

Quantum chemical investigation of spectroscopic, electronic and NLO properties of (1E, 4E)-1-(3-nitrophenyl)-5-phenylpenta-1,4-dien-3-one

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Abstract

In the present work the optimized molecular geometry and harmonic vibrational frequencies of chalcone derivative were calculated by DFT/B3LYP method with 6–31G (d,p) basis set. The vibrational assignments were performed on the basis of the potential energy distribution (PED) of the vibrational modes. Natural bond orbital (NBO) analysis has been performed on title compound using B3LYP/6–31G (d,p) and HSEh1PBE /6–31G (d,p) levels in order to elucidate intermolecular hydrogen bonding, intermolecular charge transfer (ICT) and delocalization of electron density. Mulliken atomic charges, natural population analysis (NPA) and atomic polar tensors (APT) were performed. The nonlinear optical properties of the title compound are also calculated and discussed. Molecular electrostatic potential and HOMO-LUMO energy levels are also computed. Ultraviolet–visible spectrum of the title compound has been calculated using TD–DFT method. The molecular orbital contributions were studied by density of states (DOSs). Global reactivity descriptors have been calculated using the HOMO and LUMO to predict compound reactivity.

Keywords: DFT; HOMO; LUMO; NBO; NLO; NPA.

1. Introduction

In recent times, chalcone derivatives have received great attention due to their anti-infective, especially antifungal and antibacterial activities (Zangade et al. 2010, Abonia et al. 2012, Tala-Tapeh et al. 2015). It has reported that the potential biological activities of chalcones, such as, anti-inflammatory (Ballesteros et al. 1995, Won et al. 2005), antitumor (Kumar et al. 2003), antimalarial (Domínguez et al. 2005, Awasthi et al. 2009), inhibition of key enzymes (Rao et al. 2009), cytotoxicity (Reddy et al. 2012), antiplatelet (Zhao et al. 2005), antileishmanial (Aponete et al. 2010), antiviral (Biradar et al. 2010), inhibitor of colon cancer cell growth (Mizuno et al. 2010), Radical-scavenging (Nabi et al. 2011), antidyslipidemic (Shukla et al. 2011), antidiabetic agents (Hsieh et al. 2012), vasorelaxant (Dong et al. 2010), antiprotozoal (Hayat et al. 2011) etc. In recent years, chalcones have been used in the field of material science as nonlinear optical (Shettigar et al. 2008, Asiri et al. 2014), optical limiting (Shettigar et al. 2006), electrochemical sensing (Delavaux-Nicot et al. 2007) and langmuir film (Gasull et al. 2002). Various materials containing chalcone moiety are notable for their second harmonic generation (Goto et al. 1991). The structure of the title compound was studied by the help of density functional theory (DFT) with B3LYP and HSEh1PBE functionals and 6-31G (d, p) basis set. The vibrational assignments have been performed based on potential energy distribution (PED). We have also performed natural bond orbital (NBO) calculation to provide a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Molecular electrostatic potential (MEP) surface and HOMO-

LUMO orbitals of the title compound have been investigated by using B3LYP and HSEh1PBE levels of density functional theory (DFT) with 6–31G (d,p) as basis set. In order to show the nonlinear optic (NLO) activity of title compound, the dipole moment, linear polarizability and first hyperpolarizability were obtained. Mulliken atomic charge, natural population analysis (NPA) and atomic polar tensors (APT) were computed by DFT method. The global reactivity descriptors, namely, hardness, softness, chemical potential and electrophilicity index are also calculated to understand the reactive nature of the compound.

2. Computational details

All theoretical calculations were carried out with help of Gaussian 09 program package (Frisch et al. 2009) using B3LYP (Becke's three parameter hybrid functional with the LYP correlation functional) (Lee et al. 1988, Becke et al. 1993) and HSEh1PBE (the recommended version of the full Heyd-Scuseria-Ernzerhof functional, referred to as HSE06 in literature) (Heyd et al. 2004, Heyd et al. 2004) methods in conjunction with 6–31G(d, p) basis set. The molecular structure, MEP surfaces and HOMO-LUMO levels were visualized with the help of Gauss View program (Frisch et al. 2009). The theoretical vibrational spectra of the title compound were interpreted by means of PED using the VEDA 4 program (Jamroz et al. 2004). The calculated wavenumbers were scaled with scaling factor of 0.946 for B3LYP and 0.941 for HSEh1PBE. Natural bond orbital (NBO) calculations were performed using NBO 3.1 program (Glendening et al. 1998) as implemented in the Gaussian 09 package at the DFT/B3LYP and DFT/HSEh1PBE

levels. The second order Fock–matrix was carried out to evaluate the donor (i) and acceptor (j) interaction in the NBO basis (Foster et al. 1980, Reed et al. 1983, Reed et al. 1985, Reed et al. 1985, Reed et al. 1988, Szafran et al. 2007, Sebastian et al. 2010, Tamer et al. 2015, Altürk et al. 2015). For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associated as:

$$E^{(2)} = q_i \frac{F(i,j)^2}{\epsilon_i - \epsilon_j} \quad (1)$$

The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donor and electron acceptor, i.e. a more donating tendency from electron donors to acceptors and a greater extent of conjugation of the whole system. Ultraviolet–visible spectrum, excitation energies, absorbance and oscillator strengths for the title compound were obtained in the framework of TD–DFT (Cancès et al. 1997, Stratmann et al. 1998) calculations using B3LYP/6–31G (d,p) and HSEh1PBE/6–31G (d,p) functionals. Density of state (DOS) diagram of the title compound derived using the GaussSum 2.2 program (O'Boyle et al. 2008) was used to calculate group contributions to the molecular orbitals. Molecular electrostatic potential (MEP) surfaces have been investigated by using B3LYP and HSEh1PBE levels of DFT method with 6–31G (d, p) basis set. Mulliken atomic charges, natural population analysis (NPA) and atomic polar tensors (APT) (Ferreira 1993) were calculated by determining the electron population of each atom. To study the nonlinear optical properties (NLO), parameters such as dipole moment (μ), polarizability (α) and the first–order hyperpolarizability (β) are determined using B3LYP and HSEh1PBE functionals with 6–31G(d,p) basis sets. The total dipole moments (μ), polarizability (α) and first–order hyperpolarizability (β) are evaluated using the following equations:

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

$$\alpha = \frac{1}{3}(\alpha_x + \alpha_y + \alpha_z) \quad (3)$$

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

The complete equation for calculating the magnitude of first–order hyper polarizability from Gaussian 09 output is given as follows:

$$\beta_{\text{tot}} = \left[(\beta_{xxx}^2 + \beta_{xyy}^2 + \beta_{xzz}^2)^2 + (\beta_{xxy}^2 + \beta_{yyx}^2 + \beta_{yzz}^2)^2 + (\beta_{xxz}^2 + \beta_{yyz}^2 + \beta_{zzz}^2)^2 \right]^{1/2} \quad (5)$$

