Structural and NLO Properties of Novel Organic 4-Bromo-4-Nitrostilbene Crystal: Experimental and DFT Study

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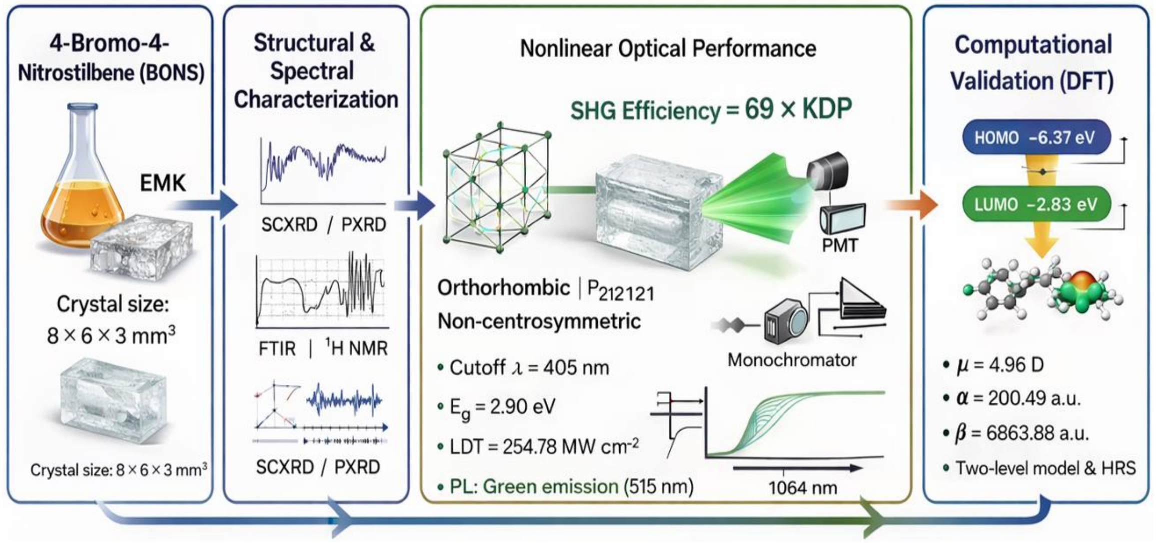
Abstract

A new organic nonlinear optical single crystal of 4-Bromo-4-Nitrostilbene (BONS) was synthesized and high quality single crystals of size 8 × 6 × 3 mm^3 grown from the solvent ethyl methyl ketone (EMK) by the slow evaporation method. Single crystal X-ray diffraction study confirmed the orthorhombic character of BONS with the space group $P2_12_12_1$, a prerequisite for second harmonic generation. Powder X-ray diffraction study further confirmed the grown crystal's crystallinity and purity. Functional group and bond characterization was done by the FTIR study while the ^1H NMR study confirmed the proton surroundings of the grown molecule. Optical transmittance study by the use of the UV-Vis spectrum showed the threshold wavelength of 405 nm and the band gap of 2.90 eV. Vickers micro-hardness test was used to determine the mechanical stability of the grown crystal while the laser damage threshold of the grown crystal was analyzed by the use of the Nd: YAG laser. The result showed a strong green emission of 515.44 nm. The nonlinear optical efficiency of the grown molecule was analyzed by the use of the Kurtz and Perry method and showed a high efficiency of about 69 times more than the KDP crystal. Density functional theory study was done to confirm the electronic and molecular geometry of the grown molecule's nonlinear optical properties. The result indicated a high charge transfer character of the molecule, hence the high nonlinear optical efficiency. The study indicated a high reliability of the DFT study and hence the molecule can very likely be used for nonlinear optical and optoeletronic applications.

Keywords: Organic compound; Crystal growth; Nonlinear optical materials; DFT

Graphical Abstract



Comprehensive Experimental and DFT Investigation of Structural, Spectral, Mechanical, and Nonlinear Optical Properties of a Novel Organic Crystal: 4-Bromo-4-Nitrostilbene (BONS)

Introduction

In recent years, the fast development of photonic and optoelectronic technology has been associated with an increased need for new nonlinear optical materials with higher efficiency, stability, and fast response properties. These materials are very important for a variety of applications, such as optical switching, frequency conversion, signal modulation, laser technology, and data storage. While the development of nonlinear optical materials based on inorganic materials has been very active, the lower nonlinear coefficients, lack of tunability, and difficult fabrication processes have pushed researchers to investigate new materials with higher properties [1].

Under these circumstances, organic nonlinear optical materials have recently gained immense interest as promising candidates owing to their high inherent optical susceptibilities, ultrafast electronic response times, flexibility, and high resistance to laser-induced damage. Second-order nonlinear optical effects are dominated in organic materials by delocalized π-electron systems that enable effective intra-molecular charge transfer. Molecules with high conjugation, D-π-A geometry, and highly electron-withdrawing or electron-donating groups are usually highly polarizable and hyper polarizable molecules whose effects directly translate into the second-order nonlinear optical properties [2].

From various organic NLO chromophores, stilbene derivatives have been of particular interest, mainly due to their advantageous molecular planarity, robust π-conjugation, high optical clarity, and efficient green light emission properties. Some stilbene derivatives, including DAST, DSNS, and MMONS, have been found to possess outstanding second-harmonic generation (SHG) conversion efficiency and crystalline stability. Notably, substituted nitro stilbenes are most prominently studied, as electron withdrawal offered by nitro substituents in these stilbenes has been found to result in increased charge transfer along the stilbene molecule, thereby leading to improved second-harmonic generation efficiency [3].

One of the most efficient strategies to increase macroscopic NLO response is to design molecules with a preference for a no centrosymmetric packing arrangement. While most organic molecules demonstrate a large molecular hyperpolarizability, a centrosymmetric crystal packing arrangement can limit their NLO response. Therefore, molecular design efforts to align molecules in an optimal head-to-tail fashion and adopt a no centrosymmetric packing arrangement remain crucial for demonstrating efficient macroscopic NLO materials. A substituent approach, particularly with halogen elements, has been an effective strategy to modulate intermolecular interactions, crystal symmetry, and optical properties [4].

Therefore, in this context, 4-Bromo-4-Nitrostilbene (BONS) acts as one of the most promising organic NLO materials, in which the concurrent presence of a strong electron withdrawing nitro functionality and a bromo functionality simultaneously increases the intramolecular charge transfer properties as well as the growth of no centrosymmetric crystals. The presence of the bromo atom not only alters the electronic properties of the molecule, which influences the charge transfer properties, but also helps in the stabilization of the crystal lattice through intermolecular forces, thus simultaneously imparting the required optical and mechanical properties for optoelectronic devices [5].

