Published by :
https://www.ijert.org/
An International Peer-Reviewed Journal

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 15 Issue 05 , May - 2026

Nonlinear optical properties NBO analysis UV spectral analysis of imidazole derivative by using DFT

Dr. Gaurav Mishra

Associate Professor

Department of Physics K.S. Saket P G College Ayodhya-224123

Abstract - Due to presence of heteroatom nitrogen *π* charge transport from donor to acceptor in imidazole derivative shown important application in nonlinear optical response. In present paper geometry of imidazole derivative is optimized by using combination DFT/B3LYP method and 6-311+G(d,p) basis set. The Fukai function of title molecule is computed by using Mullican charges on neutral anion cation state. The nonlinear optical properties of title molecule is computed by using several parameters dipole moment mean polarizability anisotropic polarizability molar refractivity hyperpolarizability etc. The hyperpolarizability of title molecule due to lowering of HOMO LUMO energy gap so several electronic reactivity of title molecule is computed by frontier molecular orbitals energy. The NBO analysis of title molecule to explain intermolecular charge transfer from donor to acceptor atoms. The TDDFT calculation of title molecule is used to discuss high hyperpolarizability which is 2.5 times hyperpolarizability of reference candidate.

Key Word: NLO Fukai Function, NBO, TDDFT

INTRODUCTION

The quantum chemical methods are useful tool to determine electronic properties charge transport properties of any chemical system. In this process firstly geometry of given system is optimized. In optimization process minima on the potential energy surface, with these minimum energy structures representing equilibrium structures. The electronic properties of any chemical system is determined by energy of frontier Molecular orbital by using quantum chemical method. Now day quantum chemical methods are important tool to determine nonlinear optical properties of liquid crystal molecules. Nonlinear optical (NLO) materials play a crucial role in modern photonic and optoelectronic technologies such as optical switching, frequency conversion, and telecommunications [1-3]. The imidazole derivatives have attracted considerable attention because of their conjugated π-electron from donor to acceptor are responsible for nonlinear optical behaviour of liquid crystal [4-5]. The Imidazole derivatives are widely used as NLO materials. The imidazole derivatives are used in Optical data storage. Laser technology. Electro-optic modulators. Nonlinear photonic devices. Their high thermal stability and tunable electronic properties make them promising candidates for advanced optical applications. The electronic properties of any liquid crystal molecule determine its reactivity by using several parameters. The high reactivity of chemical system causes easy polarization so more charge transport within molecule. This process establishes intermolecular charge transfer from donor to acceptor atmos. Over past few decade density functional theory inquorate with hybrid functional provide vast application in field of liquid crystal molecules[6-8]. Organic molecules, particularly heterocyclic compounds, are widely investigated due to their structural tunability and strong electronic responses. Among them, imidazole derivatives have attracted considerable attention because of their conjugated π-electron system and ability to support intramolecular charge transfer (ICT). In present communication we have computed electro optical properties of one of important heterocyclic imidazole ring derivate by using DFT/6-311+G(d. p) basis set. The absorption properties of title molecule is discussed by using time dependent density functional theory (TDDFT) by using same level theory which helps to understanding more insight of NLO properties of title molecule. The nature and strength of charge transport within in molecule is computed by using natural bond analysis (NBO) by using same level theory.

Computational details

Initial geometry of title molecule is design by using Gauss View 5.0[9] and geometry of title molecule is optimized by using DFT/B3LYP method 6-311+G(d, p) basis set [10-12] without any symmetry constrain. The whole calculations in present communication are performed by using G09 program package [13]. The NBO analysis on title molecule has been done by using NBO4.1 program package inbuilt G09 code. The NLO parameters like dipole moment polarizability anisotropic polarizability first order hyperpolarizability of title molecule is computed in Cartesian coordinate x.y.z by given equations

Dipole Moment $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$ (1)

Mean Polarizability $\alpha = \frac{\alpha_{xx}+\alpha_{yy}+\alpha_{zz}}{3}$ (2)

Anisotropic Polarizability $\Delta\alpha = [\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2}{2}]^{1/2}$ (3)

Hyperpolarizabilty $\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$ (4)

(4)

The following formula is used to calculate molecular refractivity using the Lorenz–Lorentz formula:

$MR = \left[\frac{n^2-1}{n^2+2}\right]\left(\frac{MW}{\rho}\right) = 1.333\text{л}N\alpha$ -------------------------(5)