The α_{tot} and β_{tot} values of Gaussian output are in atomic units (a.u.) therefore they were converted into electrostatic units (esu) (for α ; 1 a.u. = 0.1482×10^{-24} esu, for β ; 1 a.u. = 8.6393×10^{-33} esu). The chemical reactivity descriptors of compounds such as electronegativity (χ), chemical potential (μ), hardness (η), softness (S), and electrophilicity index (ω) are evaluated using following equations (Parr et al. 1978, Parr et al. 1983, Parr et al. 1999, Chattaraj et al. 2003, Pearson 2005):

$$\chi = \frac{I + A}{2} \quad (6)$$

$$\mu = -\frac{I + A}{2} \quad (7)$$

$$\eta = \frac{I - A}{2} \quad (8)$$

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

$$\omega = \frac{\mu^2}{2\eta} \quad (10)$$

3. Results and discussion

3.1. Optimized structure and hydrogen bonding

The bond lengths, bond angles and dihedral angles corresponding to the optimized geometry of the title compound have been obtained using the DFT/B3LYP/6–31(d,p) and DFT/HSEh1PBE /6–31(d,p) methods and the corresponding results are reported in Table 1. The optimized geometry of the title compound is illustrated in Fig. 1. The benzene C–C bond lengths observed in the region of 1.378–1.399 Å (Samshuddin et al. 2012) have been calculated at the range of 1.390–1.410 Å for B3LYP level and 1.386–1.406 Å for HSEh1PBE level. The C7=C8 and C10=C11 bond lengths are observed as 1.332, 1.333 Å (Samshuddin et al. 2012). In our calculations, these bond length are found to be 1.346, 1.346 Å for B3LYP level and 1.343, 1.346 Å for HSEh1PBE level. For the title compound, the C=O bond lengths (B3LYP /XRD) are 1.2308/1.2287 Å which are in agreement with reported values (Samshuddin et al. 2012). The bond length between C and N is 0.001 Å times higher than the experimental value (1.465 Å). The bond length of O–N is differed from 0.003 Å to 0.01 Å with experimental value (1.2270 and 1.2202 Å). The average ON distance of 1.2301 Å in the nitro group is an indication of clearly double bonds. The bond angle O1–N1–O2 (124.78°) of nitro group which is closer to experimental data (123.25°). The calculated O1–N1–C3 and O2–N1–C3 angles are 117.68 and 117.54, respectively, about 0.7° smaller than the experimental results. The N1–C3–C2 and N1–C3–C4 bond angles observed as 118.73° and 118.61° (Samshuddin et al. 2012) have been also calculated as 118.79 and 118.83 for B3LYP, 118.75 and 118.80 for HSEh1PBE levels. From Table 1, it can be noted that there is a good agreement between the experimental and theoretical geometric parameters.

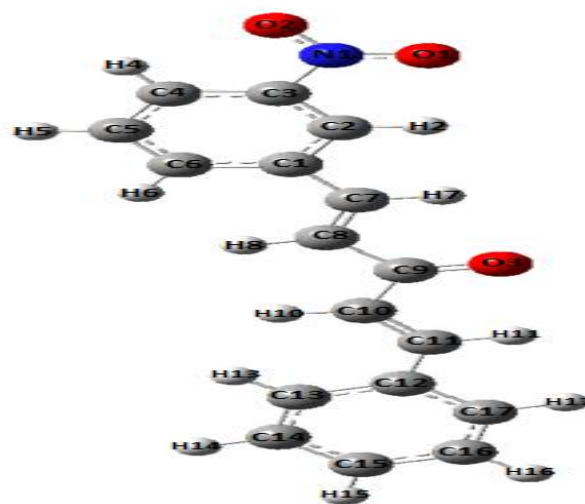


Fig. 1: The Optimized Structure of the Title Compound.

3.2. Natural bond orbital analysis

The natural bond orbital analysis have been performed by using B3LYP and HSEh1PBE methods with 6–31G (d, p) basis set. The perturbation energies of significant donor–acceptor interactions from the NBO analysis were summarized in Table 2. As concluded from the calculated NBO results, the strongest stabilization energies within title compound are defined as π (C7–C8) $\rightarrow \pi^*$ (C9–O3) with the energies of 19.32 and 18.84 kcal/mol at B3LYP and HSEh1PBE levels, respectively. The important intramolecular hyper–conjugative interactions are: n2 (O1) $\rightarrow \sigma^*$ (C3–N1), n2 (O1) $\rightarrow \sigma^*$ (N1–O2), n2 (O2) $\rightarrow \sigma^*$ (C3–N1), n2 (O2) $\rightarrow \sigma^*$ (N1–O1), n3 (O2) $\rightarrow$ (N1–O1), n2 (O3) $\rightarrow \sigma^*$ (C8–C9), n2 (O3) $\rightarrow \sigma^*$ (C9–C10) with stabilization energies 12.84, 19.30, 12.77, 19.22, 164.16, 19.79, 19.17 kJ/mol at B3LYP. The corresponding electron density values are 1.89710e, 1.89771e, 1.44242e and

1.88050e. The magnitude of charge transfer from the lone pairs of n3 (O2) to anti-bonding (N1–O1), π orbitals amount to stabilization of 164.16kcal/mol. The highly probable transition in this compound are (C1–C2) to (C3–C4) ($\pi \rightarrow \pi^*$, 20.56 kcal/mol), (C1–C2) to (C5–C6) ($\pi \rightarrow \pi^*$, 20.01 kcal/mol), (C3–C4) to (C1–C2) ($\pi \rightarrow \pi^*$, 21.60 kcal/mol), (C3–C4) to (C5–C6) ($\pi \rightarrow \pi^*$, 16.48 kcal/mol), (C5–C6) to (C1–C2) ($\pi \rightarrow \pi^*$, 18.23 kcal/mol), (C5–C6) to (C3–C4) ($\pi \rightarrow \pi^*$, 22.60 kcal/mol), these six transitions corre-

spond to three pairs of orbitals within the first aromatic ring. $E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).

^{An} Energy difference between donor and acceptor i and j NBO orbitals.

^B F (i, j) is the Fock matrix element between i and j NBO orbitals.

Table 1: The Calculated Geometric Parameters of the Title Compound

Bond lengths (Å)	X-ray	DFT	Bond angles (°)	X-ray	DFT	Dihedral angles (°)	X-ray	DFT
O1–N1	1.227	1.229	O1–N1–O2	123.25	124.78	O1–N1–C3–C2	6.3	0.0
O2–N1	1.220	1.230	O1–N1–C3	118.38	117.68	O1–N1–C3–C4	–172.4	–179.9
O3–C9	1.228	1.230	O2–N1–C3	118.36	117.54	O2–N1–C3–C2	–173.8	–179.9
N1–C3	1.465	1.475	C2–C1–C6	118.32	118.12	O2–N1–C3–C4	7.4	0.0
C1–C2	1.394	1.404	C2–C1–C7	118.78	118.43	C6–C1–C2–C3	–1.6	–0.0
C1–C6	1.399	1.410	C6–C1–C7	122.89	123.45	C7–C1–C2–C3	177.6	180.0
C1–C7	1.467	1.464	C1–C2–C3	119.22	119.69	C2–C1–C6–C5	0.6	0.0
C2–C3	1.384	1.390	N1–C3–C2	118.73	118.79	C7–C1–C6–C5	–178.6	–180.0
C3–C4	1.383	1.392	N1–C3–C4	118.61	118.83	C2–C1–C7–C8	–173.2	–179.9
C4–C5	1.385	1.395	C2–C3–C4	122.65	122.37	C6–C1–C7–C8	6.1	0.0
C5–C6	1.383	1.392	C3–C4–C5	118.09	118.06	C1–C2–C3–N1	–177.1	–180.0
C7–C8	1.332	1.346	C4–C5–C6	120.27	120.54	C1–C2–C3–C4	1.5	0.0
C8–C9	1.482	1.489	C1–C6–C5	121.43	121.22	N1–C3–C4–C5	178.4	–180.0
C9–C10	1.479	1.481	C1–C7–C8	126.52	127.86	C2–C3–C4–C5	–0.2	–0.0
C10–C11	1.333	1.346	C7–C8–C9	122.11	120.49	C3–C4–C5–C6	–0.8	0.0
C11–C12	1.468	1.461	O3–C9–C8	122.43	121.46	C1–C7–C8–C9	–177.4	180.0
C12–C13	1.395	1.409	O3–C9–C10	122.50	122.34	C7–C8–C9–O3	–11.3	0.0
C12–C17	1.397	1.407	C8–C9–C10	115.02	116.19	C7–C8–C9–C10	166.1	–180.0
C13–C14	1.387	1.409	C9–C10–C11	121.79	120.56	O3–C9–C10–C11	21.9	0.0
C14–C15	1.386	1.399	C10–C11–C12	126.80	128.29	C8–C9–C10–C11	–155.4	–180.0
C15–C16	1.378	1.395	C11–C12–C13	122.53	123.34	C9–C10–C11–C12	176.1	180.
C16–C17	1.389	1.393	C11–C12–C17	118.99	118.49	C10–C11–C12–C13	10.4	0.0
			C13–C12–C17	118.46	118.18	C10–C11–C12–C17	–170.9	–180.0
			C12–C13–C14	120.55	120.73	C11–C12–C13–C14	178.3	–180.0
			C13–C14–C15	120.36	120.31	C17–C12–C13–C14	–0.3	0.0
			C14–C15–C16	119.65	119.74	C11–C12–C17–C16	–177.9	180.0
			C15–C16–C17	120.37	119.94	C13–C12–C17–C16	0.8	–0.0
			C12–C17–C16	120.61	121.10	C12–C13–C14–C15	–0.3	–0.0
						C13–C14–C15–C16	0.4	0.0
						C14–C15–C16–C17	0.0	–0.0