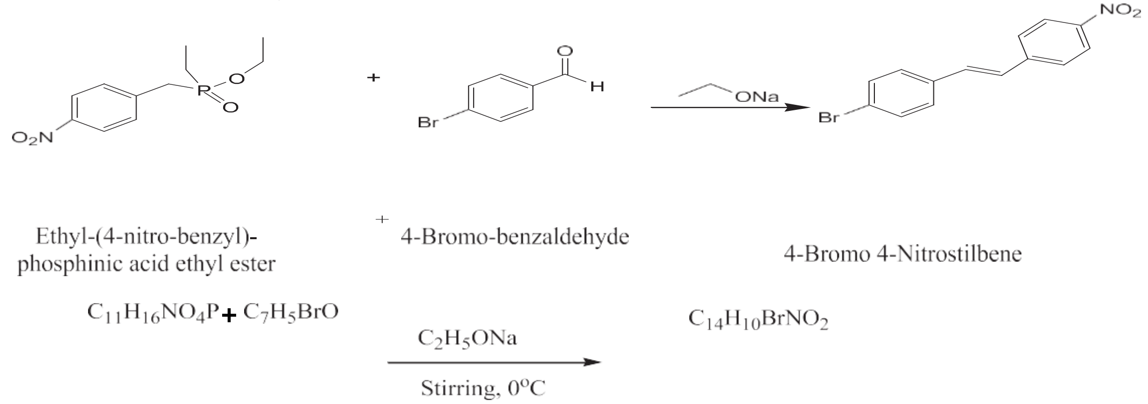
Even as the synthesis and characterization studies offer proof by example, the computational studies offer an important complement in elucidating the underlying reason for the occurrence of the nonlinear optical phenomenon at the molecular level. With the development of density functional theory (DFT) calculations, it has become an essential task to explore the relationship between the structure and the associated electronic, optical, and second-order nonlinear properties. By a calculational approach, an interrogation of parameters such as optimized geometry, frontier molecular orbital, band-gap energy, polarizability, and hyperpolarizability can be made. Further, the two-level approach and hyper-Rayleigh scattering calculate the second-order nonlinear optical susceptibility and establish a clear chemical linkage between the microscopic electronic transitions and the second-harmonic generation [6].

The integration of experimental data with the predictions of molecular calculations opens up the possibility of carrying out a more reliable analysis of structure-property correlations and enhances the validation of newly synthesized NLO materials. For stilbene-based molecules such as those in the BONS series, molecular calculations provide valuable clues on the influence of substituents on charge transfer, electronic delocalization, and nonlinear susceptibilities, and hence on the analysis of SHG response data and optical transparency values [7].

In the current research, a thorough experimental and computational investigation of 4-Bromo-4-Nitrostilbene, commonly referred to as BONS, is performed. This includes material synthesis, single crystal growth via slow evaporation, and a thorough investigation of structural, spectral, optical, thermal, mechanical, and NLO properties, while on the other hand, density functional theory calculations are used for an examination of electronic structure, polarizability, first hyperpolarizability, and NLO behaviors via DFT calculations. Through a strong correlation between experimental results and computational observations, it seems that BONS exhibits a high potential for use as an efficient NLO material for optoelectronics and photonics applications.

Experimental Methodology

High-quality single crystals of 4-Bromo-4-Nitrostilbene (BONS) were grown using the slow evaporation method. BONS was prepared in the laboratory using the base-catalysed condensation method with an equimolar quantity of high-quality diethyl p-nitro benzyl phosphonate and 4-bromobenzaldehyde in the presence of sodium ethoxide as the catalyst in an ethanol medium. A constant stirring of the reaction mixture was performed in an ice bath using a temperature-controlled water bath to regulate the temperature. Once the process was completed, the solvent was removed, and the crude BONS was purified using the recrystallization method. The purified BONS sample was further dissolved in ethyl methyl ketone (EMK) resulting in the formation of a saturated solution. This was filtered using a Whatman filter paper and left for slow evaporation. High-quality optically clear single crystals measuring 8mm × 6mm × 3mm were grown in five days. The grown BONS crystals were utilized for various experiments. These experiments include single crystal and powder X-ray diffraction analysis, FTIR and ^{1}H NMR analysis for identifying the functional groups and the molecular structure confirmation. Further analysis was conducted using UV visible spectroscopy. Solubility and band gap analysis were also undertaken. TG/DTA analysis was carried out using the TA instruments. Vickers hardness analysis was conducted using the microhardness tester. Further analysis was performed using the photoluminescence study. Finally, the laser damage threshold test was carried out using the Nd:YAG laser. Second harmonic generation was also carried out using the powder method suggested by the researcher Kurtz Perry [8, 9].



$$C11H16NO4P\ + C7H5BrO\ \frac{C2H5ONa0}{\circ\, C, stirring} \rightarrow\ C14H10BrNO2$$

Results and Discussion

Single-Crystal and Powder X-ray Diffraction Analyses

Single-crystal X-ray diffraction studies were carried out on the grown crystal of 4-Bromo-4-Nitrostilbene (BONS) using a Bruker kappa APEX diffractometer for analyzing the crystallographic dimensions and symmetry of BONS crystal. This test proved that BONS crystallizes in space group b with a noncentrosymmetric unit cell $P2_12_12_1$, a requirement for exhibiting second-order nonlinearity for a material. The refined cell dimensions for BONS were determined, given by a = 7.126(8) Å, b = 8.747(8) Å, c = 20.220(16) Å, along with a unit cell volume of V = 1260.34 Å^3. The absence of a center of symmetry for BONS helps ratify the experimental evidence of nonlinearity associated with the material.

Powder X-ray diffraction (PXRD) analysis was performed on a Bruker D8 Advance diffraction machine using Cu Kα radiation (wavelength λ = 1.5406 Å) to confirm the phase purity and crystalline structure of the prepared material. Diffraction data was collected between 2θ = 10°–35° with an interval of 0.02°. The collected PXRD data is represented in Fig. 2. The measured lattice parameters using the TREOR indexing software were found to be in an excellent match to that measured using single-crystal XRD analysis, confirming the accuracy and correctness of the data. Judging by the 2θ values, the major diffraction peaks were successfully indexed using the APPLEMAN software, verifying the correctness of the crystalline structure of the BONS crystal.

