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Investigation of Nonlinear Optical Response of Organic Compound Pyrrolidine-2,5-dione

Shradha Lakhera[1], Meenakshi Rana[1*], Kamal Devlal[1]

[1]Department of Physics, School of Sciences, Uttarakhand Open University,

Haldwani, 263139, Uttarakhand, India

**Corresponding author: mrana@uou.ac.in*

Abstract

In the present work, the computational investigation has been done for detecting NLO responses of Pyrrolidine-2,5-dione (P2D). The structure of P2D is optimized to ground state energy level by B3LYP/6-311G basis set using density functional theory (DFT). Optimized geometry is used for determining the Mulliken charges, and molecular electrostatic potential (MEP) surface. Frontier molecular orbitals (FMO), spectral behavior and the high value of dipole moment (μ_{total}), polarizability (α) and first order hyperpolarizability (β) shows the high polarizabile nature of P2D.

Keywords: Nonlinear optical material; Pyrrolidine-2,5-dione; Mulliken charges; Polarizability density functional theory

1. Introduction

The nonlinear optical (NLO) materials are the materials that show the modified behavior of the field under the externally applied field [1]. These materials show π-conjugation in alternate single and double bonds in aromatic rings present in their structures [2,3]. NLO materials are in high demand due to their wide multidisciplinary applications in engineering in the mechanical field as well as in chemical and biological sciences [4].

Pyrrolidine is one such organic compound having conjugation between the bonds hence, it might show the NLO response [5]. Pyrrolidine-2,5-dione (P2D) is a five-membered compound having four carbon and one nitrogen atom [6]. It is a heteromonocyclic derivative of Pyrrolidine having wide applications in pharmaceutical raw material, preparation of drugs, rubber accelerators and inhibitors, and epoxy resin curing agents [7]. The computational analysis of NLO properties of P2D have been reported in this work. Mulliken charge analysis, frontier molecular orbitals (FMO), molecular electrostatic potential (MEP), and spectral analysis (UV-Vis, FTIR, Raman), dipole moment (μ_{total}), polarizability (α) and hyperpolarizabilities (β) are computed to get idea about NLO responses of the compound.

2. Computational tools and methods

The structure is optimized to the ground state with the help of software "Gaussian 09" and analyzed by "Gauss view 5.0.8" [8]. Spectral calculations like a Raman, FTIR and FMO are further calculated with the help of optimized geometry. These energies are used to calculate ionization potential (IP), energy gap (ΔE), electron affinity (EA), chemical potential (CP), and electronegativity (χ). These parameters are calculated with the help of Koopman's equations [9,10]. Polarizability parameters α and β are also calculated to check the NLO response of P2D.

3. Results and Discussion

3.1 Structure and charge analysis

Optimized structure (Inset of Figure 1) of P2D have an aromatic ring having two carbonyl (C=O) group and one nitro (NO_2) group. P2D have electrostatic potential energy equal to 15376.01 eV, which is the representation of intramolecular interactions of the molecule [10]. High value of dipole moment (5.97Debye) suggests that compound have high intramolecular interactions. These intramolecular interactions lead to high polarizability of the probe molecule. More the molecule is polarizable, more it will respond to NLO properties.

The mulliken charge distribution of the P2D (Figure 1) shows the positive charge contribution of hydrogen (H) atoms and negative charge contribution of oxygen (O), nitrogen (N) and carbon (C) atoms. Charge analysis of P2D suggests that 9C and 10C are the carbon atoms associated to C=O group shows maximum positive charge of 0.593e and 0.592e respectively.

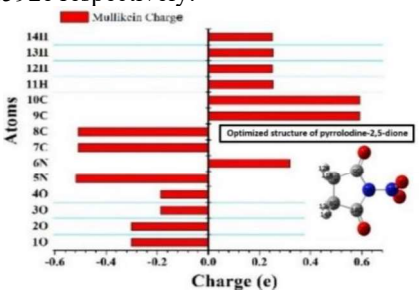

Fig. 1. Mulliken charge distribution graph of P2D. Inset of Figure 1 represent Optimized structure of P2D.

The oxygen atoms associated to C=O groups (1O and 2O) shows negative charge (-0.30 each) impact on the functional group. However, the 6N atoms of NO_2 group shows 0.318e positive charge (Figure 1). A huge charge variation between the functional groups within the compound shows the possibility of

intramolecular charge transfer (ICT) in the system.

