

Quantum chemical, spectroscopic and third order nonlinear optical investigations on 3-(3-bromophenyl)-1-imidazol-1-yl-propenone

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Imidazole is a five-membered heterocyclic moiety that possesses three carbon, two nitrogen, four hydrogen atoms, and two double bonds. It contains two nitrogen atoms, in which one nitrogen bears a hydrogen atom, and the other is called pyrrole type nitrogen. Due to the presence of a positive charge on either of two nitrogen atom, it shows two equivalent tautomeric forms. Among the different heterocyclic compounds, imidazole is better known due to its broad range of chemical and biological properties. Imidazole has become an important synthon in the development of new drugs. In this study, 3-(3-bromophenyl)-1-imidazol-1-yl-propenone have been prepared and characterized in a systematic manner. For synthesised molecule, atomic charges, frontier orbital energies and the thermodynamic properties have been calculated with theoretical Density Functional method. The synthesised molecule has been subjected to NMR, FTIR and UV analysis. The molecule shows interesting nonlinear optical (NLO) properties by the Z-scan technique. This study evokes the interest of researchers regarding the development of imidazole based tempting NLO compounds that could be beneficial in modern hi-tech applications.

Keywords: Imidazole, DFT, FTIR, nonlinear optics

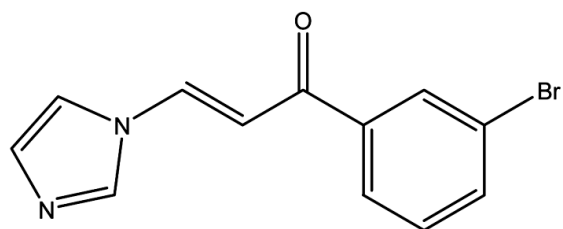
Azole compounds are an important class of nitrogen heterocycles with electron-rich property. This special structure endows azole-based derivatives easily bind with the enzymes and receptors in organisms through noncovalent interactions such as hydrogen bonds, coordination bonds, ion-dipole, cation- π , π - π stacking and hydrophobic effect as well as van der Waals force, thereby possessing various applications. The development of derivatives based on heterocyclic scaffolds is a fast emerging subject in medicinal chemistry. Azole compounds in particular play a remarkably important role in the field of medicinal chemistry. A great deal of azole-based antibacterial and antifungal agents have been extensively studied as drug candidates, and some of them have been used in the clinic, for instance itraconazole, fluconazole, Posaconazole and voriconazole, which suggests the great development value of azole compounds¹.

The development of second-order nonlinear optical chromophores is an exciting discipline with emerging applications including electro-optic modulators, optical data storage devices, telecommunications and optical switches². In particular, organic chromophores containing a donor- π -acceptor system show effective

intramolecular charge transfer from the donor to the acceptor, leading to a dipolar push-pull structure featuring low-energy and intense charge transfer absorptions³. The polarizability and the linear and nonlinear optical properties of these systems depend on their chemical structure, on the electronic behaviour of the appended donors and acceptors, and on the length of the π -conjugated linker⁴.

The use of heteroaromatic scaffolds, as π -backbones in NLO active chromophores, provides high chemical and thermal robustness. In addition, they may act as auxiliary donors or acceptors, improving the optical nonlinearity of the chromophores⁵. Among them, imidazole moieties have been incorporated in chromophore systems as strong electron acceptors because of their high electron deficiency originating from two asymmetric nitrogen atoms that lower the π^* level of the conjugated system⁶. Among the different heterocyclic compounds, imidazole is better known due to its broad range of chemical and biological properties.

