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Geometry Optimization Electrooptical Properties UV spectra analysis of 2,4-Dichloro-N-(3-methylphenyl)-Benzenesulfonamide by Quantum Chemical Method

Gaurav Mishra
Department of Physics K S Saket P. G. College Ayodhya, India

***Abstract*-- In present communication geometry optimization of 2,4-Dichloro-N-(3-methylphenyl)- benzenesulfonamide has been performed by using of combination of DFT/B3LYP method and 6-311+G (d, p) basis set. The chemical reactivity of title molecule is determined by global reactivity descriptor by using frontier molecular orbital. The energy gap between HOMO and LUMO orbital shows that title molecule is chemical reactive. The chemical softness chemical hardness chemical potential electronegativity ionization potential of title molecule is used to describe electronic properties. The HOMO and LUMO plots of title molecule show nature of chemical reactivity. The nonlinear optical behaviour of title molecule is determined by using several parameters like dipole moment polarizability hyperpolarizability order parameter anisotropic polarizability etc. The transition of electron from donor to acceptor orbital is responsible for electron delocalization and intermolecular charge transfer is computed by NBO analysis. The large hyperpolarizability of title molecule is explained by using TDDFT calculation by using same level theory.**

***Keyword*-- HOMO. LUMO.NLO, TDDFT**

I. INTRODUCTION

The geometry reactivity electronic properties of any organic molecules are determined by using Quantum chemical methods. In organic chemistry, the arrangement of electrons governs chemical bonding, stability, and reactivity. Quantum chemical techniques are very useful tool to determine spectroscopic properties, having infrared (IR), nuclear magnetic resonance (NMR), and ultraviolet–visible (UV–Vis) spectra [1-2]. The excited energy sates of any chemical molecule are computed by Time-dependent extensions of density functional theory, which allow accurate modeling of excited states and electronic transitions. The reaction mechanisms are explaining by finding transition states, intermediates, and activation energies along reaction pathways. These reaction mechanisms provide new path for experimentalist to design more efficient synthetic routes. The nonlinear optical parameters e.g. dipole moment, polarizability, and hyperpolarizability, are computed on optimized geometry which are useful to understand intermolecular interactions.

The higher first order hyperpolarizability is useful for developing nonlinear optical materials[3-4] Benzenesulfonamide is building block in pharmaceutical and chemical synthesis, particularly for emerging sulfonamide antibiotics, dyes, and herbicides. The carbonic anhydrase inhibitor often cast-off in biochemical research termed as cause eye, skin, and respiratory frustration [5-6]. The sulfonyl group attached to a benzene ring is termed as Benzenesulfonamide which is soluble in organic solvents like methanol, ethanol, and acetone. In synthesis of drug Benzenesulfonamide is a key intermediate product which are useful for pharmaceutical application like sulfonamide-based anti-infectives. Benzenesulfonamide is utilized in the manufacturing of plasticizers, resin, and sulfonamide derivatives. Thimme Gowda et.al synthesize and characterize Benzenesulfonamide derivates 2,4-Dichloro-N-(3-methylphenyl)- benzenesulfonamide [7]. In present communication geometry optimization of 2,4-Dichloro-N-(3-methylphenyl)- benzenesulfon has been carried out by using DFT/B3LYP method and 6-311+G (d, p) basis set and optimized geometry of 2,4-Dichloro-N-(3-methylphenyl)-benzenesulfon is compared with observed results which established validity of quantum chemical method. The electronic property of title molecule is computed by several electronic parameters by using energies frontier molecular orbital. The nonlinear optical properties of title molecule are computed on optimized geometry which helps to understand intermolecular charge transfer within title molecule. The electronic transition from ground state to excited state by using TDDFT method. In best of our knowledge no such study has been carried out by any researcher.

II. COMPUTATIONAL METHOD

The initial geometry of title molecule is designed on gauss view 6.0 program [8]. The initial geometry of title molecule is optimized geometry by using combination of DFT/B3LYP method and 6-311+G (d, p) basis set by using. The initial geometry optimized without any symmetry constrain by using Gauss 09 program package [9].

The gradient corrected density functional theory with the three-parameter hybrid functional (B3) [10-11] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [12] has computed by molecular structure electronic property of title molecule. The gauss view 6.0 utilized to draw HOMO-LUMO, MESP couture of title molecule. The **Global reactivity parameters** of title molecule are computed by using energy of frontier molecular orbital HOMO and LUMO.