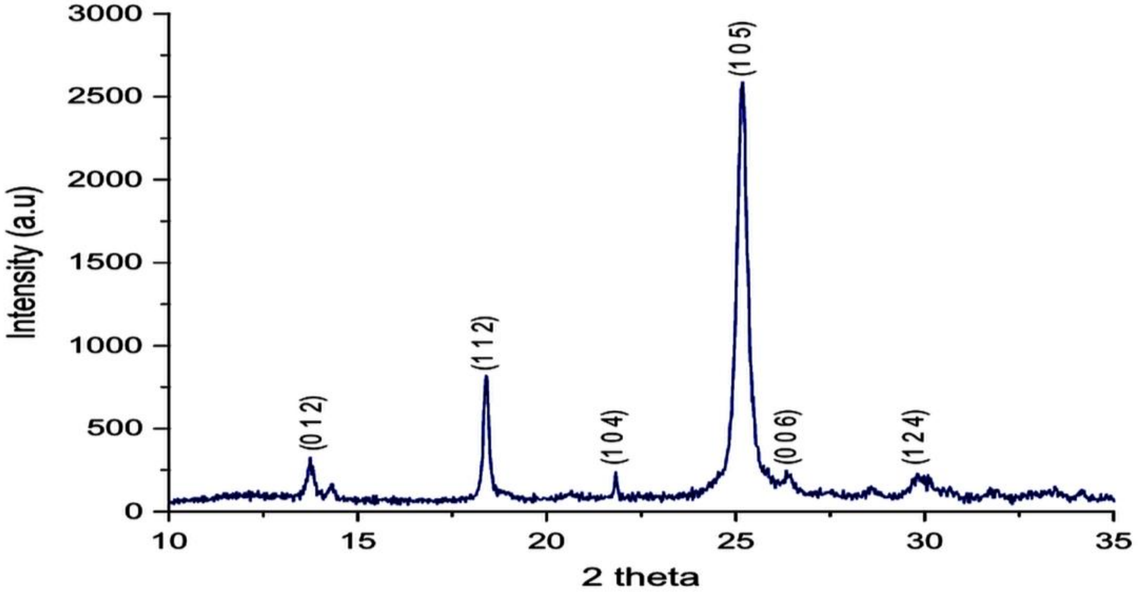


Figure 1: XRD of 4-Bromo-4-Nitrostilbene crystal

Fourier Transform Infrared (FTIR) Spectral Analysis

The Fourier transform infrared spectroscopy analysis was performed with a Shimadzu IRAffinity spectrometer to confirm the existence and identification of the functional groups in the synthesized 4-Bromo-4-Nitrostilbene crystal. The FTIR spectrum was recorded in the wavenumber region ranging from 400 to 4000 cm^{-1}, and the resulting spectrum is displayed in Fig. 2. Characteristic absorption bands that corresponded to the molecular vibrations of BONS are obviously confirmed and thus validated the formation of the compound.

The C–Br stretching vibrations were observed at 522.71 cm^{-1} and 623.01 cm^{-1}, which confirm the presence of the bromo substituent in the molecular structure. Thus, the NO_2 group has prominent absorption bands at 948.98 cm^{-1} and 1398.89 cm^{-1} assignable to symmetric and asymmetric stretching vibrations, respectively. The strong absorption band at 1633.71 cm^{-1} is attributed to the olefinic C=C stretching vibration, confirming the stilbene backbone formation in BONS. Furthermore, some absorption bands observed at 3078.39 cm^{-1}, 3101.39 cm^{-1}, and 3186.40 cm^{-1} are assigned to aromatic C–H stretching vibrations, which further support the aromatic character of the compound [8]. Overall, FTIR spectral features are in good agreement with the expected vibrational modes of BONS, confirming thereby the presence of all essential functional groups and validating the successful synthesis of the title compound.

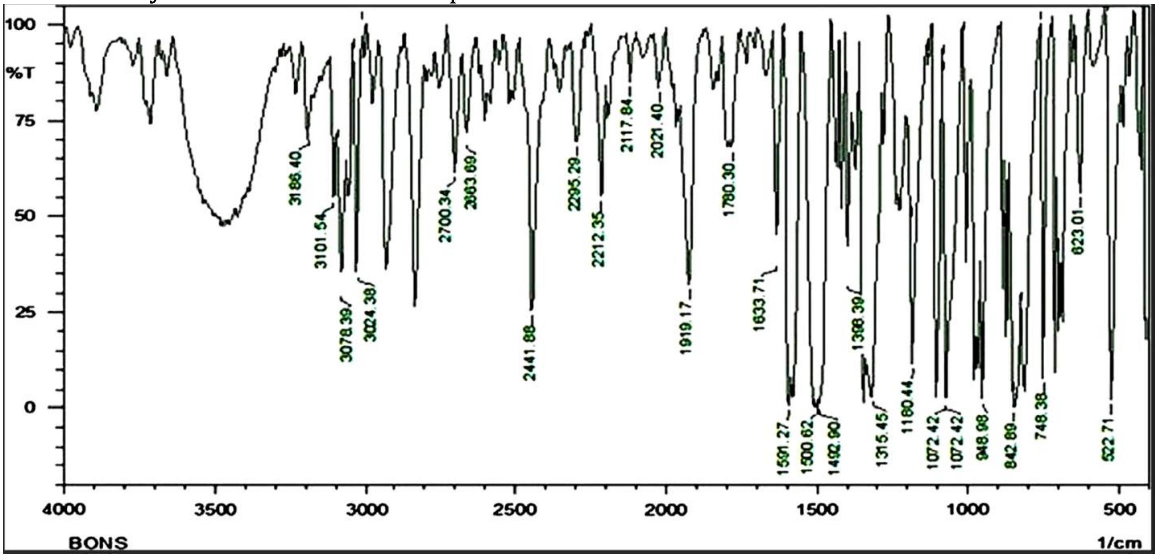


Figure 2: FTIR of 4-Bromo-4-Nitrostilbene crystal

H NMR Spectral Analysis

The ^{1}H NMR spectrum of the synthesized 4-Bromo-4-Nitrostilbene (BONS) was recorded in a $CDCl_3$ solvent using a Bruker spectrometer with a frequency of 400 MHz, and the spectrum is presented in Fig. 3. From the recorded spectrum, it can be observed that the spectrum duly shows the presence of protons in different environments, as expected in the proposed molecular structure of BONS. The presence of the two vinylic protons in the stilbene moiety of BONS can be noted as typical doublets in the spectrum at δ = 8.237 ppm and 8.232 ppm, integrating to two protons (2H), thus indicating the successful synthesis of the stilbene linkage in the target molecule. The spectrum shows the presence of the eight aromatic protons in the phenyl rings of the molecule as a series of doublets in the range of δ = 7.124-8.226 ppm, integrating to eight protons (8H), thus indicating the successful synthesis of the BONS molecule [11].