A detailed literature survey has revealed that the synthesised molecules have neither been reported nor efficiently investigated in terms of NLO response



3-(3-Bromo-phenyl)-1-imidazol-1-yl-propenone

Scheme 1 — Structure of 3-(3-Bromophenyl)-1-imidazol-1-yl-propenone

so far. Therefore, an exclusive computational investigation has been done to explore their NLO response parameters through various DFT-based analyses. So, the present DFT calculations provide a detailed account of the electronic structure, electronic transitions, molecular surfaces, global reactivity descriptors, natural population, and NLO response. Furthermore, the synthesised molecule 3-(3-bromophenyl)-1-imidazol-1-yl-propenone (Scheme 1) is subjected to various experimental analysis to understand the various properties of the molecule.

Methods and Materials

Experimental Section

Characterization techniques

In order to confirm the chemical structure, the ^1H NMR and ^{13}C NMR spectra were recorded by employing a Bruker 500 MHz spectrometer in deuterated solvents using DMSO (dimethyl sulfoxide- d_6) as the internal reference standard. In the present work, functional group was identified using a JASCO-FT-IR 5300 infrared spectrometer in the frequency region of $400\text{--}4000\text{ cm}^{-1}$ by employing the KBr pellet technique with a spectral resolution of 4.0 cm^{-1} . Optical absorption spectrum were recorded at room temperature using a Perkin-Elmer Lambda 35 Spectrophotometer in the wavelength region of $200\text{--}850\text{ nm}$. The theoretical quantum chemical studies were performed at DFT-B3LYP (Becke's three-parameter (B3) exchange in conjunction with the Lee-Yang-Parr's (LYP) correlation functional) method with 6-31++G (d,p) basis set using Gaussian 09 program⁷⁻⁹. The molecular structure was optimized from crystallographic information file (CIF) as source and all calculations were computed by this optimized structure only. GaussView 5.0 visualization program has been employed to shape HOMO, LUMO orbitals¹⁰.