Table.2: Second-Order Perturbation Theory Analysis of Flock Matrix in NBO Basis Corresponding to the Intra-Molecular Bonds of the Title Compound.

Donor (i)	ED (i) (e)	Acceptor (j)	ED (j) (e)	$E^{(2)}$ (kcal mol ^{–1})	$\epsilon_j \epsilon_i^a$ (a.u.)	$F(i,j)^b$ (a.u.)
π (C1–C2)	1.60465	π^* (C3–C4)	0.37340	20.56	0.27	0.067
π (C1–C2)		π^* (C5–C6)	0.28810	20.01	0.28	0.069
π (C1–C2)		π^* (C7–C8)	0.09427	15.49	0.30	0.066
π (C3–C4)	1.64122	π^* (C1–C2)	0.34153	21.60	0.30	0.072
π (C3–C4)		π^* (C5–C6)	0.28810	16.48	0.29	0.063
π (C3–C4)		π^* (N1–O1)	0.62218	27.22	0.15	0.061
π (C5–C6)	1.65472	π^* (C1–C2)	0.34153	18.23	0.29	0.064
π (C5–C6)		π^* (C3–C4)	0.37340	22.60	0.28	0.071
π (C7–C8)	1.84165	π^* (C1–C2)	0.34153	12.29	0.29	0.056
π (C7–C8)		π^* (C9–O3)	0.23046	19.32	0.30	0.069
π (C10–C11)	1.83189	π^* (C9–O3)	0.23046	21.62	0.29	0.072
π (C10–C11)		π^* (C12–C17)	0.37438	11.59	0.30	0.055
π (C12–C17)	1.61495	π^* (C10–C11)	0.10872	17.10	0.29	0.068
π (C12–C17)		π^* (C13–C14)	0.29620	19.18	0.28	0.067
π (C12–C17)		π^* (C15–C16)	0.32266	19.60	0.28	0.067
π (C13–C14)	1.67848	π^* (C12–C17)	0.37438	18.85	0.28	0.066
π (C13–C14)		π^* (C15–C16)	0.32266	20.22	0.28	0.068
π (C15–C16)	1.65023	π^* (C12–C17)	0.37438	21.18	0.28	0.069
π (C15–C16)		π^* (C13–C14)	0.29620	18.97	0.28	0.066
π (N1–O1)	1.98600	n3 (O2)	1.44242	12.35	0.18	0.078
n2(O1)	1.89710	σ^* (C3–N1)	0.10609	12.84	0.57	0.076
n2 (O1)		σ^* (N1–O2)	0.05664	19.30	0.71	0.105
n2 (O2)	1.89771	σ^* (C3–N1)	0.10609	12.77	0.57	0.076
n2 (O2)		σ^* (N1–O1)	0.05650	19.22	0.71	0.105
n3 (O2)	1.44242	π^* (N1–O1)	0.62218	164.16	0.14	0.139
n2 (O3)	1.88050	σ^* (C8–C9)	0.06002	19.79	0.69	0.106
n2 (O3)		σ^* (C9–C10)	0.05765	19.17	0.70	0.105
π^* (C1–C2)	0.34153	π^* (C7–C8)	0.09427	47.80	0.02	0.064
π^* (C9–O3)	0.23046	π^* (C7–C8)	0.09427	67.07	0.02	0.072
π^* (C9–O3)		π^* (C10–C11)	0.10872	53.10	0.02	0.072
π^* (C12–C17)	0.37438	π^* (C10–C11)	0.10872	107.46	0.01	0.067
π^* (N1–O1)	0.62218	π^* (C3–C4)	0.37340	15.69	0.14	0.059

Table 3: Selected NBO Results Showing Formation of Lewis and Non– Lewis Orbitals of the Title Compound Using B3LYP/631G (D, P) Level of Theory