Several global reactivity parameters [13-17] are computed by using following equation

Energy band gap = (ε_{LUMO} - ε_{HOMO}--------(1)

Electronegativity (χ) = $\frac{IP+EA}{2}$----------------(2)

Chemical potential $\mu = -\chi$------------------(3)

Global hardness $\eta = \frac{IP-EA}{2}$-------------------(4)

Global softness (S = $\frac{1}{2\eta}$ -------------------(5)

Global electrophilicity index $\omega = \frac{\mu^2}{2\eta}$ -------(6)

Electron Donating Power (ω^-) $\omega^- = \frac{(3IP+EA)^2}{16(IP-EA)}$**-------(7)**

Electron Accepting Power (ω^+) $= \frac{(IP+3EA)^2}{16(IP-EA)}$**---------(8)**

In the cartesian coordinate system dipole moment (μ), mean polarizability (α), anisotropy in polarizability (Δα), and first-order hyperpolarizability (β)[18-19] is computed by below equation.

Mean Polarizability $\alpha = \frac{\alpha_{xx}+\alpha_{yy}+\alpha_{zz}}{3}$ (9)

Anisotropic Polarizability $\Delta\alpha = [\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2}{2}]^{1/2}$ (10)

Hyperpolarizabilty $\beta = [(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{xxy}+\beta_{yzz})^2+(\beta_{zzz}+\beta_{xxz}+\beta_{yyz})^2]^{1/2}$ (11)

Order parameter $S = \frac{\alpha_e-\alpha_0}{\alpha_e+\alpha_0}$ (12)

III. GEOMETRY OPTIMIZATION

The energy of optimized geometry of title molecule is -981.54 a,u, with no symmetry so C1 point group symmetry. The title molecule shows Monoclinic, P21/c crystal structure with a = 7.9031 (7) Å b = 14.507 (1) Å c = 12.715 (1) Å β = 99.895 (8)°[7]. The computed bond length and corresponding observed bond length are compared in atvle-1. The optimized geometry in 2D and 3D of title molecule are shown in Fig-1. The optimized geometry of title molecule with chemical formula C13H11Cl2NO2S, the conformations of the N—C bonds in the C—SO2—NH—C sections have uncivilized spins with admiration to the S O bonds.

The computed dihedral angle between the both benzene rings is 68.5 which is well matched with observed value. The computed aromatic C–C bond lengths show slight deviation 0.01–0.02 Å with corresponding observed value which is characteristic of delocalized π-systems. The observed S–N bond length is 1.615 Å, however S=O bonds lie in between 1.42–1.43 Å are also well matched with computed value. In the optimized geometry, these bonds are usually slightly longer due to the absence of crystal packing forces, but the difference remains small. Overall computed Bond lengths show very close agreement with observed value however computed and observed bond angle show small deviations. The packing effect in crystal geometry shows alight deviation in Dihedral angles

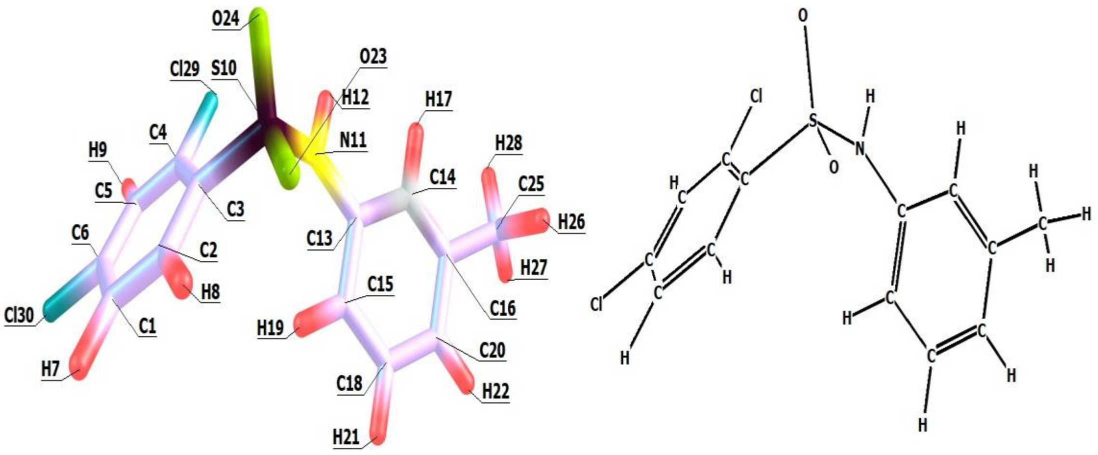

Fig-1 optimized geometry of title molecule in 2D(right) 3D (left)

