm^{-1} Range: Bands corresponding to the stretching and deformation vibrations of the C–O–C and oxazole rings are located in this range. These bands were observed to have medium to low intensity in the IR spectrum.

1000-500 cm^{-1} Range: Bands corresponding to the ring deformation and torsion vibrations of the molecule. The low-frequency region of the spectrum provides information about the flexibility of the molecular structure and the intramolecular bonds.

Infrared (IR) Spectrum Summary: The band with the highest intensity was observed at a frequency of 737.68 cm^{-1}. This primarily corresponds to the out-of-plane deformation vibrations of the C-H bonds.

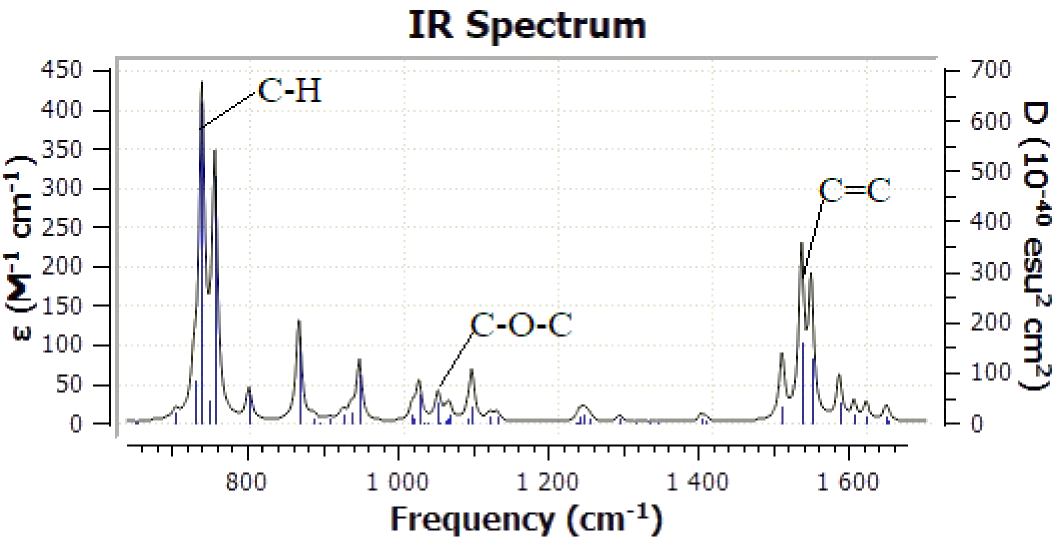


Figure 3. IR spectrum of the PPO molecule.

The Raman spectrum has a higher sensitivity compared to the IR spectrum in displaying symmetric vibrations. In the spectral analysis:

C–C and C–O–C Stretching vibrations: These bands appear with high intensity in the Raman spectrum, corresponding to the main structural vibrations of the molecule.

Aromatic rings: The symmetric C=C stretching vibrations in the phenyl groups stand out more clearly in the Raman spectrum. This is particularly noticeable in the 1600-1500 cm^{-1} range of the spectrum.

C–H Vibrations: Aromatic C–H bonds are also noticeable in the Raman spectrum, but their intensity may be lower compared to the IR spectrum.

Raman spectrum summary: The strongest Raman activity was recorded at 1565.81 cm^{-1}. This band is associated with the stretching vibrations of the C=C bonds in the aromatic rings and is considered the most diagnostic peak in the Raman spectrum.