Bond (AB)	ED/energy(a.u.)	EDA (%)	EDB (%)	NBO	S (%)	p (%)
Σ (C1–C2)	1.97144	50.65	49.35	0.7117 ($sp^{2.01}$) C+0.7025 ($sp^{1.00}$) C	33.26 35.41	66.70 64.55
Σ (C1–C6)	1.97586	51.04	48.96	0.7144 ($sp^{1.95}$) C+0.6997 ($sp^{1.88}$) C	33.87 34.73	66.09 65.23
Σ (C1–C7)	1.97679	51.52	48.48	0.7178 ($sp^{2.05}$) C+0.6963 ($sp^{1.96}$) C	32.82 33.75	67.14 66.20
Σ (C2–C3)	1.97644	49.06	50.94	0.7004 ($sp^{1.94}$) C+0.7137 ($sp^{1.64}$) C	34.05 37.90	65.90 62.07
Σ (C3–C4)	1.97665	51.15	48.85	0.7152 ($sp^{1.65}$) C+0.6989 ($sp^{1.97}$) C	37.77 33.61	62.19 66.34
Σ (C3–N1)	1.98966	37.82	62.18	0.6150 ($sp^{3.12}$) C+0.7885 ($sp^{1.77}$) N	24.26 36.08	75.61 63.88
Σ (C4–C5)	1.97626	50.37	49.63	0.7097 ($sp^{1.83}$) C+0.7045 ($sp^{1.88}$) C	35.38 34.76	64.59 65.20
Σ (C5–C6)	1.98121	49.84	50.16	0.7060 ($sp^{1.83}$) C+0.7082 ($sp^{1.80}$) C	35.27 35.70	64.69 64.27
Σ (C7–C8)	1.98316	50.33	49.67	0.7094 ($sp^{1.64}$) C+0.7048 ($sp^{1.65}$) C	37.86 37.79	62.11 62.18
Σ (C8–C9)	1.98075	51.60	48.40	0.7183 ($sp^{2.08}$) C+0.6957 ($sp^{1.91}$) C	32.41 34.38	67.54 65.57
Σ (C9–C10)	1.98122	48.72	51.28	0.6980 ($sp^{1.84}$) C+0.7161 ($sp^{2.08}$) C	35.24 32.43	64.71 67.53
Σ (C9–O3)	1.99534	34.66	65.34	0.5888 ($sp^{2.30}$) C+0.8083 ($sp^{1.39}$) O	30.30 41.76	69.59 57.91
Σ (C10–C11)	1.98305	49.79	50.21	0.7056 ($sp^{1.65}$) C+0.7086 ($sp^{1.65}$) C	37.73 37.69	62.23 62.27
Σ (C11–C12)	1.97734	48.94	51.06	0.6995 ($sp^{1.92}$) C+0.7146 ($sp^{2.08}$) C	34.29 32.42	65.67 67.54
Σ (C12–C13)	1.97486	51.08	48.92	0.7147 ($sp^{1.94}$) C+0.6994 ($sp^{1.88}$) C	33.97 34.71	65.99 65.25
Σ (C12–C17)	1.97555	51.17	48.83	0.7153 ($sp^{1.98}$) C+0.6988 ($sp^{1.86}$) C	33.57 34.91	66.40 65.05
Σ (C13–C14)	1.98056	50.21	49.79	0.7086 ($sp^{1.79}$) C+0.7056 ($sp^{1.83}$) C	35.81 35.30	64.15 64.66
Σ (C14–C15)	1.98102	50.08	49.92	0.7076 ($sp^{1.85}$) C+0.7066 ($sp^{1.86}$) C	35.01 35.01	64.95 64.95
Σ (C15–C16)	1.98107	49.96	50.04	0.7068 ($sp^{1.84}$) C+0.7074 ($sp^{1.85}$) C	35.19 35.06	64.77 64.90
Σ (C16–C17)	1.98083	49.84	50.16	0.7059 ($sp^{1.84}$) C+0.7083 ($sp^{1.81}$) C	35.15 35.62	64.81 64.34
Σ (N1–O1)	1.99579	48.58	51.42	0.6970 ($sp^{2.13}$) N+0.7171 ($sp^{2.97}$) O	31.92 25.14	67.98 74.71
Σ (N1–O2)	1.99578	48.58	51.42	0.6970 ($sp^{2.13}$) N+0.7171 ($sp^{2.98}$) O	31.89 25.12	68.01 74.74
Π (C1–C2)	1.60465	52.47	47.53	0.7244 ($sp^{1.00}$) C+ 0.6894 ($sp^{1.00}$) C	0.00 0.00	99.97 99.95
Π (C3–C4)	1.64122	54.84	45.16	0.7405 ($sp^{1.00}$) C+ 0.6720 ($sp^{1.00}$) C	0.00 0.00	99.99 99.95
Π (C5–C6)	1.65472	51.48	48.52	0.7175 ($sp^{1.00}$) C+ 0.6965 ($sp^{1.00}$) C	0.00 0.00	99.96 99.96
Π (C7–C8)	1.84165	46.94	53.06	0.6851 ($sp^{1.00}$) C+ 0.7284 ($sp^{1.00}$) C	0.00 0.00	99.94 99.96
Π (C9–O3)	1.96464	32.49	67.51	0.5700 ($sp^{1.00}$) C+ 0.8217 ($sp^{1.00}$) O	0.00 0.00	99.85 99.70
Π (C10–C11)	1.83189	54.56	45.44	0.7386 ($sp^{1.00}$) C+ 0.6741 ($sp^{1.00}$) C	0.00 0.00	99.96 99.94
Π (C12–C17)	1.61495	51.56	48.44	0.7180 ($sp^{1.00}$) C+ 0.6960 ($sp^{1.00}$) C	0.00 0.00	99.98 99.96
Π (C13–C14)	1.67848	49.46	50.54	0.7033 ($sp^{1.00}$) C+ 0.7109 ($sp^{1.00}$) C	0.00 0.00	99.96 99.96
Π (C15–C16)	1.65023	49.43	50.57	0.7030 ($sp^{1.00}$) C+ 0.7112 ($sp^{1.00}$) C	0.00 0.00	99.96 99.96
Π (N1–O1)	1.98600	40.04	59.96	0.6327 ($sp^{1.00}$) N+ 0.7744 ($sp^{1.00}$) O	0.00 0.00	99.73 99.75
n1(O1)	1.98113			$sp^{0.34}$	74.83	25.16
n2(O1)	1.89710			$sp^{99.99}$	0.14	99.76
n1(O2)	1.98117			$sp^{0.34}$	74.86	25.14
n2(O2)	1.89771			$sp^{99.99}$	0.14	99.76
n3(O2)	1.44242			$sp^{1.00}$	0.00	99.78
n1(O3)	1.97822			$sp^{0.72}$	58.20	41.76
n2(O3)	1.88050	–	–	$sp^{1.00}$	0.00	99.80
σ^* (C1–C2)	0.02070	49.35	50.65	0.7025 ($sp^{2.01}$) C – 0.7117 ($sp^{1.82}$) C	33.26 35.41	66.70 64.55
σ^* (C1–C6)	0.02493	48.96	51.04	0.6997 ($sp^{1.95}$) C – 0.7144 ($sp^{1.88}$) C	33.87 34.73	66.09 65.23

Table 3: (Continued)