The energies of frontier molecular orbitals (E_{HOMO}, E_{LUMO}), energy band gap ($E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$), electronegativity ($\chi$), chemical potential ($\mu$), global hardness ($\eta$), global softness ($S$), and global electrophilicity index (ω) of title molecule are computed by using following equations [17-19]

$$\chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) \qquad (6)$$

$$\mu = -\chi = \frac{1}{2}(E_{LUMO} + E_{HOMO}) \qquad (7)$$

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \qquad (8)$$

$$S = \frac{1}{2\eta} \qquad (9)$$

Electronic Properties

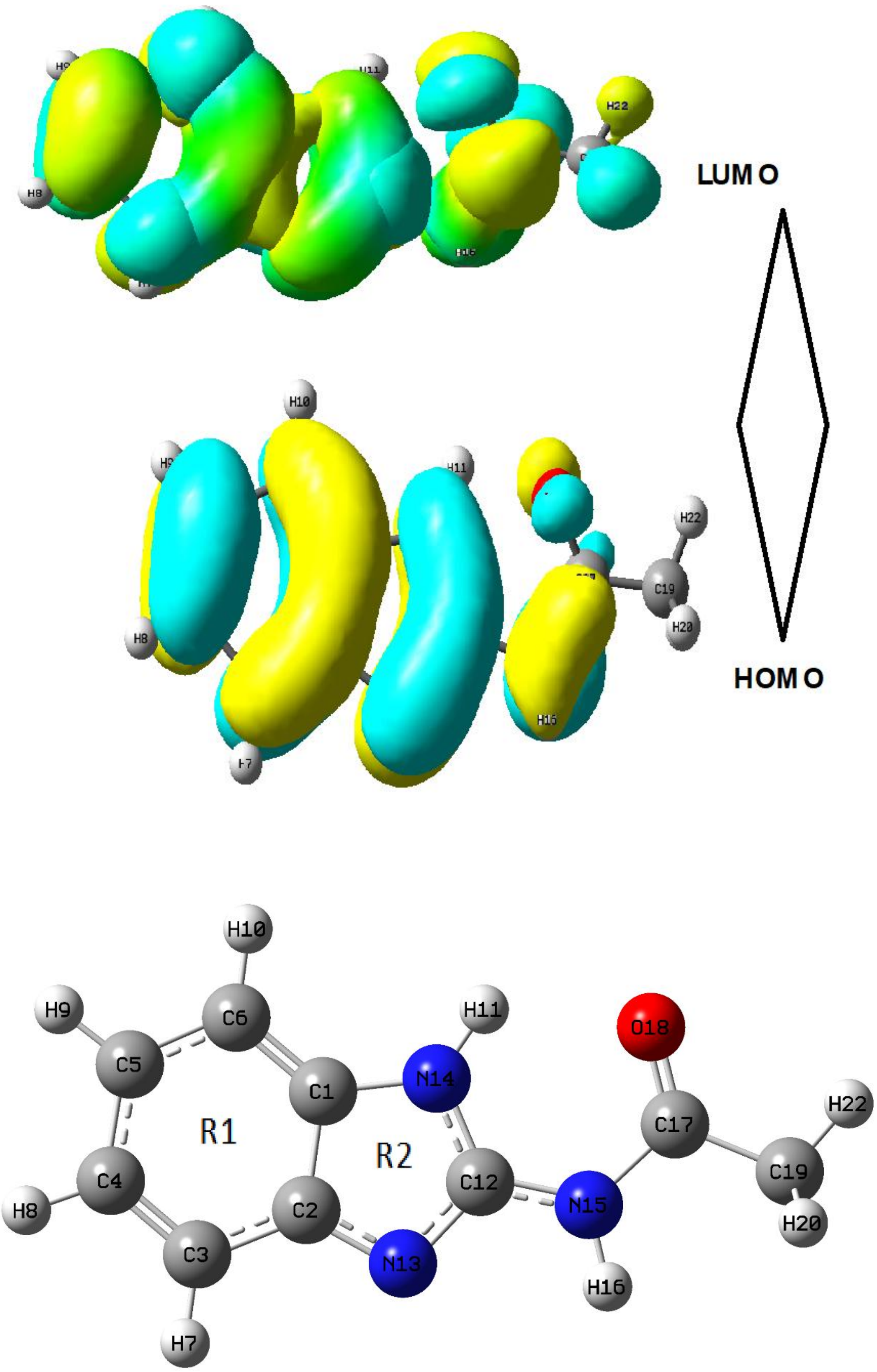

Fig-1 HOMO LUMO plot(upper) and optimized geometry(Lower) of title molecule

In any chemical; system chemical reactivity of any system is determined by Frontier molecular orbital (FMO) especially highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Several reactivity parameters of title molecule based on HOMO and LUMO are listed in table-1. The energy value HOMO energy -5.07 eV shows ability to donate electron however the LUMO energy =1.58eV shows ability to accept electrons in title molecule. The relatively high HOMO energy shown molecule has good ability to donate electron however, low LUMO energy with HOMO–LUMO energy gap ($\Delta E = 3.49$ eV)support charge transport from donor to acceptor in intramolecular charge transfer interactions. The HOMO LUMO plot of title molecule along with optimized geometry of title molecule is shown in Fig-1. The LUMO distributed over whole molecule however HOMO sitributed over whole molecule except methyl group so charge transfer from -CH_3 group to aromatic ring,

Molecules having smaller band gaps generally exhibit higher polarizability and stronger nonlinear optical response because electronic excitation occurs more easily between the frontier orbitals. The electronegativity value ($\chi = 3.33$ eV)reproduces the electron appealing capability of the molecule, while the negative chemical potential ($\mu = -3.33$ eV)confirms the thermodynamic stability of the molecular system. The global hardness ($\eta = 1.75$ eV)indicates resistance toward charge transfer and deformation of the electron cloud. The global reactivity descriptors show molecule having medium stability, significant charge transfer capability, and favorable electronic softness improves nonlinear optical applications and molecular electronic devices.