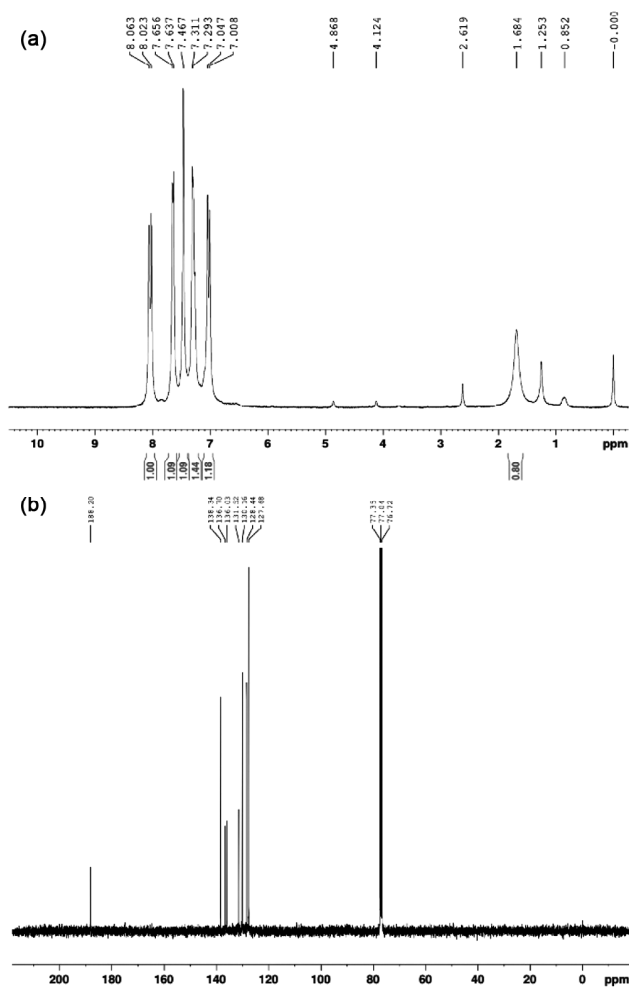
Results and Discussion

NMR Spectral Analysis

Nuclear magnetic resonance (NMR) is a versatile technique employed to identify the molecular structure. The ^1H NMR and ^{13}C NMR spectra of title molecule were recorded using DMSO as solvent. The recorded ^1H and ^{13}C NMR spectra are shown in Fig. 1a and b, respectively. In the ^1H NMR spectrum, the appearance of 11 distinct proton signals confirms the formation of the crystal. The signals at δ 8.063 and 8.023 ppm are due to the CH proton of the Bromophenyl moiety. The peaks centered at δ 7.656 and 7.637 ppm are assigned to the CH proton of imidazole moiety. The centered at δ 7.467 ppm owes to the proton of -N-CH- molecular group. The CH aromatic proton signals appeared at δ 7.311 and 7.293 ppm. The signals at δ 7.047 and 7.008 ppm are due to the proton of the propene moiety. The signals observed at δ 1.684 and 1.253 ppm represents the protons due to methine group of the molecule. The appearance of carbon signals in the spectrum explicitly confirms the molecular structure of the complex. The carbon signal at δ 188.2 ppm owes to the highly deshielded carboxyl carbon atoms of the molecule. The carbon signal at δ 138.3 ppm is attributed to the carbon in the aromatic ring. The carbon signal at δ 136.7 ppm is attributed to the carbon of the -N-CH- molecular group. The carbon signal at δ 136.0 ppm is due to the carbon of the imidazole moiety in the molecule. The signal at δ 131.5 ppm owes to the carbon of the alkylbenzene group. The carbon signal at δ 130.1 ppm is attributed to the carbon in the alkene functional group. The carbon signal at δ 128.4 ppm is due to the carbon in the aromatic ring. The methine group carbon signal observed at δ 127.7 ppm is attributed to the carbon in the aromatic ring. The carbon signals about δ 77 ppm is due to the carbon of the bromophenyl moiety in the molecule. Thus, the molecular structure of complex stands confirmed from the ^1H and ^{13}C NMR spectral data.

FTIR measurements

The well assignment of the bands, observed in the vibrational spectra is an indispensable step for solving the structural problems of any molecule. The IR spectrum of title molecule in the region $4000\text{--}400\text{ cm}^{-1}$ is shown graphically in Fig. 2 and the corresponding vibrational wavenumbers are given in Table 1. The details of the various vibrations and their assignments are discussed in the subsequent sections. The absorption band appearing at 2922 cm^{-1} is due to

Fig. 1 — (a) ^1H and (b) ^{13}C NMR spectrum of the compound

aromatic C-H stretching vibration of the molecule. The sharp absorption band at 2858 cm^{-1} is due to the aliphatic C-H stretching vibration. The $\text{C}=\text{C}$ stretching vibration of propene moiety is observed at 1653 cm^{-1} . The $\text{C}=\text{C}$ stretching vibration of benzene appears at 1585 cm^{-1} . The band at 1463 cm^{-1} is due to the C-N asymmetric stretching vibration of the molecule. For imidazole moiety, the C-N symmetric stretching vibration is observed at 1384 cm^{-1} . The C-H scissoring vibration of aliphatic group of the molecule is observed at 1330 cm^{-1} . The scissoring vibration of aromatic ring is observed at 1188 cm^{-1} . The band at 1103 cm^{-1} is due to the benzene ring stretching vibration of the molecule. The C-H scissoring vibration of imidazole moiety is observed at 1037 cm^{-1} . The C-H wagging vibration of bromophenyl group is observed at 995 cm^{-1} . The peak at 775 cm^{-1} is assigned to CH wagging vibration.