Bond (AB)	ED/energy(a.u.)	EDA (%)	EDB (%)	NBO	S (%)	p (%)
$\Sigma^*(\text{C1-C7})$	0.02262	48.48	51.52	0.6963 ($\text{sp}^{2.05}$) C – 0.7178 ($\text{sp}^{1.96}$) C	32.82	67.14
$\Sigma^*(\text{C2-C3})$	0.02039	50.94	49.06	0.7137 ($\text{sp}^{1.94}$) C – 0.7004 ($\text{sp}^{1.64}$) C	33.75	66.20
$\Sigma^*(\text{C3-C4})$	0.02198	48.85	51.15	0.6989 ($\text{sp}^{1.65}$) C – 0.7152 ($\text{sp}^{1.97}$) C	34.05	65.90
$\Sigma^*(\text{C3-N1})$	0.10609	62.18	37.82	0.7885 ($\text{sp}^{3.12}$) C – 0.6150 ($\text{sp}^{1.77}$) N	37.90	62.07
$\Sigma^*(\text{C4-C5})$	0.01565	49.63	50.37	0.7045 ($\text{sp}^{1.83}$) C – 0.7097 ($\text{sp}^{1.88}$) C	37.77	62.19
$\Sigma^*(\text{C5-C6})$	0.01399	50.16	49.84	0.7082 ($\text{sp}^{1.83}$) C – 0.7060 ($\text{sp}^{1.80}$) C	33.61	66.34
$\Sigma^*(\text{C7-C8})$	0.01221	49.67	50.33	0.7048 ($\text{sp}^{1.64}$) C – 0.7094 ($\text{sp}^{1.65}$) C	24.26	75.61
$\Sigma^*(\text{C8-C9})$	0.06002	48.40	51.60	0.6957 ($\text{sp}^{2.08}$) C – 0.7183 ($\text{sp}^{1.91}$) C	36.08	63.88
$\Sigma^*(\text{C9-C10})$	0.05765	51.28	48.72	0.7161 ($\text{sp}^{1.84}$) C – 0.6980 ($\text{sp}^{2.08}$) C	35.38	64.59
$\Sigma^*(\text{C9-O3})$	0.01094	65.34	34.66	0.8083 ($\text{sp}^{2.30}$) C – 0.5888 ($\text{sp}^{1.39}$) O	34.76	65.20
$\Sigma^*(\text{C10-C11})$	0.01248	50.21	49.79	0.7086 ($\text{sp}^{1.65}$) C – 0.7056 ($\text{sp}^{1.65}$) C	35.27	64.69
$\Sigma^*(\text{C11-C12})$	0.02243	51.06	48.94	0.7146 ($\text{sp}^{1.92}$) C – 0.6995 ($\text{sp}^{2.08}$) C	35.70	64.27
$\Sigma^*(\text{C12-C13})$	0.02492	48.92	51.08	0.6994 ($\text{sp}^{1.94}$) C – 0.7147 ($\text{sp}^{1.88}$) C	37.86	62.11
$\Sigma^*(\text{C12-C17})$	0.02104	48.83	51.17	0.6988 ($\text{sp}^{1.98}$) C – 0.7153 ($\text{sp}^{1.86}$) C	37.79	62.18
$\Sigma^*(\text{C13-C14})$	0.01407	49.79	50.21	0.7056 ($\text{sp}^{1.79}$) C – 0.7086 ($\text{sp}^{1.83}$) C	32.41	67.54
$\Sigma^*(\text{C14-C15})$	0.01583	49.92	50.08	0.7066 ($\text{sp}^{1.85}$) C – 0.7076 ($\text{sp}^{1.86}$) C	34.38	65.57
$\Sigma^*(\text{C15-C16})$	0.01564	50.04	49.96	0.7074 ($\text{sp}^{1.84}$) C – 0.7068 ($\text{sp}^{1.85}$) C	35.24	64.71
$\Sigma^*(\text{C16-C17})$	0.01408	50.16	49.84	0.7083 ($\text{sp}^{1.84}$) C – 0.7059 ($\text{sp}^{1.81}$) C	32.43	67.53
$\Sigma^*(\text{N1-O1})$	0.05650	51.42	48.58	0.7171 ($\text{sp}^{2.13}$) N – 0.6970 ($\text{sp}^{2.97}$) O	30.30	69.59
$\Sigma^*(\text{N1-O2})$	0.05664	51.42	48.58	0.7171 ($\text{sp}^{2.13}$) N – 0.6970 ($\text{sp}^{2.98}$) O	41.76	57.91
$\Pi^*(\text{C1-C2})$	0.34153	47.53	52.47	0.6894 ($\text{sp}^{1.00}$) C – 0.7244 ($\text{sp}^{1.00}$) C	37.73	62.23
$\Pi^*(\text{C3-C4})$	0.37340	45.16	54.84	0.6720 ($\text{sp}^{1.00}$) C – 0.7405 ($\text{sp}^{1.00}$) C	37.69	62.27
$\Pi^*(\text{C5-C6})$	0.28810	48.52	51.48	0.6965 ($\text{sp}^{1.00}$) C – 0.7175 ($\text{sp}^{1.00}$) C	34.29	65.67
$\Pi^*(\text{C7-C8})$	0.09427	53.06	46.94	0.7284 ($\text{sp}^{1.00}$) C – 0.6851 ($\text{sp}^{1.00}$) C	32.42	67.54
$\Pi^*(\text{C9-O3})$	0.23046	67.51	32.49	0.8217 ($\text{sp}^{1.00}$) C – 0.5700 ($\text{sp}^{1.00}$) O	33.97	65.99
$\Pi^*(\text{C10-C11})$	0.10872	45.44	54.56	0.6741 ($\text{sp}^{1.00}$) C – 0.7386 ($\text{sp}^{1.00}$) C	34.71	65.25
$\Pi^*(\text{C12-C17})$	0.37438	48.44	51.56	0.6960 ($\text{sp}^{1.00}$) C – 0.7180 ($\text{sp}^{1.00}$) C	33.57	66.40
$\Pi^*(\text{C13-C14})$	0.29620	50.54	49.46	0.7109 ($\text{sp}^{1.00}$) C – 0.7033 ($\text{sp}^{1.00}$) C	34.91	65.05
$\Pi^*(\text{C15-C16})$	0.32266	50.57	49.43	0.7112 ($\text{sp}^{1.00}$) C – 0.7030 ($\text{sp}^{1.00}$) C	35.81	64.15
$\Pi^*(\text{N1-O1})$	0.62218	59.96	40.04	0.7744 ($\text{sp}^{1.00}$) N – 0.6327 ($\text{sp}^{1.00}$) O	35.30	64.66
					35.01	64.95
					35.19	64.77
					35.06	64.90
					35.15	64.81
					35.62	64.34
					31.92	67.98
					25.14	74.71
					31.89	68.01
					25.12	74.74
					0.00	99.97
					0.00	99.95
					0.00	99.99
					0.00	99.95
					0.00	99.96
					0.00	99.96
					0.00	99.94
					0.00	99.96
					0.00	99.85
					0.00	99.70
					0.00	99.96
					0.00	99.94
					0.00	99.98
					0.00	99.96
					0.00	99.96
					0.00	99.96
					0.00	99.96
					0.00	99.73
					0.00	99.75

Table 4: The Molecular Electric Dipole Moment M (Debye), Polarizability A_{tot} ($\times 10^{-23}$ Esu) and First Order Hyperpolarizability B_{tot} ($\times 10^{-30}$ Esu) Values of Title Compound

Parameters	B3LYP	Parameters	B3LYP
μ_x	-5.075	β_{xxx}	-2452.638
μ_y	5.120	β_{xxy}	-1540.676
μ_z	0.000	β_{xyy}	-25.275
μ (D)	7.210	β_{vvv}	59.765
α_{xx}	454.420	β_{xxz}	-1.398
α_{xy}	-3.548	β_{xvz}	-0.173
α_{yy}	200.126	β_{yyz}	-0.443
α_{xz}	0.005	β_{xzz}	-1.200
α_{yz}	-0.001	β_{yzz}	3.105
α_{zz}	64.036	β_{zzz}	0.992
α_{tot} (a.u)	239.528	β_{tot} (a.u)	2886.158
$\alpha_{\text{tot}} \times 10^{-23}$ (esu)	3.545	$\beta_{\text{tot}} \times 10^{-30}$ (esu)	24.936

The intra-molecular interactions due to the orbital overlap of π (C12–C17) over π^* (C13–C14) and π^* (C15–C16) with energies 19.18 kcal/mol and 19.60 kcal/mol, π (C13–C14) over π^* (C12–C17) and π^* (C15–C16) with stabilization energies 18.85 kcal/mol and 20.22 kcal/mol and π (C15–C16) over π^* (C12–C17) and π^* (C13–C14) with energies 21.18 kcal/mol and 18.97 kcal/mol. these six transitions correspond to three pairs of orbitals within the second aromatic ring. Further the other high energy interactions involving the delocalization of π^* electrons of aromatic with the anti-bonding π^* electrons of aromatic corresponds to π^* (C12–C17) $\rightarrow \pi^*$ (C10–C11) and π^* (C1–C2) / π^* (C7–C8) stabilizes the compound by stabilization energy in the range of 47.80107.46kJ/mol.

The large hyperconjugative interaction energies which are presented in Table 2 display the presence of intramolecular charge transfer (ICT) in title compound. It is well known that ICT induce the nonlinear optical properties of molecular systems.

The second order perturbation energies of significant donor-acceptor interactions and occupancy of electrons and p-character in significant NBO natural atomic hybrid orbitals were presented in Table 3. Selected bond taken from Table 3, σ (C9–O3) is composed of 0.5888 ($sp^{2.30}$) C+0.8083 ($sp^{1.39}$) O. The numbers 0.5888 and 0.8083 represent the polarization co-efficient. The biggest value of the polarization coefficient, indicate higher value of the electronegativity. The weights are obtained from the squares of the coefficients as $(0.8083)^2 \approx 0.65334889$, corresponding to 65.34 % localization on oxygen atom. In a similar way, the 34.66 % localization on carbon is obtained. The oxygen has larger percentage of this NBO, at 65.34 % and gives the larger polarization coefficient of 0.8083 because it has higher electro negativity. In σ (C3–N1)orbital with 1.98966 electrons has 37.82 % C3character in a $sp^{2.06}$ hybrid and has 36.43% C9 character in $asp^{3.12}$ hybrid. The nitrogen has larger percentage of NBO at 62.18 % and gives the larger polarization coefficient of 0.7885 because of its higher electro negativity.

3.3. Frontier molecular orbital analysis

The HOMOLUMO energy gap of the title compound was computed at DFT/B3LYP/6-31G (d, p) and DFT/ HSEH1PBE /6-31G (d, p) levels. The electron density plots of the HOMO and LUMO for the title compound is presented in Fig. 2. The energy band gap is 3.7567 eV from B3LYP and 3.4010 from HSEH1PBE shown in Fig. 2. The small value of band gap reflects the chemical activity of the compound and encourages the application of the title compound as nonlinear optical materials.