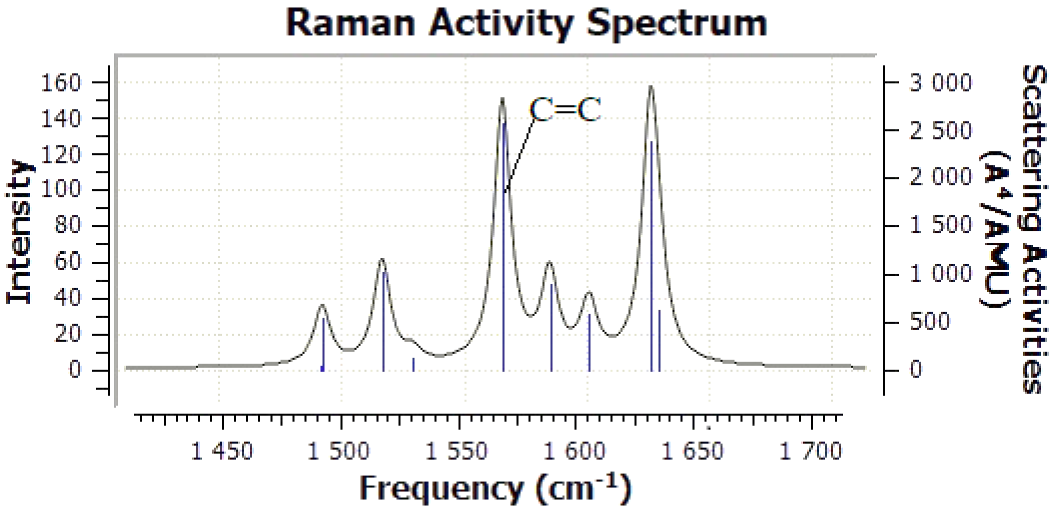


Figure 4. Raman spectrum of the PPO molecule.

The combined analysis of the IR and Raman spectra is crucial for determining the molecule's symmetry and functional groups. For the PPO molecule: The aromatic phenyl groups and the oxazole ring generate the principal bands in the molecular spectrum. The IR spectrum primarily reflects asymmetric vibrations, while the Raman spectrum primarily reflects symmetric vibrations. Low-frequency bands provide information about the molecular structure and deformation vibrations. Intensities in the spectral scales depend on the symmetry and polarization of the electron cloud distribution within the molecule. The thermodynamic properties of the PPO molecule are presented in Table 4.

Table 4. The thermodynamic properties of the PPO molecule.

Thermodynamic property	Value	Unit
Imaginary frequency	0	-
Temperature	298.150	Kelvin
Pressure	1.00000	atm
Scaling factor (or Scaled frequencies)	0.8929	-
Electronic energy (EE)	-19167.1473	eV
Zero-point energy (ZPE) correction	5.4289	eV
Thermal correction to entropy	5.7891	eV
Thermal energy correction	5.8148	eV
Thermal free energy correction	4.3305	eV
EE + Zero-point energy	-19161.7184	eV
EE + Thermal energy correction	-19161.3582	eV
EE + Thermal enthalpy correction	-19161.3325	eV
EE + Thermal free energy correction	-19162.8169	eV
E (Thermal)	133.500	kcal/mol
Heat capacity (C_v)	54.959	cal/mol·Kelvin
Entropy (S)	114.806	cal/mol·Kelvin

The determined thermodynamic data can be useful in explaining the molecule's stability, its tendency toward reactions, and its temperature-dependent properties.

The calculated energy gap (ΔE) of 4.18 eV indicates that the PPO molecule stands on the boundary between semiconductors and dielectrics in terms of electronic conductivity. The large energy gap ensures the molecule's chemical hardness, making it suitable for long-term use in radiation detectors.

The negative value of the LUMO energy is attributed to the specific nature of the 3-21+G* basis set; however, the energy gap provides good agreement with experimental UV absorption spectra. The strong signal in the Raman spectrum 1565 cm^{-1} suggests that the molecule possesses a conjugated π -system, which is a key factor for the luminescence process.

CONCLUSION

This work presents a comprehensive quantum-chemical analysis of the PPO molecule at the *B3LYP/3-21+G level of theory**. The optimal geometry and the global minimum energy -704.379 Hartree of the molecule were determined. The HOMO-LUMO energy gap was calculated to be 4.18 eV, which explains the molecule's optical transparency and stability. The IR and Raman spectra were analyzed, and the frequencies of the characteristic vibrational modes were identified. The IR and Raman spectral analysis enables the scientific determination of the structural features of the PPO molecule, the interaction between the aromatic and heterocyclic groups, and the vibrational behavior of the molecule. This data is useful in molecular modeling and the analysis of chemical reactions. Furthermore, the obtained results serve as a valuable resource for designing new PPO-based scintillation materials and for the preliminary assessment of their spectral properties.

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