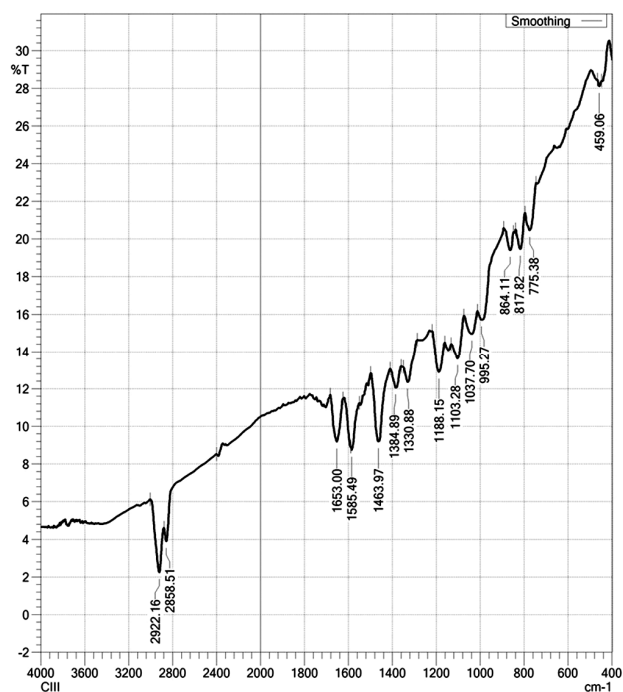


Fig. 2 — FT-IR Spectrum of the compound

Table 1 — Comparative FT-IR and Raman analysis

FTIR	Vibrational Analysis	Raman
2922	CH stretching of aromatic ring	3083
2858	CH stretching	3036
1653	C=C vib of Propene moiety	1646
		1620
1585	C=C vib of benzene ring	1588
1463	CN asymmetry Stretch	1470
1384	CN symmetry Stretch	1339
		1313
1330	CH sis aliphatic group	1281
1188	CH sis of aromatic ring	1142
1103	Benzene ring stretching vibration	
1037	CH Sis of imidazole moiety	1108
995	CH wagging of Bromo phenyl	
775	CH Wagging	775
459	c-c wagging of Propene moiety	
	Asymmetric bending of Benzene ring	645

The peak appeared at 459 cm^{-1} is assigned to C-C wagging vibration of propene moiety of the molecule.

Raman Spectroscopy

The title molecule was also subjected to Raman spectroscopy (Fig. 3). The observed frequency for the molecule is listed in the Table 1 and shown in the Fig. The peak observed at 3083 cm^{-1} is attributed to