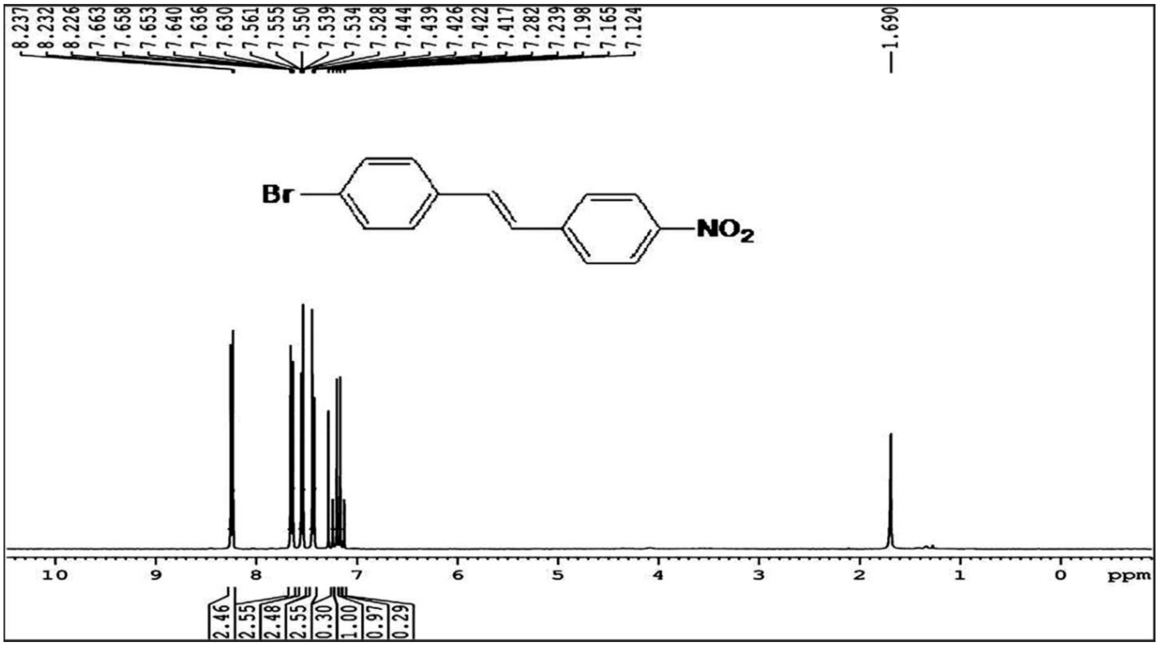


Figure 3: NMR of 4-Bromo-4-Nitrostilbene crystal

UV–Vis–NIR Absorption Spectrum

Optical absorption spectrum of the BONS single crystal of thickness 2 mm has been carried out using ELICO SL218 Double-Beam UV-Vis-NIR Spectrophotometer within a wavelength range of 190-1100 nm. Figure 4 shows optical absorption spectrum of the crystal. Optical absorption spectrum of organic materials for nonlinear optical applications depends on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In this experiment, a minimum excitation point lies between 380-389nm due to π-electrons transitions [9]. Notably, the crystal does not possess any substantial absorption over the entire visible to Near-IR region with a sharp cut-off point of 405nm, showing optical transparency of the crystal. The optical band gap value (Eg) of the BONS crystal could be estimated from the fundamental absorption edge at 405 nm. Band gap energy could be calculated by the relation $E_g = 1.24/\lambda$ ev. Where (λ) is the cutoff wavelength in micrometers (0.405µm). The result of the calculation of the band gap shows that it was 2.90eV; this indicates that the BONS crystal has a wide band gap suitable for the nonlinear optical application. The transparency of the BONS crystal in the visible region, coupled with a suitable band gap, makes it an efficient nonlinear optical material [12].

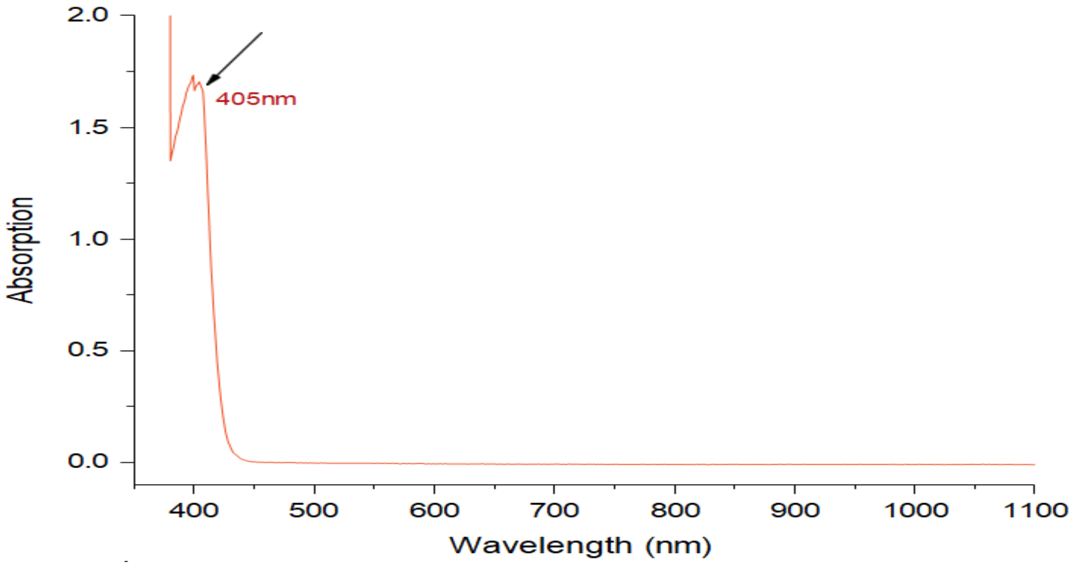


Figure 4: UV-Vis of 4-Bromo-4-Nitrostilbene crystal

Thermal Analysis

Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA) of the grown crystal of 4-Bromo-4-Nitrostilbene (BONS) were done using a TA Instruments SBT Q600 Thermogravimetric analyzer in a nitrogen environment, and the respective plots are shown in Fig. 5. From the DTA graph, it was noted that there was a sharp endothermic peak at 204.48 °C, marking the melting point of the crystal, representing its well-crystalline nature [10]. There were no phase transitions before the melting point, marking the stability in structure up to that particular temperature. A series of two prominent exothermic peaks were noticed at 366.29 °C and 521.29 °C, marking the major decomposition phases of the compound. The BONS crystal was found to be thermally stable up to 233.39 °C, marking the onset of the degradation process. After the melting point, two major regions of exothermic transitions were noticed at 366.29 °C and 521.29 °C, marking the major degradation areas for the respective compound. The TGA graph revealed three major regions of weight loss at 233.39–385.75 °C, 385.75–496.80 °C, and 496.80–544.01 °C. A marked weight loss was noticed in the initial regions due to the initial degradation of the molecules, followed by a constant degradation process. The final residue was noticed at 544.01 °C, marking the complete degradation of the compound at higher temperatures [13, 14].