Table-1 Various electronic reactivity parameters (eV) of the title molecule by using the B3LYP functional

HOMO	**LUMO**	**ΔE**	**χ**	**μ**	**η**	**S(eV−1)**	**ω**
−5.07	−1.58	3.49	3.33	-3.33	.75	0.286	3.17

Fukai Function (FF)

The most reactive site of any chemical system is computed by Fukui Function[20-21] analysis in term of Mullican atomic charges in neutral anion and cationic state of system by using following equation

$f_k^+ = q_k(N+1) - q_k(N)$ For nucleophilic attack

$f_k^- = q_k(N) - q_k(N-1)$ for electrophilic attack

$f_k^0 = \frac{1}{2}(f_k^+ + f_k^-)$ for radical attack:

In this equation $q_k(N)$, $q_k(N+1)$, and $q_k(N-1)$are the atomic charges of the neutral, anionic, and cationic species, respectively. The computed f_k^+ For nucleophilic attack f_k^- for electrophilic attack f_k^0 for radical attack are listed in table-2 by using Mullican atomic charges in neutral anion and cationic state of system. From this table highest f_k^+ are corresponding C12 exhibits the which shown C12 atom is the most favorable site for nucleophilic attack however maximum f_k^-value for O18 most electron-rich center and therefore highly susceptible toward electrophilic attack. The maximum radical exposure at C12 and C17, showing these atoms plays a dominant role during charge transfer developments. Local softness (Sf_k)offer extra provision for chemical reactivity are also listed in table-2 which again shown that this center provides similar trends. In intermolecular charge transfer process charge transport from O18(donor) to C12(Acceptor) are responsible for enhanced nonlinear optical (NLO) behavior.

Table-2 Computed Fukai function of title molecule by using same level theory

Atoms	**q0**	**q+1**	**q-1**	**f_k^+**	**f_k^-**	**f_k^o**	**Sfk+**	**Sfk-**	**Sfk0**
C1	0.3409	0.3972	0.3505	0.0563	-0.0096	0.2219	0.0115	-0.0020	0.0454
C2	0.2870	0.2830	0.2567	-0.0040	0.0303	0.1547	-0.0008	0.0062	0.0316
C3	-0.1612	-0.1241	-0.2303	0.0371	0.0691	-0.0089	0.0076	0.0141	-0.0018