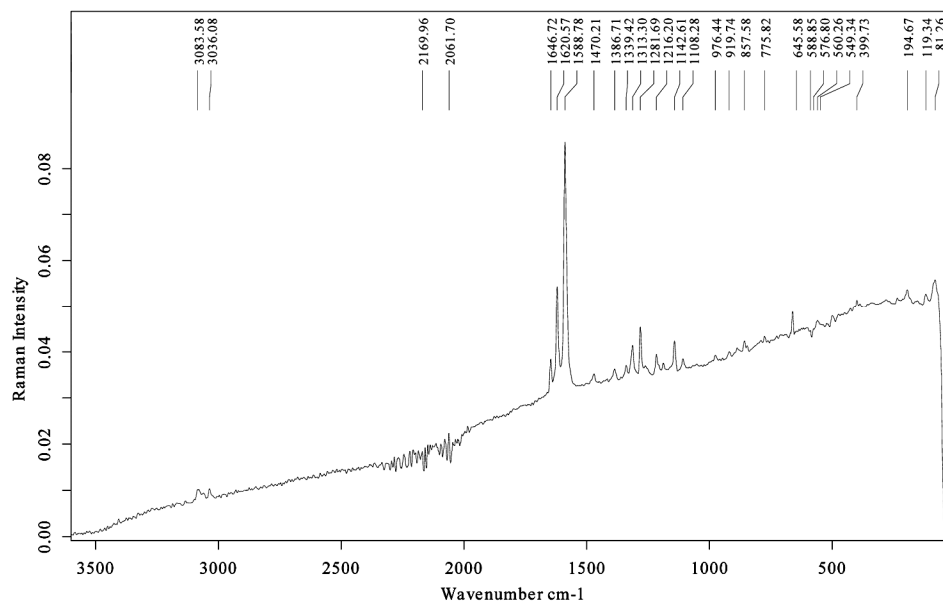


Fig. 3 — FT-Raman spectra of 3-(3-Bromophenyl)-1-imidazol-1-yl-propenone

aromatic C-H stretching vibration of the molecule. The band at 3036 cm^{-1} is attributed to the aliphatic C-H stretching vibration. The bands at 1646 and 1620 cm^{-1} are due to C=C stretching vibration of the propene moiety. The C=C stretching vibration of benzene ring appears at 1588 cm^{-1} in the Raman spectrum. The band at 1470 cm^{-1} is assigned to the C-N asymmetry stretching vibration of imidazole. The C-N symmetry stretching vibration is observed at 1336 cm^{-1} . The Raman C-H scissoring vibration of aliphatic group is observed at 1281 cm^{-1} . The C-H scissoring vibration of aromatic ring is observed at 1142 cm^{-1} . The peak at 775 cm^{-1} is assigned to C-H wagging vibration. The peak at 645 cm^{-1} is due to asymmetric bending vibration of the benzene ring.

UV Absorption Studies

The UV-Vis-NIR spectral analysis is carried out on the material to study linear optical characteristics of the material. Ultra violet and visible radiation interacts with matter which causes electron transitions from the ground to a high energy state. UV absorption spectra arise from the transition of electrons within a molecule from a lower electronic energy level to a higher one. Three distinct types of electrons are involved in organic molecules such as the σ -electrons (involved in saturated bonds), the π -electrons (involved in bonding between the atoms in molecules and in the electrons which can be excited by UV radiation). When an atom or molecule absorbs the

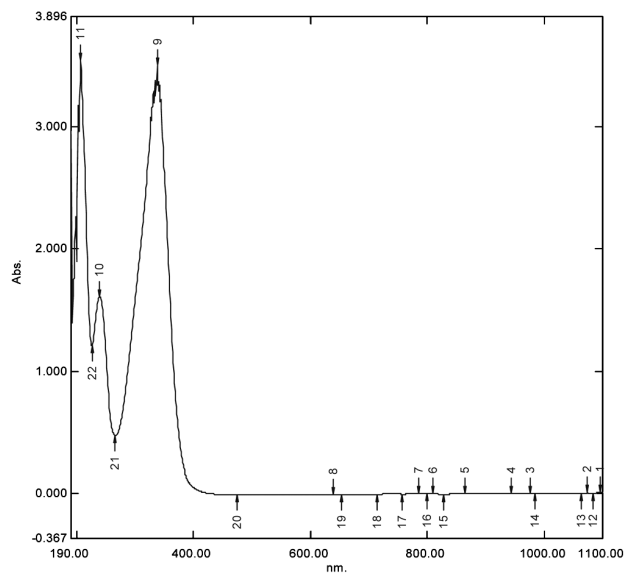


Fig. 4 — Optical absorption spectrum

energy, electrons are promoted from their ground state to an excited state¹¹. The absorption spectra of title molecule was recorded in methanol (MeOH) solvent and obtained spectrum are displayed in Fig. 4. The UV-vis spectrum of the molecule shows a weaker absorption band at 239 nm and a maximum absorption peak at 338 nm . The latter absorption peak is considered as the characteristic absorption peak of the 3-(3-Bromophenyl)-1-imidazol-1-yl-propenone. These observed peaks are due to π - π^* and n - π^* transition of 3-(3-Bromophenyl)-1-imidazol-1-yl-