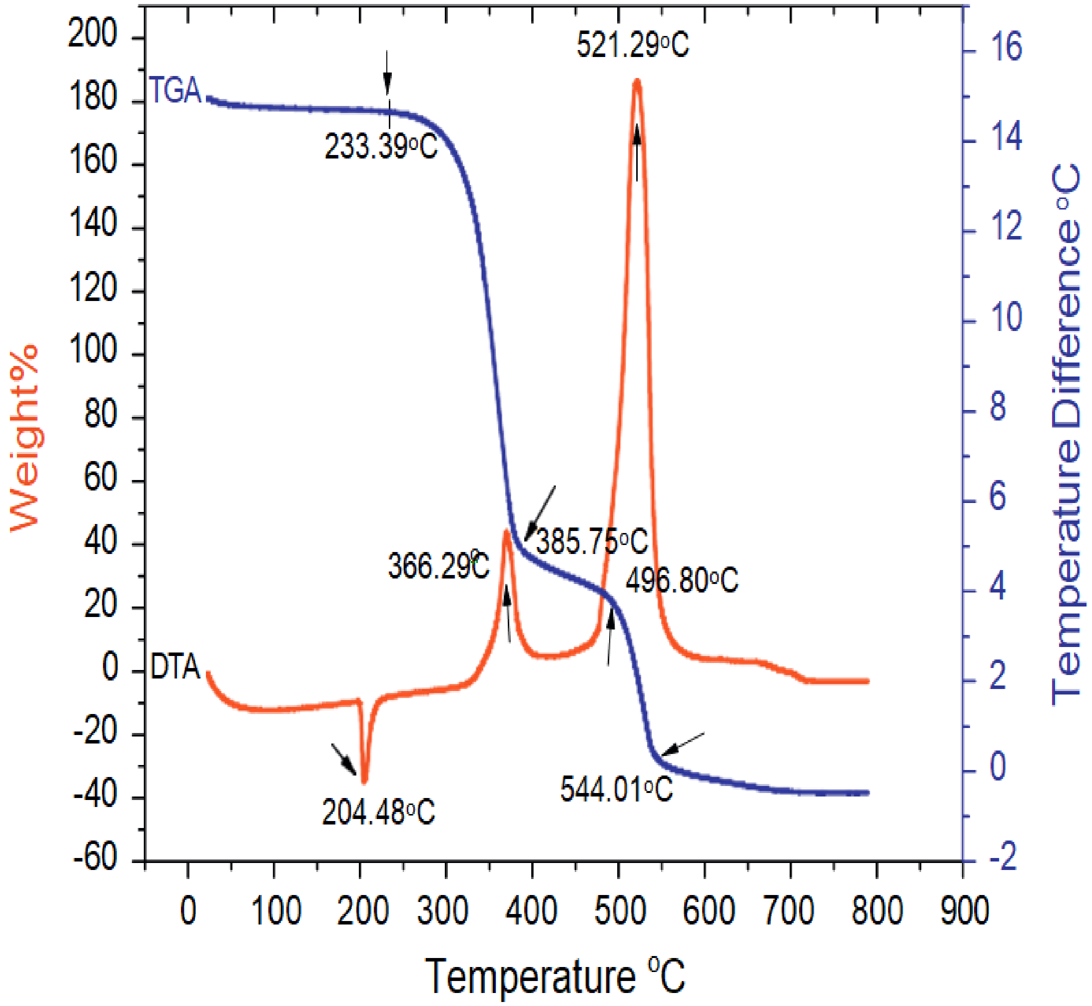


Figure 5: TGA and DTA of 4-Bromo-4-Nitrostilbene crystal

Mass Spectral Analysis

The high-resolution mass spectrometric analysis of the BONS crystal was done using the JEOL GC MATE II GC-MS double-focusing mass analyzer, and the obtained spectrum is shown in Fig. 6. The presence of the molecular ion peak with m/z = 302.9895 accurately represents the molecular weight of the BONS molecule and hence confirms the formation of the desired molecule. Fragmentation of the molecular ion peak was observed to give a prominent peak corresponding to m/z = 153.7669 and is represented by the nitro-substituted aromatic moiety. Another distinct fragment peak corresponding to m/z = 178.0783 was obtained due to the loss of the bromine ion from the parent molecule [11]. Such fragmentation features of the obtained spectrum once again confirm the molecular composition of the BONS crystal [15,16].

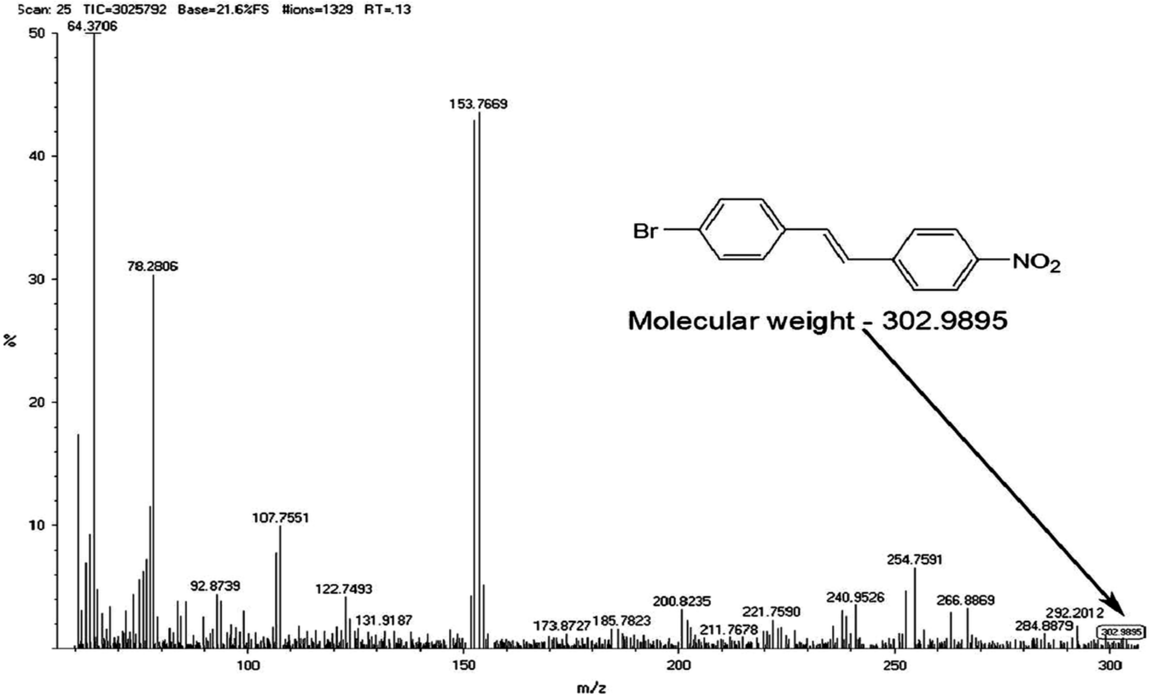


Figure 6: MASS Spectra of 4-Bromo-4-Nitrostilbene crystal

Mechanical Properties

To assess the mechanical strength of the BONS crystal grown, a Mitutoyo MH112 microhardness tester from Japan, which utilizes a Vickers diamond indenter, was used. In semiconductor technology, the determination of the microhardness of materials is important to ascertain the usability of the substance for the manufacture of optoelectronic devices. For the determination of the Vickers hardness number (H_v), the equation HV = $1.8544P/d^2$ applies, where the variables are the applied load (P, kg) and the diagonal length of the indentation (d, mm). These tests were carried out at loads of 10, 25, 50, and 100g, and the corresponding values are shown in the graphical representation of Fig. 7. On the observation, the value of the hardness number increased with the applied load. This shows the higher resistance to plastic deformation. Cracks were recorded when the applied load exceeded the limit of 100g, which signifies the maximum allowable load. Furthermore, the relationship exhibits the Reverse Indentation Size Effect (RISE) [12]. These make it clear that the BONS crystal has the required strength for optoelectronic device applications.