C4	-0.1483	-0.1277	-0.1427	0.0205	-0.0055	-0.0564	0.0042	-0.0011	-0.0115
C5	-0.1508	-0.1090	-0.1683	0.0418	0.0175	-0.0248	0.0086	0.0036	-0.0051
C6	-0.1596	-0.1468	-0.2078	0.0129	0.0482	-0.0429	0.0026	0.0098	-0.0088
H7	0.1318	0.2138	0.0747	0.0820	0.0571	0.1764	0.0168	0.0117	0.0361
H8	0.1222	0.2048	0.0627	0.0825	0.0595	0.1734	0.0169	0.0122	0.0354
H9	0.1231	0.2130	0.0636	0.0899	0.0595	0.1812	0.0184	0.0122	0.0370
H10	0.1193	0.2076	0.0805	0.0882	0.0389	0.1673	0.0180	0.0079	0.0342
H11	0.3586	0.4070	0.3498	0.0484	0.0087	0.2321	0.0099	0.0018	0.0474
C12	0.5868	0.8156	0.6770	0.2288	-0.0902	0.4771	0.0468	-0.0184	0.0975
N13	-0.6010	-0.5181	-0.6357	0.0829	0.0347	-0.2002	0.0169	0.0071	-0.0409
N14	-0.7012	-0.7218	-0.7426	-0.0206	0.0414	-0.3505	-0.0042	0.0085	-0.0716
N15	-0.6199	-0.6810	-0.6817	-0.0611	0.0618	-0.3402	-0.0125	0.0126	-0.0695
H16	0.3725	0.3981	0.3013	0.0256	0.0711	0.2474	0.0052	0.0145	0.0506
C17	0.5234	0.6152	0.4205	0.0918	0.1028	0.4049	0.0188	0.0210	0.0828
O18	-0.4907	-0.4385	-0.6432	0.0522	0.1525	-0.1169	0.0107	0.0312	-0.0239
C19	-0.5379	-0.5602	-0.4855	-0.0224	-0.0524	-0.3175	-0.0046	-0.0107	-0.0649
H20	0.2009	0.2164	0.0927	0.0155	0.1082	0.1701	0.0032	0.0221	0.0348
H21	0.1903	0.2164	0.0855	0.0262	0.1047	0.1737	0.0053	0.0214	0.0355
H22	-0.1165	-0.0811	-0.1939	0.0354	0.0774	0.0158	0.0072	0.0158	0.0032

NLO properties

The nonlinear optical properties of any chemical system is determined by several parameters e.g. electric polarizability and first-order hyperpolarizability parameters are listed in table-3. The computed mean polarizability ($\alpha_{\text{total}} = 68.47$)shows capability of the electron cloud to develop distorted by application an external electric field. Higher polarizability values caused by enhanced electronic delocalization and improved charge transfer within the molecular framework. The anisotropic polarizability ($\alpha_{\text{aniso}} = 26.22$)reproduces the directional necessity of electronic polarization. The reasonable anisotropic shows that the charge distribution in various direction. The moderate anisotropy mainly due to conjugated π-electron systems and donor–acceptor interactions, which facilitate intramolecular charge transfer processes. The calculated molar refractivity value ($MR = 255.9$)is directly related to molecular volume and polarizability. The computed MR for title molecule shows presence of notable electronic polarization and conjugation within the molecular structure.

The first-order hyperpolarizability is important parameter to compute nonlinear optical activity. The computed hyperpolarizability value ($\beta_{\text{total}} = 104.23\ \text{a.u.}$)is 2.41 times larger than that of reference molecule Urea. Let us discuss this by using NBO analysis.

NBO analysis

The NBO analysis of title molecule is listed in table-4. The NBO analysis shows that Enhances conjugation and β due to charge transfer from π(C_1- C_2) to π*(C_5=C_6) by 25.6 kcal/mol of title molecule. Another Strong ICT, increases β due to charge transfer from LP (2)N_{14} to π*(C_5=C_6) by 32.1 kcal/mol. The high β value of title molecule due delocalization from π(C17=C16) to π*(C_{12}=N_{15}) by 18.4kcal/mol. The Improves polarization due to charge transfer from LP(2)O_{18} to π*(C_{17}=O_{18}) by 28.7 kcal/mol. The charge transfer from LP (2)N_{14} to π*(C=C) Ring stabilize upto 22.8 kcal/mol. The Aromatic stabilization in title molecule is due to charge transfer from π(C- C)ring to π*(C=C)Ring by 22.8 kcal/mol. The enhanced β value may originate from efficient intramolecular charge transfer between electron donor and acceptor groups through the conjugated molecular backbone.