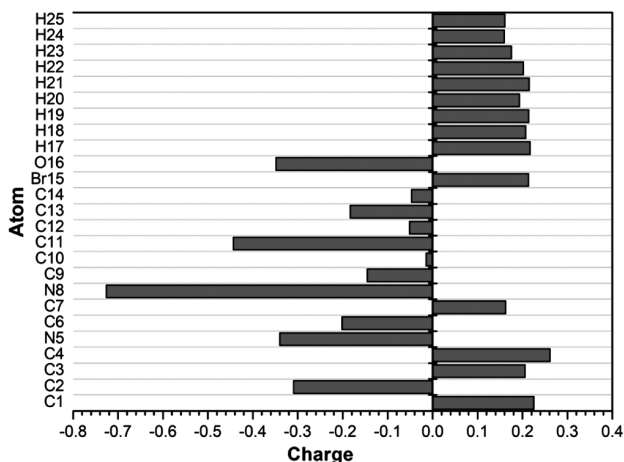


Fig. 5 — Mulliken charge distribution analysis

propenone molecule. From the spectrum, it is clear that UV cut-off wavelength of grown crystal is noted at 340 nm for the title molecule.

Mulliken Atomic Charge

A major function for the application of quantum chemical calculation to a molecular system was the Mulliken calculation of Atomic Charges. Atomic charges depend on the dipole moment, molecular polarisation, electronic structure and many of molecular system characteristics. The charge distributions over the atoms advocate the creation, in the molecule, of donor and acceptor pairs. Fig. 5 shows the calculated Mulliken load distribution in the molecular structure. There are more negative charges for oxygen and nitrogen atoms while the positive charge is present for all hydrogen atoms. Furthermore, Mulliken atomic charges also show that the nitrogen atoms have a highest negative atomic charge in the molecule. The atomic charges variations of hydrogen atoms are formed by hydrogen bonding. The total of the atomic charge of all atoms, however, retains neutrality with regard to charge. Mulliken population analysis is a useful way for interpreting and predicting the reagent behaviours of a wide range of chemical systems for both electrophilicity and nuclear reactions to take into account the differences in electrostatics of atoms within Mulliken population methodology.

HOMO-LUMO Analysis

The highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are called Frontier Molecular Orbitals (FMOs) as they lie on the outermost limits of the

compound electrons. The frontier orbit gap helps to distinguish the chemical reactivity of the molecule and its kinetic stability. A small frontier orbital divide molecule is commonly referred to as the soft molecule and has high chemical reactivity and low kinetic stability¹². Furthermore, FMOs are important to determine a molecule's capacity for light absorption. In the optical, electrical as well as in quantum chemical applications, FMOs play an important role. HOMO-LUMO energy gap characterizes electron acceptance capacity. In interacting molecular orbitals, the two interacting are the molecular orbital (HOMO), usually of the highest energy, and the compound's lowest non occupied molecular orbital (LUMO). These orbitals are a pair of compound orbitals that allow them to interact stronger. The calculation was carried out in the gas phase, in order to assess the energetic behaviour of the title compound. Figure shows that the molecule will eventually transfer charges. The HOMO value is calculated at -0.25923 eV and LUMO is at -0.10306 eV. The HOMO and LUMO energy separation is 0.15617 eV. The transmission of energy between the HOMO and LUMO makes the material intramolecular charging active.

The energy gap value also helps us identify a molecule's chemical reactivity and kinetic stability. A small molecule band gap energy is usually associated with high chemical reactivity and low film stability. In determining biochemical pathways for electron transfer, photosynthesis, oxidative phosphorylation and oxidative stress, the energy ionisation (I) and electron affinity (A) are of great importance. The energy of ionisation is directly proportional to the compound electrochemical oxidation potential. An idea of the stability of free radicals and anions is the electron affinity. By the theorem of Koopmans¹³ $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$ can express energy and electrons affinity by means of orbital energies HOMO and LUMO. From the value of ionization energy and electron affinity, Mulliken electronegativity (χ) can be calculated from the equation $\chi = (I+A)/2$. The chemical potential (μ) is the negative value of the electronegativity. Softness (S) is a property of the molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness ($S = 1/2\eta$). The hardness is calculated using the expression $\eta = (I-A)/2$ ¹⁴. Parr *et al.* have proposed the global electrophilicity power of a system¹⁵. This index measures the stabilization in energy when the system acquires an additional electronic charge from the environment. The values of electronegativity, chemical hardness, softness,