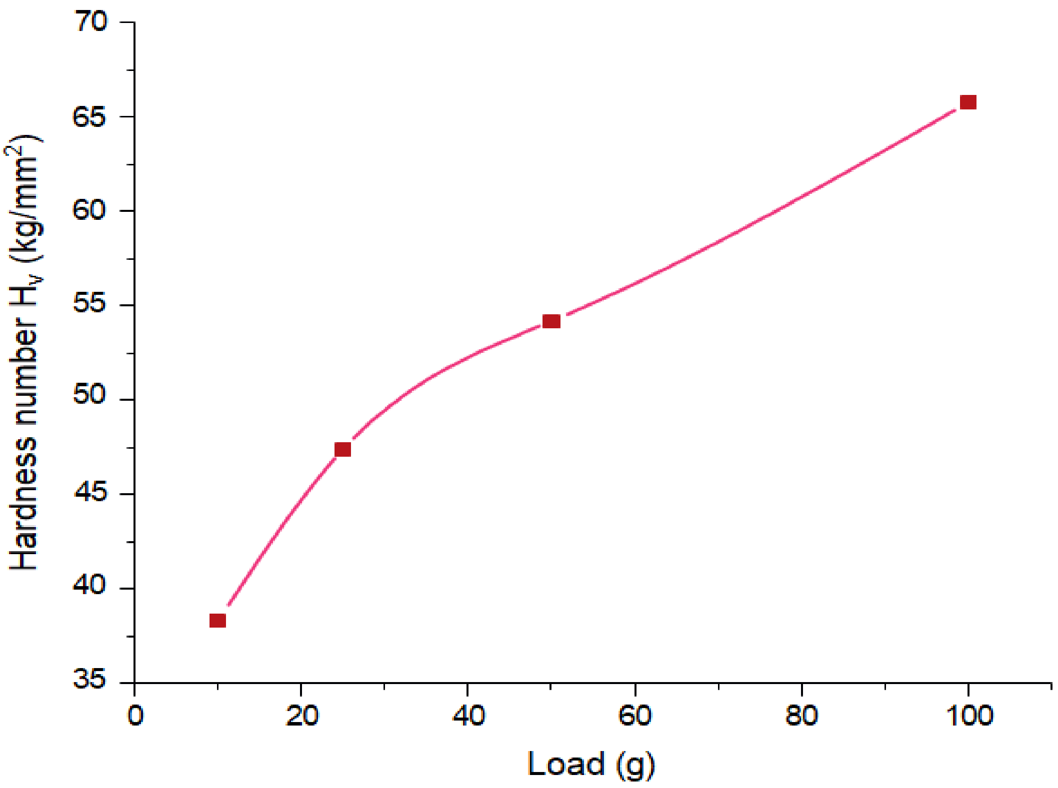


Figure 7: Mechanical Strength of 4-Bromo-4-Nitrostilbene crystal

Laser Damage Threshold (LDT) Measurement

For NLO applications, laser materials need to be strong enough to resist the strong laser beam. The laser damage threshold (LDT) of the BONS crystal was measured using a Q-switched Nd: YAG laser, which operated at its fundamental wavelength of 1064 nm with a pulse width of 10 ns. A highly polished crystal of size 8 × 6 × 3 mm^3 was used for measurement. A visible lesion appeared at the laser surface at an incident energy of 80 mJ, while cracks appeared on the crystal surface at higher energies. For the measurement of the laser damage threshold, the relation [Pd = E/(π r2 τ)] has been used, based on the pulse energy (mJ), radius of the laser spot (mm), and pulse width (ns). The LDT of the BONS crystal has been evaluated to be 254.78 MWcm^{-2}, which revealed its significant resistance against high-powered laser light [17, 18].

Photoluminescence (PL) Spectrum

The photoluminescence (PL) spectra of BONS crystals were recorded by a Jobin Yvon- Spex fluorescence spectrophotometer with a high-intensity 450 W xenon discharge lamp as an exciting light source. The fluorescence spectra were recorded from 450 to 600 nm, and these crystals were excited at a wavelength of 350 nm at a resolution of 0.2 nm. The recorded photoluminescence spectra were presented as shown below (Fig. 8). A broad bright peak (1,550,136.54 a.u.) corresponding to an intense emission at a wavelength of 515.44 nm, which falls under the green region, justified its excellent property as a bright green light emitter. This indicates a high recombination and proves that BONS crystals are excellent materials for a bright green light emitter for use in a nonlinear optical device [19, 20].

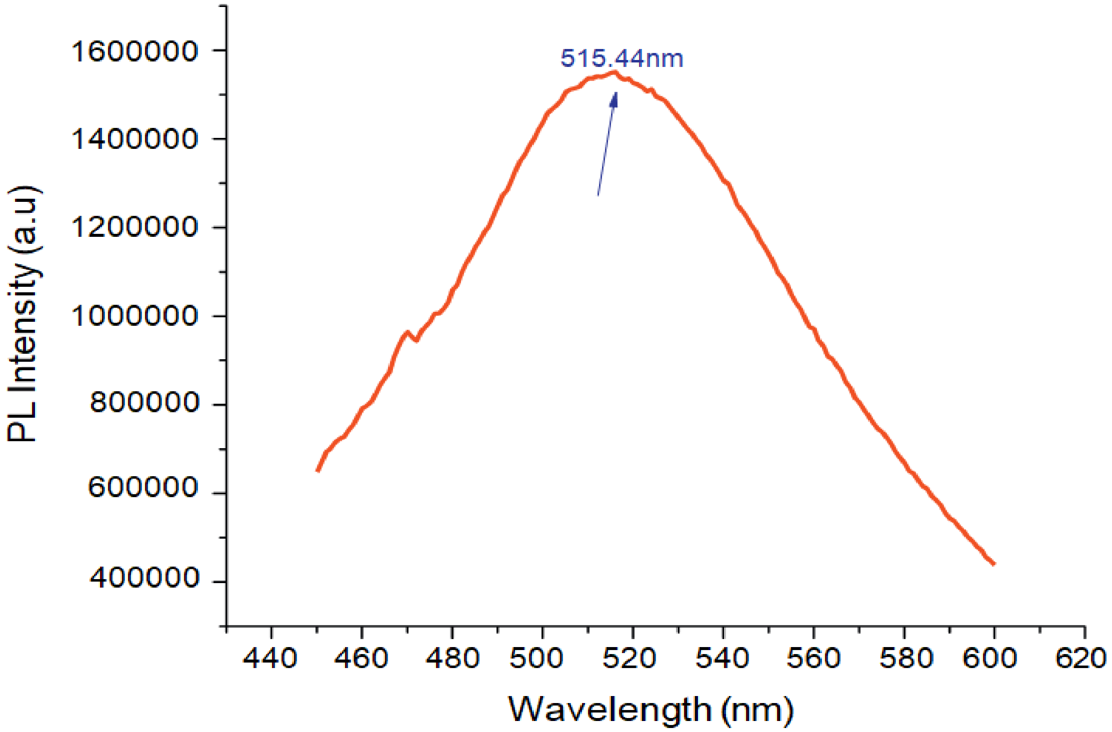


Figure 8: Photoluminescence (PL) spectra of 4-Bromo-4-Nitrostilbene crystal

Computational Methodology

To supplement and confirm the experimental results, DFT calculations were conducted on the BONS molecule. These calculations involved the assessment of the nonlinear optical properties of the molecule. Geometry optimization was carried out on the molecule. FMO studies were conducted on the DFT-optimized molecule. During FMO studies, calculations of HOMO-LUMO energy partition and band gaps of the optimized molecules were performed. Additionally, calculations of molecular polarizability and first hyperpolarizability of the optimized molecule were conducted. These calculations were geared towards estimating the efficiency of the nonlinear optical response. Theoretical calculations were conducted on the optimized molecule and helped in supplementing experimental results. They indicated good correspondence between the experimental and theoretical results. Theoretical calculations validated the functionality of the optimized BONS molecule in nonlinear optics [21-28].

Geometry Analysis

The geometry of the 4-Bromo-4-Nitrostilbene molecule was completely optimized using the density functional theory method in order to identify the most stable form of the molecule. This is presented in Table 1 and Figure 9. It is observed that the optimized structure has an ideal conjugated system with an aromatic C-C bond length of 1.386 – 1.413 Å. However, the olefinic linkage between the two phenyl rings is shorter (C10-C9 = 1.347 Å), indicating the presence of an equally strong C=C double bond that helps in intramolecular charge transfer. For the molecule, the bromine-oxygen single-bond length was found to be 1.931 Å. This is in accordance with the reported bond-length data for other aryl bromides. However, the N-O double-bond length of 1.285 Å is indicative of symmetric N=O double-bonding. On the other hand, the various aromatic angle measurements around the conjugated system indicate an angle of nearly 120°. This is an important aspect since it confirms the near-planarity and sp^2-hybridized nature of the conjugated system. However, slight deviations are noticed for the non-heteroatomic bonds C10-C9-C6 = 126.378° and C11-C10-C9 = 126.599°. These deviations are due to the sterical effects caused by the nitro and bromo groups. It is evident that the optimized geometry is an indicator of the presence of an almost rigid and planar structure with intensified conjugation and charge delocalization. This is important since strong conjugation and charge delocalization are essential for the enhancement of the second-harmonic generation efficiency of the Title compound.