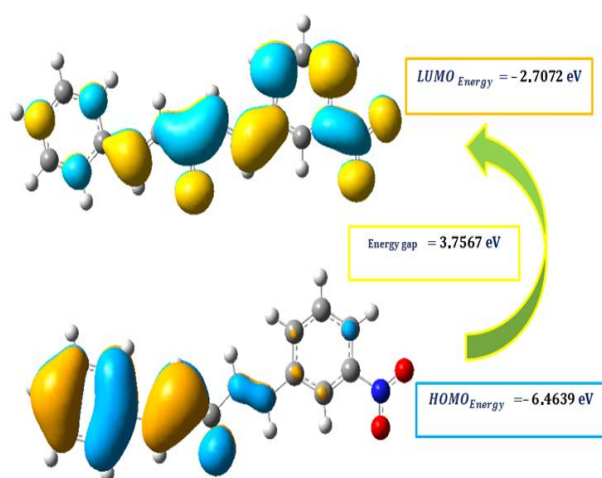


Fig. 2: The Molecular Orbitals and Energies for the HOMO and LUMO of the Title Compound.

3.4. Molecular electrostatic potential (MESP) analysis

Electrostatic potential in the MEP plot is increasing in the order of red < orange < yellow < green < blue. Electrostatic potential surface has been plotted for the title compound with B3LYP/6-31G (d,p) basis set using the computer software Gauss view as shown in Fig. 3. The negative regions are mainly localized on the nitro group and oxygen atom, a maximum positive region is localized on the hydrogen atoms indicating a possible site for nucleophilic attack.

3.5. Nonlinear optical properties

The non-linear optic properties (NLO) of the title compound was studied by calculating the dipole moment, polarizability and first order polarizability using B3LYP and HSEh1PBE methods with 6-31G (d,p) basis set. The NLO properties are summarized in Table 4.

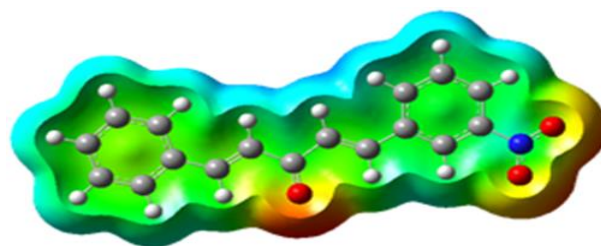


Fig. 3: Molecular Electrostatic Potential Map Obtained with B3LYP/6-31G (D, P) Level.

The calculated molecular dipole moment 7.2100 and 7.1500D for B3LYP and HSEh1PBE levels, respectively. The calculated molecular polarizability (α) values equal 35.498×10^{-23} and 35.093×10^{-23} (e.s.u) for B3LYP and HSEh1PBE levels, respectively. The first order static hyperpolarizability (β) parameter has been calculated as 24.936×10^{-30} and 23.9523×10^{-30} (e.s.u.) respectively. Our title compound with greater dipole moment and hyperpolarizability value shows that the compound has large NLO optical property.

3.6. Vibrational assignments

The title compound consists of 34 atoms, which has 96 normal modes of vibration. The vibrational band assignments were made by the aid of potential energy distribution (PED) using VEDA program. Vibrational frequency assignments of the title compound are reported in Table 5. The calculated infrared spectra of the title compound are shown in Fig. 4. Generally, the aromatic structure shows the presence of CH stretching vibration in the region 3100–3000 cm^{-1} (Silverstein et al. 1981, Wade 1992, Rastogi et al. 2002). In this present study, the C–H stretching vibrations are observed at 3074 to 3023 cm^{-1} [mode number 96 to 90] by B3LYP/6-31G (d,P) method. The PED corresponding to this pure mode of title compound contributed 86% to 99%. The C–C–H in plane bending vibrations are normally occurred as a number of strong to weak intensity bands in the region 1300–1000 cm^{-1} . The theoretical wave numbers for B3LYP level at 1456, 1443, 1411, 1166, 1143, 1134, 1126 and 1058 cm^{-1} (mode no 75, 74, 73, 61, 60, 59, 58, 56) are assigned as C–C stretching vibrations with PED contributions of 60, 52, 46, 34, 76, 64, 79 and 21 %, respectively. The C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 1000–750 cm^{-1} . The C–C stretching vibrations of aromatic compounds are expected in the range from 1650 to 1200 cm^{-1} . The theoretical wave numbers for B3LYP level at 1585, 1570, 1545, 1541, 1533, 1391, 1306, 1052, 1296, 1052 and 998 cm^{-1} (mode no 81, 80, 78, 77, 76, 72, 65, 55, 69, 53) are assigned as C–C stretching vibrations with PED contributions of 61, 36, 69, 58, 41, 45, 40, 53, 31 and 69 %, respectively. The C=O stretching modes are expected around 1600 to 850 cm^{-1} . The C=O stretching vibrations are computed at 1659 cm^{-1} , stretching; δ , Scissoring; ρ , rocking; β , out-of-plane defor-

mation; ω , wagging; τ , twisting; s, symmetric; as, antisymmetric. M–1 for B3LYP level, and 1679 cm^{-1} for HSEh1PBE levels. Percentage PED analysis is given in the brackets and PED contribution less than 10% is neglected.

Table 5: Vibrational Frequency Assignments of the Title Compound.