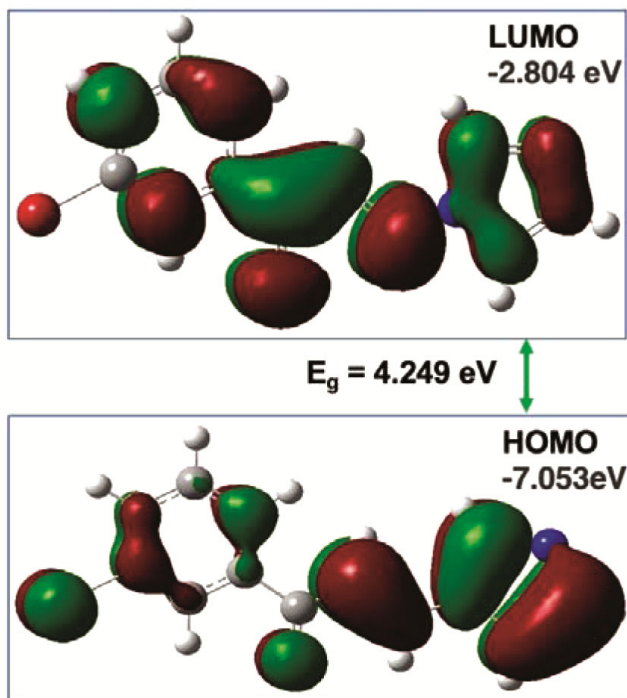


Fig. 6 — HOMO-LUMO analysis

and electrophilicity index of the title molecule are 0.1811 eV, 0.07808 eV, 6.4032 eV, and 0.2101 eV in gas phase, respectively (Fig. 6).

Z-scan

Z-scan technique is common technique for measuring both the non-linear (n_2) and the non-linear $\chi^{(3)}$ ¹⁶ refractive index. The sample was moved through the axial direction through a focal area ($-Z$ to $+Z$) which is the direction of laser beam propagation. The intensity dependent absorption of the material was measured when the sample was moved through the focus and without placing the open aperture on the detector. By monitoring the transformation through a small aperture at the far field position (closed aperture), the amplitude of the phase shift is measured carefully. The open and closed aperture measurements of the standard transmission (T) are shown in Fig. 7a and b. From the following relation, the value of $\chi^{(3)}$ was calculated.

$$|\chi^{(3)}| = [(Re\chi^{(3)})^2 + (Im\chi^{(3)})^2]^{\frac{1}{2}}$$

The estimated nonlinear refractive index (n_2), nonlinear absorption coefficient and third order susceptibility values of single crystal was $0.754 \times 10^{-7} \text{ cm}^2/\text{W}$, $2.883 \times 10^{-4} \text{ cm/W}$ and $2.704 \times 10^{-7} \text{ esu}$