Table1
Computed bond length and corresponding observed bond length

S.N.	Bond length	Computed(A^0)	Observed(A^0)
1	C=C)R1	1.393-1.400	1.372-1.394
2	(C=C)R2	1.393-1.403	1.371-1.394
3	C-CH3	1.511	1.455
4	C-Cl	1.747-1.750	1.733-1.737
5	C-S	1.807	1.7734
6	S=O	1.4610-1.4609	1.420-1.434
7	S-N	1.694	1.615
8	C-N	1.447	1.435

IV. ELECTRONIC PROPERTIES

The electronic properties of any chemical system are uniquely described by frontier molecular orbital FMO. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital are termed as frontier molecular orbital. The energy required transition of electron from HOMO to LUMO molecular orbital is termed as band gap. A system with lower energy gap is more polarize means less kinetic stability and vice versa. The HOMO energy level lies at −6.26 eV however LUMO energy of title molecule lies at −1.57 eV. The kinetic stability and electronic excitation behavior of title molecule is directly related with HOMO–LUMO energy gap ($\Delta E = 4.69$ eV). The HOMO primarily acts as donor however LUMO termed as acceptor so transition of electron from HOMO to LUMO provides stability of title molecule.

The HOMO LUMO plot of title molecule is shown in Fig-2. The HOMO is distributed over dichlorobenzene ring however LUMO is distributed over benzene ring so electron transfer from dichlorobenzene ring to benzene ring stabilize title molecule. The MESP plot (fig-2) of title molecule shown highly negative regions localized oxygen and nitrogen. These atoms pull electron density toward themselves due to their high electronegativity, creating strong negative potential zone which is also supported by HOMO LUMO plot of title molecule. On the other hand, hydrogen atoms and certain carbon regions show more positive potential, indicating electron deficiency and possible sites for nucleophilic interaction. The HOMO (MO=81) is basically related with loin pair electron of LP(3)Cl_{30} is p orbital character however LUMO(MO=82) corresponds with Rydberg electron of C1 having mixed character of d and p orbitals.

The computed energy gap lies within range of organic molecule shows that system possesses good thermodynamic stability and low chemical reactivity, as electron promotion from the ground state requires comparatively higher energy. According to Koopmans' theorem, negative eigen value of HOMO is termed as electron affinity (EA) however negative eigen value of LUMO is termed as ionization potential. The computed EA =6.26eV shows moderate tendency to accept electrons and IP=1.57 eV reflects strong resistance toward electron removal. Several Global reactivity descriptors based on FMO energies are computed and listed in table-2 . These Global reactivity descriptors are useful parameter's to describe chemical reactivity of title molecule.

The capacity to attract electron is termed as electronegativity (χ = 3.92 eV however negative chemical potential (μ = −3.92 eV) confirms the stability of the electronic system. The resistance in charge transfer offered by chemical system to chemical hardness (η = 2.35 eV) and vice versa termed as softness (S = 0.213 eV^{-1}) means how ease of charge transfer. The capacity to accept electrons is termed as electrophilicity index and its computed value (ω = 3.27 eV) shows that title molecule is moderate electrophile in chemical interactions however computed electron-donating (ω^{-} = 5.76 eV) shows that title molecule work as electron donor species rather than electron-accepting (ω^{+} = 1.03 eV) powers which utilize in nonlinear optical properties of title molecule.