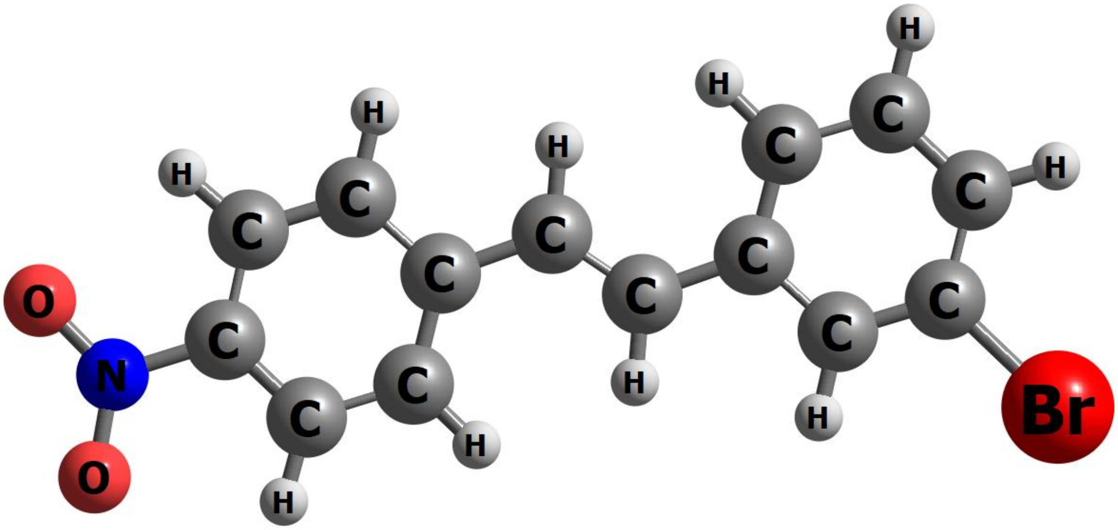


Figure 9: Optimize Geometry of 4-Bromo-4-Nitrostilbene crystal

Table 1: DFT Analysis of 4-Bromo-4-Nitrostilbene crystal

BONS	Bond length(Å)	BONS	Bond Angle (°)
C4C3	1.391	C5C4C3	119.086
C5C4	1.388	C6C5C4	121.204
C6C5	1.412	C7C6C5	118.104
C7C6	1.413	C9C6C5	118.526
C9C6	1.465	C8C3C4	121.306
C8C3	1.393	C10C9C6	126.378
C10C9	1.347	C11C10C9	126.599
C11C10	1.467	C12C11C10	118.169

C12C11	1.408	C17C11C12	118.208
C17C11	1.409	C13C12C11	120.808
C13C12	1.386	C15C13C12	120.723
C15C13	1.389	C16C17C11	120.434
C16C17	1.391	N2C3C4	119.377
N2C3	1.459	Br14C13C12	119.555
Br14C13	1.931	H19C4C3	118.566
H19C4	1.08	H20C5C4	119.597
H20C5	1.084	H21C7C6	120.097
H21C7	1.082	H22C8C3	118.32
H22C8	1.08	H23C9C6	114.392
H23C9	1.087	H24C10C9	119.197
H24C10	1.087	H25C12C11	119.784
H25C12	1.083	H26C15C13	119.974
H26C15	1.081	H27C16C15	119.392
H27C16	1.083	H28C17C11	120.089
H28C17	1.083	O1N2C3	117.236
O1N2	1.285	O18N2O1	125.563
O18N2	1.285		

Frontier Molecular Orbital (FMO) Analysis

Frontier molecular orbital theory is highly important for understanding the charge transfer characteristics of the BONS molecule. The energy values of HOMO and LUMO calculated using Frontier molecular orbital theory are −6.37 eV and −2.83 eV, respectively, with a gap energy (ΔEgap) of 3.54 eV. The moderate gap energy between HOMO and LUMO represents a balance between stability and reactivity of molecules, which is highly pertinent for nonlinear optical activities. The HOMO is found to be confined within the π-conjugated stilbene framework, which identifies regions responsible for electron donation, while LUMO is mainly concentrated within the nitro-substituted phenyl moiety, which is responsible for electron acceptance. The charge transfer process within BONS between HOMO and LUMO is efficient because of their separation, which correlates well with planar geometry and conjugated bond structure, as explained above. The donor-acceptor interactions between bromo and nitro groups in BONS contribute highly to its second-harmonic generation activities due to increased polarization within an external electric field.

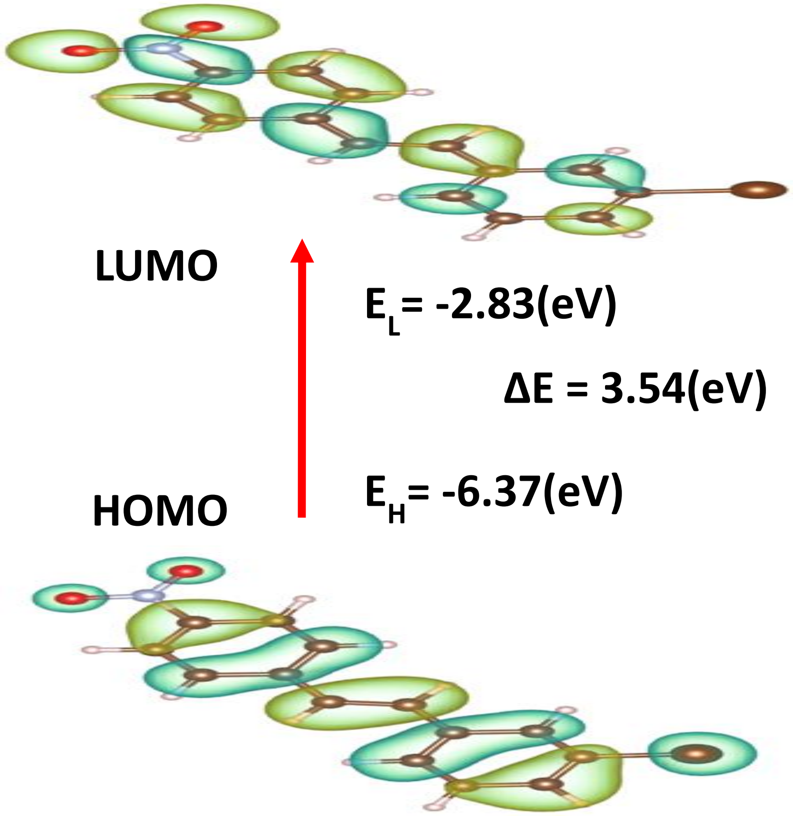


Figure 10: FMO analysis of 4-Bromo-4-Nitrostilbene crystal

Global Quantum Reactivity Descriptors

Global quantum chemical descriptors, computed from FMO energies, provide more insight into the reactivity and stability of BONS. Accordingly, the calculated ionization potential (IP) and electron affinity (EA) are 6.37 and 2.83 eV, respectively, reflecting the resistance of the molecule to electron removal and its ability to accept electrons. The computed electronegativity (χ = 4.60 eV) indicates a strong tendency to attract electrons. The chemical potential (μ = –4.60 eV) confirms the thermodynamic stability of the system. The moderate chemical hardness thus computed (η = 1.77 eV) suggests an adequate resistance to charge deformation. In contrast, the corresponding softness S = 0.28 eV^{-1} suggests sufficient polarizability, which is favorable for nonlinear optical processes. Moreover, the relatively high electrophilicity index, ω = 5.98 eV, shows that BONS is strongly electrophilic. This is explained by the presence of the nitro group, in good agreement with the optimized molecular geometry, where effective π-electron delocalization and donor-acceptor alignment enhance both reactivity and optical nonlinearity.