N	N (cm^{-1}) Unscaled	N (cm^{-1}) Scaled	IR Intensities	Force constants	Assignments with PED (%)
96	3250	3074	4.9186	6.8016	vCHA(97)
95	3237	3062	3.3991	6.7387	vCHA (99)
94	3215	3041	11.3095	6.6621	vCHA (97)
93	3212	3038	23.7172	6.6746	vCHA (94)
92	3204	3030	30.7404	6.6186	vCHA (87)
91	3200	3027	4.5376	6.5594	vCHA (96)
90	3196	3023	7.1918	6.5653	vCHA (86)
89	3188	3015	3.1220	6.5121	vCH (80)
88	3184	3011	11.7789	6.5026	vCH84)
87	3182	3010	5.3043	6.4725	vCHA (89)
86	3175	3003	3.1108	6.4611	vCH (84)
85	3171	2999	0.8418	6.4612	vCH (87)
84	3165	2993	0.6841	6.4288	vCH (95)
83	1754	1659	53.7228	13.3005	vO=C (76)
82	1686	1595	404.4244	10.2698	vC=C (53) + δ HC=C (16)
81	1676	1585	348.9516	11.7843	vCCA (61)
80	1660	1570	30.9754	9.9889	vC=C (19) + vCCA (36)
79	1649	1560	133.9619	10.8885	vC=C (55)
78	1634	1545	113.8118	12.424	vCCA (69)
77	1629	1541	50.0131	8.1016	vCCA (58)
76	1621	1533	26.4681	9.8053	vCCA (41) + δ CCCA (11)
75	1539	1456	12.4340	3.1253	δ HCCA (60)
74	1526	1443	13.8891	3.4060	δ HCCA (52)
73	1492	1411	32.6404	2.9953	vCCA (28)+ δ HCCA (46)
72	1471	1391	22.3459	4.0263	vCCA (45)+ δ HCCA (25)
71	1400	1324	313.3061	16.0304	vasON (78) + δ ONO (12)
70	1381	1306	258.2036	4.3298	vCCA (40)
69	1370	1296	27.4344	4.2871	vCCA (53) + δ HC=C (14)
68	1369	1295	49.0893	1.5729	δ HC=C (70)
67	1355	1282	16.4706	1.5810	δ HC=C (63)
66	1346	1273	8.9122	1.9745	vCC (29) + δ HC=C (37)
65	1330	1258	49.1069	1.6438	ρ HCCA (46)
64	1321	1249	29.8177	1.8979	vCC (10) + δ HC=C (12) + ρ HCCA (12)
63	1303	1232	7.3313	1.9718	vCC (23) + δ HCCA (23)
62	1236	1169	5.8638	1.5994	vCCA (20) + vCC (13) + δ HC=C (27) + δ HCCA (10)
61	1233	1166	23.9357	1.7645	vCCA (21) + δ HCCA (34)
60	1209	1143	23.5938	0.9986	vCCA (11) + δ HCCA (76)
59	1199	1134	22.7958	0.9772	vCCA (10) + δ HCCA (64)
58	1190	1126	1.0758	0.9180	vCCA (11) + δ HCCA (79)
57	1124	1063	129.7697	1.5137	vCCA (10) + vCC (21) + δ HCCA (11)
56	1119	1058	156.6727	1.3876	vCCA (11) + δ HCCA (21)
55	1112	1052	13.5393	1.1504	vCCA (31) + δ HCCA (27)
54	1106	1046	235.6977	1.1838	vCC (19) + δ HCCA (21)
53	1055	998	1.1878	1.4524	vCCA (69) + δ HCCA (14)
52	1043	986	41.0081	0.7500	ω HC=CC (76)
51	1035	979	2.9354	0.7352	ω HC=CC (78)
50	1016	961	1.1430	3.7441	vCCA (29) + δ CCCA (41)
49	1015	960	7.7061	3.6329	vCCA (25) + δ CCCA (39) + δ CC=C (17)
48	1002	948	0.3629	0.7505	τ HCCCA (71) + τ CCCCA (10)
47	997	943	0.0088	0.7695	τ HCCCA (63) + τ CCCCA (20)
46	987	934	0.2686	2.5421	vCC (59)
45	974	921	0.0029	0.7591	τ HCCCA (76) + τ CCCCA (11)
44	954	902	2.7715	0.7669	τ HCCCA (12) + τ HCCN (70)
43	937	886	0.0054	0.7814	τ HCCN (61) + τ HC=CC (13)
42	936	885	24.2823	2.2872	vNC (14) + δ CCCA (21)
41	934	883	0.0487	0.7263	τ HCCCA (73)
40	910	861	22.8718	0.9907	τ HC=CC (61) + β OCCC (12)
39	869	822	1.1823	1.8757	δ CCCA (28) + δ CNO (23)
38	864	817	0.3940	0.7159	τ HCCC (53) + τ HCCCA (16)
37	852	806	0.1326	0.5772	τ HCCC (10) + τ HCCCA (78)
36	834	789	32.7467	3.2672	δ ONO (33) + δ CCCA (13)
35	823	778	15.7483	0.6467	ω HCCCA(63) + β OCCN (10)
34	777	735	37.1860	0.7550	ω HCCCA (49) + τ CCCCA (10)
33	757	716	1.9017	2.3553	δ CNO (12) + δ ONO (13) + δ CC=C (24)
32	748	707	9.4367	1.2658	β OCCN (57)
31	717	678	36.9770	0.5752	ω HCCCA (23) + β OCCC (23)
30	696	658	2.0344	0.6677	ω HCCCA (14) + τ CCCCA (34)
29	688	651	20.9396	2.1043	δ CCCA (55) + δ ONO (12)
28	669	633	6.2325	0.8206	ω CCCCA (11) + β OCCC (25)
27	633	599	0.4296	1.5133	δ CCCA (80)
26	603	570	1.0982	1.4269	vCC (10) + δ CCCA (29) + δ CNO (11)
25	568	537	69.6510	1.2925	δ CCC (11) + δ CCCA (27)
24	559	529	18.0280	1.0257	δ CCCA (50)

23	528	499	2.5960	0.6748	τ CCCCA (45)
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Table 5: (Continued)

N	N (cm ⁻¹) Unscaled	N(cm ⁻¹) Scaled	IR Intensities	Force constants	Assignments with PED (%)
22	515	487	0.7856	0.8282	δ CNO (66)
21	498	471	7.3447	0.4217	β CCCC (63)
20	438	414	0.0543	0.3713	β CCCC (13) + τ CCCCA (54)
19	427	404	5.0972	0.6730	ν NC (16) + δ CCC (27)
18	413	391	0.0202	0.2922	τ HCCCCA (21) + τ CCCCA (73)
17	379	358	6.1811	0.6139	ν NC (29) + δ ONO (12) + δ CCCCA (11)
16	294	278	0.6106	0.3420	δ CC=C (62)
15	288	272	1.6970	0.1522	τ CCCCA (55)
14	284	269	0.0593	0.1562	τ CCCCA (34) + τ CC=CC (35)
13	272	257	4.2743	0.3510	δ CCCCA (65)
12	198	187	2.4883	0.1607	δ CCC (51)
11	187	177	0.0001	0.0511	τ C=CCC (77)
10	173	164	1.2501	0.0894	τ CCCCA (77)
09	165	156	0.2678	0.1090	ν CC (32) + δ CC=C (37)
08	104	98	0.9337	0.0336	τ C=CCC (49) + τ CCCCA (13)
07	94	89	0.6286	0.0347	δ CC=C (80)
06	83	79	0.1244	0.0198	τ CCCCA (46) + τ CC=CC (26)
05	71	67	0.7493	0.0104	τ CCCCA (17) + τ C=CCC (51)
04	48	45	0.6288	0.0179	τ CCCCA (72)
03	33	31	0.1215	0.0042	δ CC=C(76)
02	20	19	0.4246	0.0011	τ C=CCC (11) + τ CCCCA (62)
01	12	11	0.0476	0.0007	τ CCCCA (80)

Table 6: Thermo Dynamical Parameters of Title Compound Calculated at B3LYP/6-31G (D, P)

Parameters	Value	Parameters	Value
μ (D)	7.21	HOMO (eV)	-6.46
I	6.46	LUMO (eV)	-2.71
A	2.71	ΔE (eV)	3.76
χ	4.59	Zero-point vibrational energy (J/Mol)	935.70
μ	4.59	Zero-point correction (hated/particle)	0.26
η	1.88	Thermal correction to energy	0.28
S	0.94	Thermal correction to enthalpy	0.28
ω	5.60	Thermal correction to Gibbs free Ennery	0.21

Table 7: Calculated Absorption Wavelength λ (Nm), Excitation Energies E (Ev) and Oscillator Strengths (F) of the Title Compound Using TD-DFT/B3LYP/6-31G (D, P) Basis Set.

Wavelength λ (nm)	361.88	333.68
Excitation energy (eV)	3.4261	3.7157
Oscillator strengths (f)	0.4519	0.2275
Major contributions	HOMO→LUMO (97%)	H-2→LUMO (13%) H-2→L+1 (27%)
Minor contribution	H-2→LUMO (2%)	HOMO→L+1 (55%) H-4→LUMO (2%)

Table 8: Atomic Charges of the Title Compound

Atoms	Mulliken	NPA	APT	Atoms	Mulliken	NPA	APT
C1	0.110	-0.075	-0.017	N1	0.391	0.514	1.237
C2	-0.131	-0.185	-0.030	O1	-0.392	-0.378	-0.650
C3	0.236	0.057	-0.100	O2	-0.393	-0.380	-0.685
C4	-0.083	-0.206	-0.057	O3	-0.500	-0.570	-0.859
C5	-0.101	-0.231	-0.078	H2	0.144	0.276	0.109
C6	-0.089	-0.178	-0.019	H4	0.141	0.276	0.105
C7	-0.082	-0.156	0.300	H5	0.108	0.253	0.027
C8	-0.146	-0.292	-0.599	H6	0.099	0.243	0.046
C9	0.408	0.493	1.527	H7	0.129	0.259	0.064
C10	-0.146	-0.316	-0.757	H8	0.081	0.222	0.027
C11	-0.090	-0.134	0.491	H10	0.079	0.222	0.026
C12	0.127	-0.089	-0.145	H11	0.122	0.253	0.057
C13	-0.108	-0.199	-0.028	H13	0.086	0.236	0.034
C14	-0.089	-0.235	-0.070	H14	0.093	0.243	0.015
C15	-0.078	-0.220	-0.022	H15	0.094	0.243	0.018
C16	-0.088	-0.236	-0.027	H16	0.095	0.245	0.013
C17	-0.124	-0.198	0.008	H17	0.097	0.243	0.037

The C=C stretching modes are expected around 1650 to 1100 cm⁻¹ (Clothup et al. 1990, Roeges 1994) when conjugated with a carbonyl group (Socrates 1981). The carbonyl stretching vibrations appear in the region 1750–1600 cm⁻¹. In the present case, the band calculated at 1659 cm⁻¹ with PED contribution of 76 % was assigned as the carbonyl stretching vibration, which are in well agreement with the reported values for chalcone derivatives (Alwani Zainuri et al. 2017). The NO₂ group compounds are readily identified by asymmetric and symmetric stretching bands. The

asymmetric NO₂ stretching vibrations are generally observed in the region 1570–1485 cm⁻¹, while the symmetric stretch will appear between 1370–1320 cm⁻¹ (Meislich et al. 1993). In the present compound, the strong band at 1400 cm⁻¹ by DFT method has been assigned to asymmetric stretching mode of N–O.