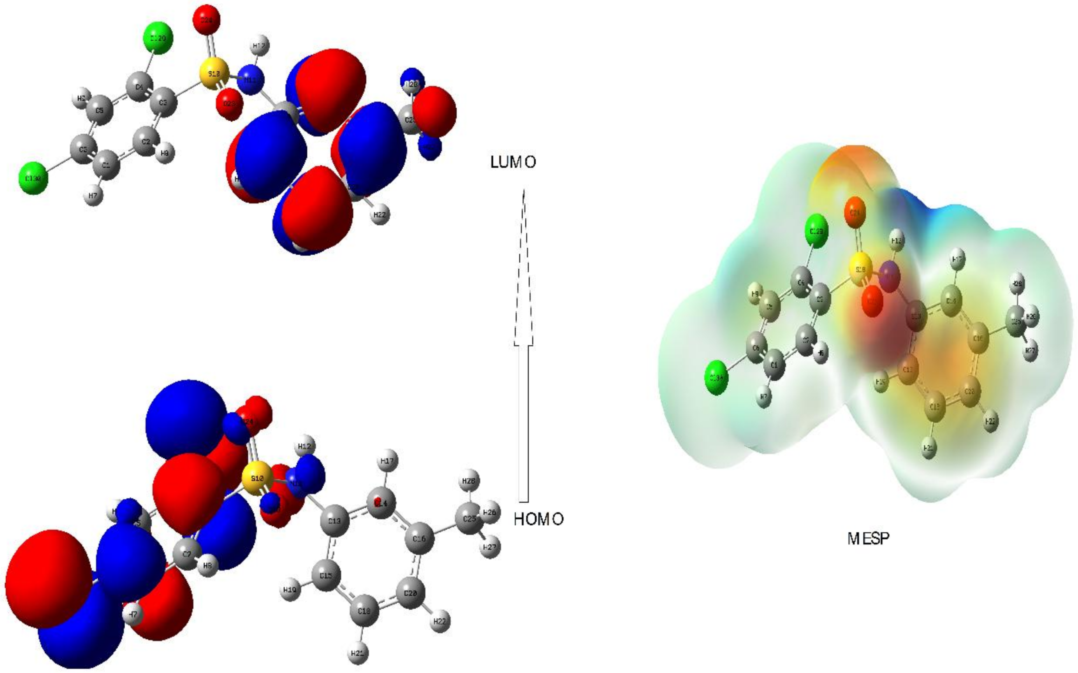

Fig-2 HOMO LUMO MESP plot of title molecule

Table-2
Chemical reactivity descriptor (eV)of title molecule by using energy of Frontier orbital

Folder	ε_H	ε_L	$\varepsilon_H - \varepsilon_L$	χ	μ	η	S	ω	$\omega-$	$\omega+$	EA	IP
A	−6.26	−1.57	4.69	3.92	-3.92	2.35	0.213	3.27	5.76	1.03	6.26	1.57

V. NONLINEAR OPTICAL BEHAVIOUR (NLO)

The nonlinear optical properties of any chemical system us determined by its charge transport properties, In present molecule -SO2 and -Cl groups are present on tutle molecule which improves charges on title molecule. The nonlinear optical properties are determined by several parameters loke dipole moment polarizability anisotropic polarizability hyperpolarizability order parameter molar refractivity e.t.c. are computed and listed in table-3. The response of electron density due to application field are determined by polarizability and hyperpolarizability and termed as optical nonlinearity.

The large computed large anisotropic polarizability ($\Delta\alpha$ = 279.85 a.u.) incorporate with moderate mean polarizability (α = 151.38 a.u.) shows that charge distribution in title molecule are highly directional dependent. The polarizability component along X direction is much higher that corresponding component along Y direction ($\alpha xx \gg \alpha yy$) indicate that polarization is more distinct along X molecular axis, which is characteristic for conjugated systems showing charge delocalization along X direction which is supported by computed molar refractivity (MR = 22.43 cm^3/mol).

The first order hyperpolarizability is 3*3*3 rank tensor having 27 components. After applying symmetry concept 27 component reduced up to 10 components. The computed total hyperpolarizability (β_0 = 218.60 a.u., corresponding to 1.89 × 10^{-30} esu) which is more than five times greater than corresponding value of reference candidate shows title molecule have nonlinear optical response. The computed large hyperpolarizability of title molecule is usually related with actual intramolecular charge transfer through π-conjugated framework. Again comparing component of hyperpolarizability along X Y,Z direction shows that greater contribution comes across βx = 187.62 as compared with βy = −40.80, βz = 104.78 a.u indicate that major charge transfer along X axis and due to significant contributions along other directions shows that electron redistribution is not strictly one-dimensional. The supplementary validation of the nonlinear response at the molecular level are also present due to significant computed hyper-Rayleigh scattering value (β_{HRS} = 114.32 a.u.) however depolarization ratio (S = 0.321) shows that mixed character NLO activity present in title molecule.