3.2 Chemical reactivity

Chemical reactivity of the molecule is determined by FMO energies. For P2D, values of HOMO and LUMO energies are -8.38eV and -3.48eV respectively and the value of energy gap (ΔE) is 4.90eV. Lower the ΔE, higher will be chances of ICT interactions. Lower ΔE valued compounds are considered chemically reactive and optically polarizable. Negative of HOMO and LUMO energies gives us values of IP (8.38eV) and EA (3.48eV) respectively. CP is the average of E_{LUMO} and E_{HOMO}, value of CP is calculated as -5.93eV. χ is calculated as average of IP and EA and for our molecule, value of χ is reported as 5.93eV. It represents the interaction of electron cloud present towards the functional groups present in the molecule. All these parameters are considered as global reactivity descriptors and helps us to get idea about reactivity and stability of the molecule.

3.4 Molecular electrostatic potential (MEP) analysis

MEP analysis helps in identifying the reactive sites and charge transfer within the molecule. The blue region shown in MEP indicates electrophilic attack site that is caused due to presence of carbon atoms (Figure 2 a). Red region indicates the nucleophilic site and charge cloud (Figure 2 a). These regions show the charge transfer within the molecule. In MEP of P2D green color is not present. This conclude that, the major part of the molecule participates in charge transfer. The more the charge transfer is, more will be the ICT within the molecule.

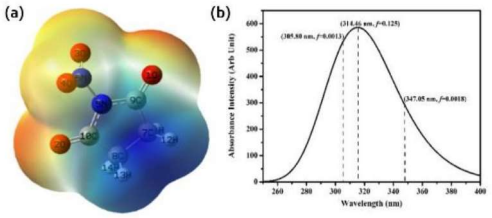

Fig. 2. a) MEP surface of P2D. b) UV-Vis absorption spectra of P2D molecule.

3.5 Vibrational analysis

High value of Raman intensity leads to high polarizability and vibrational stability of the molecule [10]. The peak at wavelength 1539 nm correspond to $\nu_{N\text{-}O}$ and $\nu_{C\text{-}O}$ mode is found at 1728cm^{-1} (Table 1). $\nu_{C\text{-}H}$ possesses maximum value of Raman intensity (786.03cm^{-1}). The high values of Raman intensity shows the high extend of the bond conjugation within the molecule and hence, high NLO behaviour.

Table 1: Computed Raman and FTIR data for P2D.

Modes	Frequency	IR	Raman activity	Raman intensity
ν_{NO}	1539.38	180.63	3.7048	126.20
ν_{CO}	1728.93	578.84	0.4468	91.28
ν_{CH}	3069.65	0.0112	210.147	786.03
ν_{CH}	3118.23	2.648	93.0489	326.40

3.6 UV-Vis analysis

For the probe system, the transition $S_0 \rightarrow S_1$ is observed at the highest wavelength 347.05nm with oscillator frequency 0.0018. The transition $S_0 \rightarrow S_2$ have oscillator strength (*f*) 0.0125 at wavelength 314.46nm (Figure 2 b). The value of *f* for transition $S_0 \rightarrow S_3$ is observed as 0.0018 at 305.80nm wavelength (Figure 2 b). These transitions show the high intramolecular interactions between the lone pair (n) electrons and the π electron. These type of interaction makes the system unstable and hence enhances the possibility of ICT.

3.7 NLO analysis

For the detection of NLO response of P2D, we have computed μ_{total}, α, and β and compared the results with known organic NLO material urea. The value of μ_{total} for P2D is computed as 2.35Debye that is higher than that of Urea (1.52 Debye). The polarizability parameters like mean isotropic polarizability (α) and anisotropy of polarizability ($\Delta\alpha$) can be calculated as 9.88×10^{-24}esu and 19.94×10^{-24}esu respectively. These values for P2D are much higher than α (5.66×10^{-24}esu) and $\Delta\alpha$ (6.30×10^{-24}esu) values of Urea. The value of β for P2D is 1.536×10^{-30}esu, which is more than β value of Urea (0.781×10^{-30}esu). These values indicate the high polarizability of P2D and validates the NLO behavior of P2D.

4. Conclusion

High value of dipole moment, chemical reactivity parameters show the better chemical reactivity of the probe molecule. The obtained high values of Raman intensity and availability of π-π* and n-π* electronic transitions in P2D shows its reactive nature. Along this, the observed high value of α and β represent the polarizable nature of the molecule. All these observations validate the strong potential candidature of P2D as an NLO material.

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