TABLE-3

Several nonlinear optical parameters of title molecule

S.N.	Parameters	values	hyperpolarizability	Value(a.u.)
1.	α_{XX}	-53.7119	β_{XXX}	82.9533
2.	α_{YY}	-73.9074	β_{YYY}	14.2427
3.	α_{ZZ}	-77.7960	β_{ZZZ}	2.2628
4.	α_{XY}	-6.310	β_{XYY}	4.3835
5.	α_{XZ}	-0.5672	β_{XXY}	-17.3943
6.	α_{YZ}	-4.6683	β_{XXZ}	*7.1884*
7	α_{total}	68.47	β_{XZZ}	16.5484
8	αaniso	26.22	β_{YZZ}	0.8314
9	MR	255.9	β_{YYZ}	-1.2628
10	µx	4.4351	β_{total}(a.u.)	104.23
11	µy	0.5737	β_{total}(e,s,u.)	9.00×10^{-31}esu(2.41times urea)
12	µz	−0.3127	β_{ver}(a.u.)	101.91(2.36times urea)
13	µtot	4.4829	β_{HRS}(a.u.)	96.55(2.25times urea)

Table: 4 NBO Analysis Relevant to NLO Properties

Donor Orbital	**Acceptor Orbital**	**E^2 (kcal/mol)**	**Energy Difference (ΔE)**	**F(i,j)**	**NLO contribution**

π(C_1- C_2)	π*(C_5=C_6)	25.6	0.28	0.065	Enhances conjugation and β
LP (2)N_{14}	π*(C_5=C_6)	32.1	0.31	0.072	Strong ICT, increases β
π(C17=C16)	π*(C_{12}=N_{15})	18.4	0.35	0.058	Extends delocalization
LP(2)O_{18}	π*(C_{17}=O_{18})	28.7	0.30	0.069	Improves polarization
π(C- C)ring	π*(C=C)Ring	15.2	0.40	0.050	Aromatic stabilization
LP (2)N_{14}	π*(C=C)Ring	22.8	0.33	0.061	Charge transfer pathway
Lp(heteroatom)	π* system	35.4	0.27	0.075	Strong D–π–A interaction
π conjugated chain	π* chain	27.9	0.29	0.068	Enhances dipole moment
LP(2) N_{12}	σ* / π*	20.6	0.32	0.060	Increases polarizability

Table-5 TDDFT calculation for the title molecule for the prominent transition peak

Transition state	f_{oe}	ΔE_{oe}	Δλmax	Δμ(D)	$\frac{\Delta\mu f_0}{\Delta E^3}$	Ele. Trans.
$S_0 \rightarrow S_1$	0.1830	2.4534	242	0.4134	2.4534	H →L+1(68%)
$S_0 \rightarrow S_2$	0.0072	2.0805	342	0.1805	0.0805	H-1→L+1(55%)
$S_0 \rightarrow S_3$	0.0040	2.0379	290	0.1345	0.0379	H →L(32%)
$S_0 \rightarrow S_5$	0.1939	**2.7459**	273	**1.234**	1.7459	H-1 →L+3(35%)
$S_0 \rightarrow S_8$	0.0166	2.1368	242	0.1458	0.1368	H →L+3(38%)
$S_0 \rightarrow S_9$	0.0445	2.3259	222	0.4459	0.3259	H →L+2(35%)
$S_0 \rightarrow S_{10}$	0.0727	**2.5165**	216	**0.3205**	0.5165	H-2→L+2(61%)

TDDFT calculation

The TDDFT calculation of title molecule (table-5) has been performed by using same level theory on optimized geometry. The UV plot of title molecule is shown in fig-2. The two-level theory utilized to discuss high hyperpolarizability of title molecule. The most prominent peak computed $S_0 \rightarrow S_3$ with oscillatory strength (f=**1.234**) at 242nm. The computed hyperpolarizability depends on transition strength change in dipole moment (Δμ = 2.4534D)and transition energy (**2.7459 eV)** corresponds to highest prominent absorption peak during electronic transition H →L (32%),