The charge transfer along dipole moment of title molecule is computed by vector component of hyperpolarizability (βver = −70.15 a.u.) which shows that direction of charge transfer is opposite along dipole moment

Overall, the combination of high polarizability, large anisotropy, and enhanced hyperpolarizability demonstrates that the molecule exhibits a strong nonlinear optical response. Let us check intermolecular π charge transport within molecule by NBO analysis which helps us insight picture of NLO behaviour.

Table 3
Nonlinear optical parameters of title molecule in a.u.

Polarizability(a.u.)		**Hyper Polarizability(a.u.)**	
αxx	255.120	βx	187.62
αyy	22.239	βy	-40.80
αzz	176.778	βz	104.78
α	151.38	β_0	218.60
MR	22.43	β_0(esu)	1.89×10^{-30}
S	0.321	β_{HRS}	114.32
$\Delta\alpha$	279.85	βver	−70.15

VI. NBO Analysis

To identify intra molecular charge interaction charge transfer and conjugate interaction are determine by Natural bond analysis **[20]**. The second order perturbation energy $E^{(2)}$ describe strength of interaction meaning higher value second order perturbation energy means strong interaction and vice versa. [21-22]. The moment of π electron from to acceptor level are accountable for nonlinear optical behaviour of title molecule. In table-4 we have categorized this π → π* interaction according with strength of interaction, In first type interaction strongest conjugation due to charge transfer from π (C=C donor) → π* (C=C acceptor) stabilize up to 28-34 kcal/mol. In second type π (aromatic ring) → π* (linker/imine) interaction which extend delocalization of charge within range 15-30kacl/mol.

The charge transfer from C=C donor ring to acceptor ring of type π → π* stabilize title molecule up to 10–25 kcal/mol which are accountable for enhancing NLO properties due to this type ICT moment. The heteroatom contribution interaction in between π (C=N or C=O) → π* (adjacent π system) stabilize title molecule up to 8-10kcal/mol. The substituent effect due to charge transition in between π (phenyl) → π* (substituent group) stabilize up to 5-15 kcal/mol. The overall π → π* improves NLO behaviour due to intermolecular charge interaction in between donor to acceptor orbital which are responsible for large hyperpolarizability of title molecule. The nonlinear optical behaviour of title molecule are describe by using TDDFT calculation.

Table-4
NBO analysis of title molecule

S.N.	**Donor Orbital**	**Acceptor orbital**	**E(2) (kcal/mol)**	**Assignment**
1	π ($C_1=C_2$),$C_3=C_4$)	π* ($C_{13}=C_{14}$, $C_{11}=C_{12}$)	28-34	Donor ring → acceptor ring (main ICT path)
2	π(C_1–C_2, C_3–C_4)	π*(C=N: C_7–N_8)	15–30	Ring → imine (C=N) conjugation
3	π(C_1–C_2)	π*(C_{10}–C_{11})	10–25	Donor phenyl → acceptor phenyl
4	π($C_7=N_8$ or $C_9=O_{10}$)	π*(C_3–C_4)	8–20	Heteroatom-assisted delocalization
5	π(C_1–C_2)	π*(C–O or C–N substituent)	5–15	π (phenyl) → π* (substituent group)
6	π(C_3–C_4)	π*(C_{10}–C_{11})	5–12	π (ring) → π* (ring) (inter-ring)
7	π(C–C)	π*(C–C / C–N	2–8	weak π → π*

VII. TDDFT Calculation

The TDDFT calculation on title molecule has been performed on optimized geometry by using same level theory. TDDFT calculation on title molecule has been done up to six level. The computed transition energy corresponding oscillatory strength transition orbital and percentage contribution in bracket change in dipole moment during transition are listed in table-5.

The Most prominent peak in UV spectra (Fig-3) computed at 303nm in which excited electron goes from HOMO to LUMO orbital having 70% contribution by absorbing 4.089 eV however second largest contribution computed corresponding $S_0 \rightarrow S_5$ transition at 242nm. The absorption of 5.119 eV energy electron transit from H →L+3(37%), H → L+5(38%), H-1→ L+2(22%) with oscillatory strength (f=0.0074).