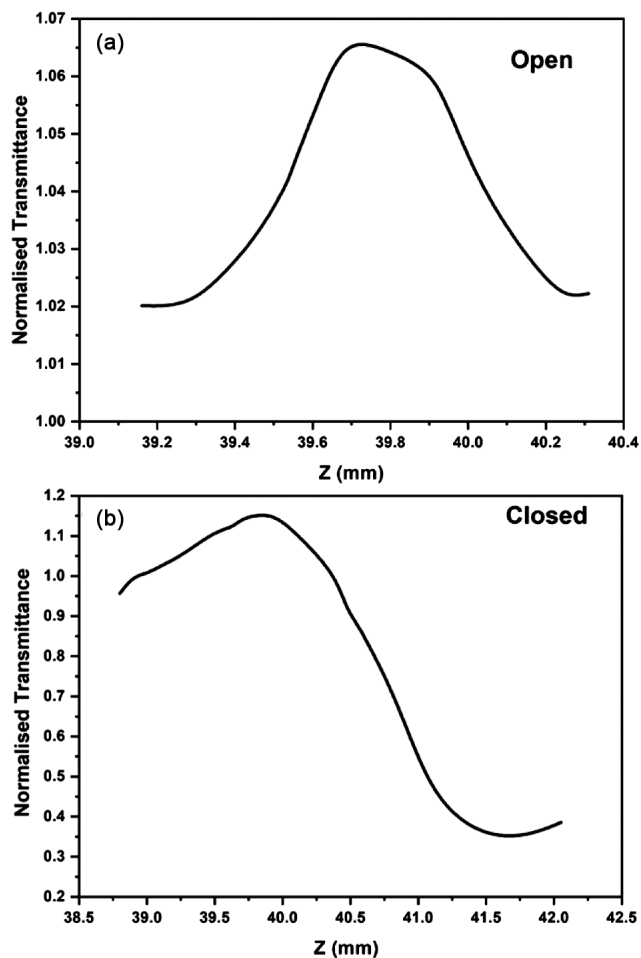


Fig. 7 — (a) Open and (b) closed aperture spectrum of Z-scan measurements

indicates that the material reveals a positive refractive index. It leads to self-focused nature and displays a process of two-photon crystal absorbance. This is one of the most important parameters for optical limits.

Thermodynamic properties

The density functional methods set at B3LYP/6-311++G are used to calculate thermodynamic characteristics of the title molecule. Based on the vibrational analysis, the theoretical harmonic frequencies were used to calculate the Zero Point Vibrational Energy, heat capacities, entropy and rotational constants for the title compound. Several thermodynamic properties such as Zero Point Vibrational Energy and C_V can be used in the calculation of other thermodynamic energy sources and estimating the direction of chemical reactions according to the thermodynamic functional relations and the use of second law of thermodynamics. The calculated

Table 2 — Thermodynamical parameters

Self-consistent field Energy (a.u.)		-3221.3134
Zero point energy (Kcal/Mol)		116.41137
Rotational constant(GHZ)		1.59360
Rotational temperature (Kelvin)		0.07648
Energy (E) (KCal/Mol)	Translational	0.889
	Rotational	0.889
	Vibrational	123.168
	Total	124.945
Specific heat (C _v) (Cal/ Mol-Kelvin)	Translational	2.981
	Rotational	2.981
	Vibrational	44.311
	Total	50.273
Entropy(S) (Cal/ Mol-Kelvin)	Translational	42.744
	Rotational	34.035
	Vibrational	47.179
	Total	123.958
Dipole moment (Debye)		1.7071

thermodynamic properties are listed in Table 2. The molecule has Zero Point Vibrational Energy as 116.41137 kcal mol⁻¹, heat capacity as 50.273 cal mol⁻¹K⁻¹, entropy as 123.958 cal/mol-K and total thermal energy as 124.945 k cal mol⁻¹. These thermodynamic data may provide useful information for the further study on the title compound.

Conclusion

An experimental and theoretical spectroscopic study concerning the structure of 3-(3-Bromophenyl)-1-imidazol-1-yl-propenone has been performed. The efficient electron withdrawing acceptors are utilized for their structural tailoring, which strengthened the charge transfer phenomena. Different spectroscopic techniques, UV-visible, FTIR, and ¹H and ¹³C NMR, are utilized for the determination of structural characterization. Besides the synthesis, a computational study was also performed in order to explore the chemical and optical characteristics. The synthesised molecular structure was confirmed with NMR spectra. The UV-vis spectrum of the molecule shows a weaker absorption band at 239 nm and a maximum absorption peak at 338 nm. Mulliken atomic charge analysis confirmed that there are more negative charges for oxygen and nitrogen

atoms while the positive charge is present for all hydrogen atoms. The HOMO and LUMO energy separation of the molecule is 0.15617 eV. Z-Scan study leads to self-focused nature and displays a process of two-photon crystal absorbance of the synthesised molecule.

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