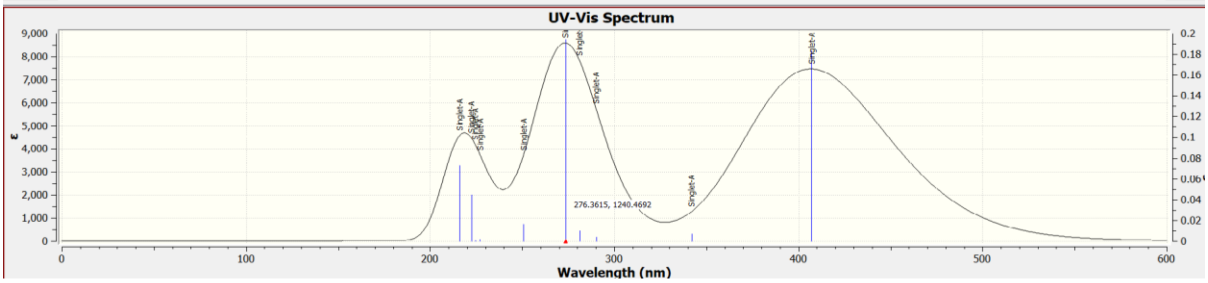

Fig-2 UV plot of title molecule

CONCLUSION

In this paper we have discussed nonlinear optical properties of **N-(1H-benzo[d]imidazol-2-yl) acetamide** by using combination of DFT/B3LYP method6-311+G(d, p) basis set. The electronic properties cleary shown that HOMO–LUMO energy gap ($\Delta E = 3.49\ \mathrm{eV}$)support charge transport from donor to acceptor in intramolecular charge transfer interactions. The global reactivity descriptors show molecule having medium stability, significant charge transfer capability, and favorable electronic softness improves nonlinear optical applications and molecular electronic devices. The Fukai function also indicate intermolecular charge transfer from O18(donor) to C12(Acceptor) are responsible for enhanced nonlinear optical (NLO) behavior. The computed hyperpolarizability value ($\beta_{\text{total}} = 104.23\ \text{a.u.}$)is 2.41 times larger than that of reference molecule Urea.The NBO analysis shows enhanced β value may originate from efficient intramolecular charge transfer between electron donor and acceptor groups through the conjugated molecular backbone. The large computed hyperpolarizability due high strength change in dipole moment ($\Delta\mu = 2.4534\mathrm{D}$)and transition energy (**2.7459 eV). This study shows that title molecule have potential to become good NLO material in future.**

REFERENCE

[1] Collings, P. J. & Hird, M. Introduction to Liquid Crystals Chemistry and Physics (Taylor & Francis, 1977).

[2] Srinivasa, H. T., Palakshamurthy, B. S., Venkatesha, M. A. & Mohammad, A. K. T. Synthesis/structural and mesomorphic properties of substituted hydrazide based calamitic molecules. Phase Trans. 92 (11), 1043–1053. Https://doi.org/10.1080/01411594.2019.1669034 (2019).

[3] Al-Mutabagani, L. A. et al. Synthesis and mesomorphic and electrical investigations of new furan liquid crystal derivatives. Front. Chem. https://doi.org/10.3389/fchem.2021.711862 (2021)

[4] Tadeusz Marek Krygowski, Beata Tamara Stępień, Sigma- and Pi-Electron Delocalization: Focus on Substituent Effects, Chemi. Rev. 105 (10), 3482–3512 (2005).

[5] Wei, Q. et al. Synthesis and mesomorphic properties of fluorinated Schiff base liquid crystals. Beijing Keji Daxue Xuebao/J. Univ. Sci. Technol. Beijing 30 (3), 285–288. https://doi.org/10.1155/2014/904657 (2008).

[6] A. K. Pandey, A. Dwivedi, K.K. Pandey, D. D. Dubey, V. Singh, Study of electro-optical behavior of nematic liquid crystal p butoxybenzylidene, p-heptylaniline (BBHA) under applied electric field by using density functional theory Journal of Molecular Liquids 420 (2025) 126839.

[7] M. Hagar, H. A. Ahmed, G.R. Saad, Synthesis and mesophase behaviour of Schiff base/ester 4-(arylideneamino)phenyl-4″-alkoxy benzoates and their binary mixtures. Journal of Molecular Liquids 273 (2019) 266-273.

[8] H.A. Ahmed, M. Hager, O.A. Alhaddad, Mesomorphic and geometrical orientation study of the relative position of fluorine atom in some thermotropic liquid crystal systems, 47, 404-413 (2020).

[9] A.Frisch, A.B.Nelson, AJ.Holder, Gauss view, Inc.Pittsburgh PA, (2005)

[10] A.D. Becke, J. Chem. Phys, 98, (1993), 5648.

[11] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 37, (1988), 785.

[12] P. Hohenberg, W. Kohn, Phys. Rev, 136, (1964), 13864.

[13] M. J. Frisch, et al Gaussian 09; Gaussian, Inc., Pittsburgh, PA, (2009).

[14] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys. 68 (1978) 3801.

[15] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512

[16] R.G Parr, L. Szentpály, S. Liu, *J. Am. Chem. Soc.*121, 1922–1924(1999).

[17] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys. 68 (1978) 3801.

[18] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512

[19] R.G Parr, L. Szentpály, S. Liu, *J. Am. Chem. Soc.*121, 1922–1924(1999).

[20] D. A. Kleinman, Phys, Rev B, 126, (1962), 1977.

[21] J. Pipek and P. Z. Mezey, J. Chem. Phys. 90, (1989), 4916.