The excitation energy in these six states les in between 4.527-5.190eV however oscillatory strength lies in between 0.0025-0.0189 a.u.. The two state level employees that hyperpolarizability of title molecule is determined transition of electron corresponding most intense peak. The hyperpolarizability of title molecule is inversely proportional to third power of excited energy(4.089eV) and proportional to oscillatory strength (f=0.0182) as well as change in dipole moment during transition (0.1818a.u.). The low transition energy and large oscillatory strength (f=0.0182) as well as change in dipole moment during transition are responsible for such large hyperpolarizability.

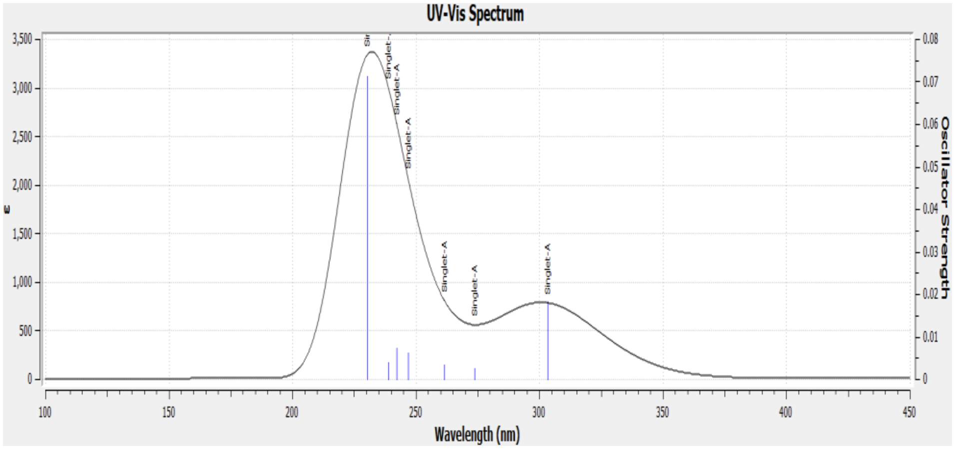

Fig-3 UV plot of title molecule by using TDDFT method

Table-5
TDDFT calculation for the title molecule for six states

States	f_{oe}	ΔE_{oe}	Δλmax	Δμ	Ele. Trans.
$S_0 \rightarrow S_1$	0.0182	4.089	303	0.1818	H →L(70%)
$S_0 \rightarrow S_2$	0.0025	4.527	274	0.0223	H →L+1(70%)
$S_0 \rightarrow S_3$	0.0033	4.741	262	0.0286	H-1 →L(70%)
$S_0 \rightarrow S_4$	0.0063	5.024	247	0.0513	H-3 → L (40%) H-3 → L+1 (15%) H-1 →L (26%) H-2 →L(41%)
$S_0 \rightarrow S_5$	0.0074	5.119	242	0.0594	H →L+3(37%) H → L+5(38%) H-1→ L+2(22%)
$S_0 \rightarrow S_6$	0.0039	5.190	239	0.030	H-1→L+2(35%)

VIII. CONCLUSION

The geometry of title molecule is optimized by using DFT/B3LYP method incorporate with 6-311G(d, p) basis set. The computed Bond lengths show very close agreement with observed value however bond angle show small deviations.

The packing effect in crystal geometry shows alight deviation in Dihedral angles. The computed electronic parameters show resistance in charge transfer ($\eta = 2.35$ eV) and vice versa termed as softness ($S = 0.213$ eV^{-1}) shows easier flow of charge within molecule.

The capacity electron-donate ($\omega^- = 5.76$ eV) is higher shows that title molecule work as electron donor species rather than electron-accepting ($\omega^+ = 1.03$ eV) powers which utilize in nonlinear optical properties of title molecule. NBO analysis shows that $\pi \rightarrow \pi^*$ improves NLO behaviour due to intermolecular charge interaction in between donor to acceptor orbital. The large hyperpolarizability of title molecule due to low excited energy(4.089eV) and high oscillatory strength (f=0.0182) as well as change in dipole moment during transition (0.1818a.u.). Overall title molecule has potential to use as good NLO candidate in future.

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