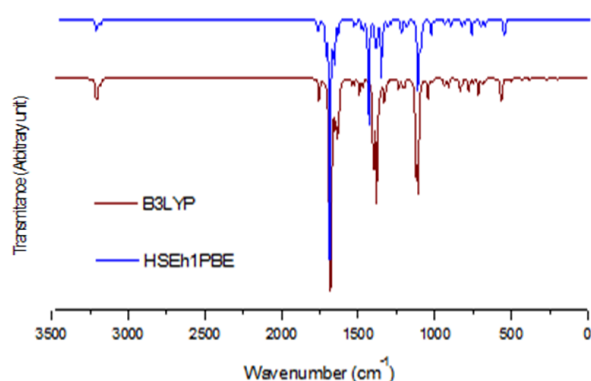


Fig. 4: The Calculated Infrared Spectra of the Title Compound.

3.7. Global reactivity descriptors and thermodynamic parameters

Energies of frontier molecular orbitals (E_{HOMO} , E_{LUMO}), have been used to calculate global chemical reactivity descriptors of compounds such as ionization potential, electron affinity, electronegativity, Global hardness, global softness, chemical potential and electrophilicity index. The calculated HOMO–LUMO energies, Energy gap are presented in Table 6. The Ionization potential (I) and an electron affinity (A) of the title compound calculated by B3LYP and HSEh1PBE levels are 6.4639, 6.3551 eV and 2.7072, 2.9543 eV respectively. The calculated values of the hardness, softness, chemical potential, electronegativity and electrophilicity index of our compound at B3LYP are 1.8784, 0.9392, -4.5855, 4.5855 and 5.5973 respectively as shown in Table 6. It is seen that the chemical potential of title compound is negative which means that these substances are stable. The values of some thermodynamic parameters of the title compound calculated using B3LYP/6- and 31G (d,p) HSEh1PBE/6-31G (d,p) levels are summarized in Table 6.

3.8. Electronic properties and UV spectra

In order to recognize electronic transitions of the title compound, calculations in gas phase were performed by using TD-DFT/B3LYP/631G (d,p) for six excited states. The calculated absorption wavelengths (λ), oscillator strengths (f), and excitation energies (E) are given Table 7. The theoretical UV–Vis spectra of the title compound are shown in Fig 5. The calculated value at 361.88 nm is attributed to HOMO→LUMO electronic transition with 97% contribution. The electronic transitions is due to $n \rightarrow \pi^*$ transition and may be attributed to the excitation of C=O group. Gauss–Sum 2.2 program was used to calculate group contributions to the molecular orbitals and prepare the density of states spectrum in Fig. 5.

3.9. Mulliken population analysis and natural population analysis

The calculated Mulliken charge values are listed in Table 8. The better represented graphical forms of our results were depicted in Fig. 6. The magnitude of the carbon atomic charge is found to be positive and negative. The magnitude of the hydrogen atomic charges is found to be only positive and is arranged in an order from 0.079012 to 0.144755 for title compound. The maximum atomic charge is obtained for C9 when compared with other atoms. This is due to the attachment of negatively charged carbon C9 atom. Negatively charged lone pair oxygen (O3) atom shows that charge is transferred from C to O ($C9 \rightarrow O3$).

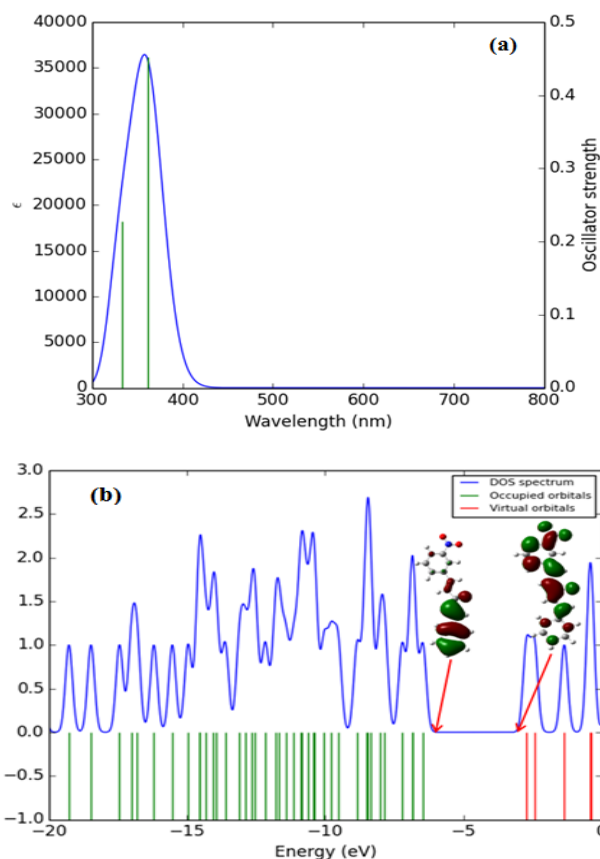


Fig. 5: Theoretical UV-Vis Spectrum (A) and Density of States (DOS) Diagram (B) of the Title Compound

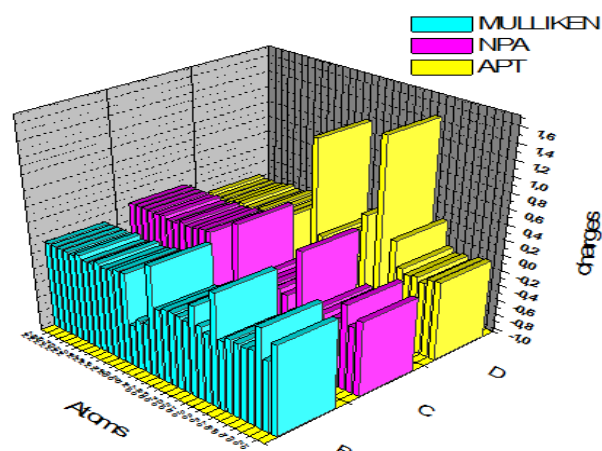


Fig. 6: The Mulliken Charges Diagram of the Title Compound.

4. Conclusion

The optimized geometrical parameters of title compound were performed and analyzed using DFT calculation based on B3LYP and HSEh1PBE levels of theory with the standard basis set 6-31G (d, p). The vibrational wavenumbers, infrared intensities and force constants were calculated and a complete vibrational analysis of the title compound has been carried out. The dipole moment, polarizability and first order hyperpolarizability of the studied compound have been calculated by DFT method which indicated that the title compound is a material which has substantial nonlinear optical character. The frontier molecular orbitals have been visualized and the HOMO–LUMO energy gap has been calculated and can be used to estimate the ionization potential, electron affinity, electronegativity, electrophilicity index, global hardness, softness and chemical potential of the compound. Finally, all these results displayed that the title compound exhibits considerable NLO properties.

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