Table 2: Global quantum chemical descriptors of 4-Bromo-4-Nitrostilbene crystal

Parameter	**Value**	**Unit**
HOMO (E_H)	–6.37	eV
LUMO (E_L)	–2.83	eV
Energy Gap ($\Delta E_{(gap)}$)	3.54	eV
Ionization Potential (IP)	6.37	eV
Electron Affinity (EA)	2.83	eV
Electronegativity (χ)	4.60	eV
Chemical Potential (μ)	–4.60	eV
Hardness (η)	1.77	eV
Softness (S)	0.28	eV^{-1}
Electrophilicity (ω)	5.98	eV

Molecular Electrostatic Potential (MEP) Analysis

Figure 11: The MEP surface provides a three-dimensional topological map of charge distribution and reactivity sites in the BONS molecule. As seen from the MEP map, prominent negative potential regions are concentrated in areas surrounding the oxygen atoms of the nitro group, which indicates preferred reactivity sites for electrophilic attack. On the other hand, areas with positive potential are mostly concentrated around the hydrogen atoms and the bromo-substituted phenyl ring, indicating nucleophilic interaction sites. This intramolecular charge separation is directly related to the results of the FMO analysis, which showed that LUMO was concentrated on the nitro group while the HOMO is distributed along the conjugated backbone. The MEP findings corroborate the calculated electronegativity and electrophilicity values, confirming strong intramolecular charge polarization. Therefore, FMO, quantum reactivity descriptors, and MEP analyses all consistently show that the electronic structure of BONS should strongly favor charge transfer, polarization, and enhanced nonlinear optical activity.

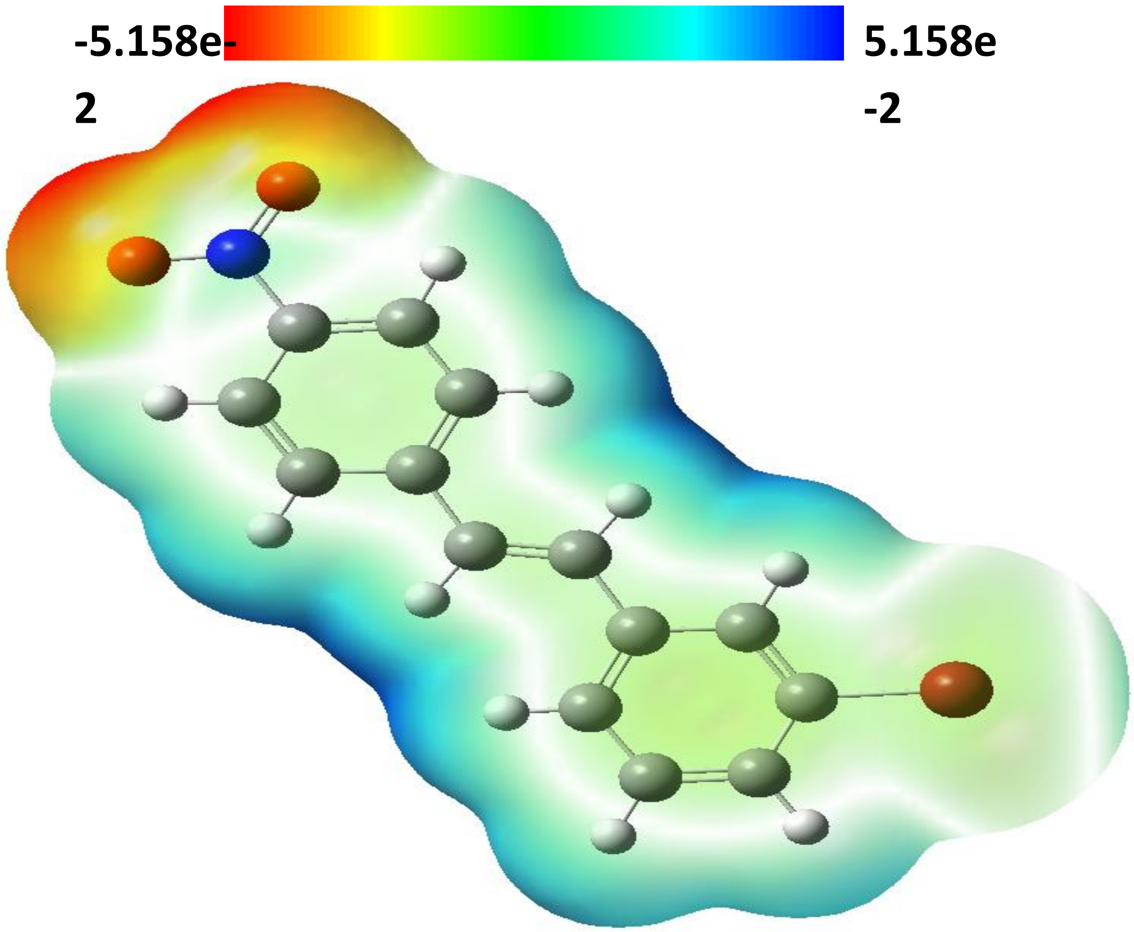


Figure 11: MESP Analysis of 4-Bromo-4-Nitrostilbene crystal

Nonlinear Optical Study

The nonlinear optical (NLO) properties of the grown crystal of 4-Bromo-4-Nitrostilbene (BONS) were explored both experimentally and theoretically with the help of density functional theory (DFT), showing excellent consistency in the validation of the observed values in table 3. The experiment was carried out using the Kurtz-Perry Powder SHG method of measuring the nonlinear optical properties of the crystal, where the powdered BONS crystal, exposed to a Q-switched Nd: YAG laser of wavelength 1064 nm and pulse width of 10 ns with a pulse energy of 2.4 mJ, displayed a strong peak in the SHG intensity at 532 nm with a corresponding output voltage of 1.5 V, while the same intensity was measured to be 21.7 mV in the standard potassium dihydrogen phosphate (KDP). This implies that the efficiency of the SHG in BONS crystal values is a whopping 69 times higher than that of the standard KDP crystal, thereby confirming the excellent nonlinear optical activity of the former crystal. The RB3LYP/3-21G calculations are in excellent support of the above observation, indicating a relatively higher value of the dipole moment (μ = 4.956 Debye), which signifies higher polarity and efficient charge transfer of the molecule in the crystal. The observed relatively higher values of the mean polarizability (α = 200.494 a.u.) and especially the giant value of the first hyperpolarizability (β = 6863.884 a.u.) of the BONS molecule indicate the excellent nonlinear optical properties of the molecule itself, which would be of significant help in its application in future photonics and optoelectronics devices for which efficiency in nonlinear optical properties would play a vital role in their successful working.

Table 3: DFT Analysis of NLO for 4-Bromo-4-Nitrostilbene crystal

Parameter	**Value**	**Unit**
Total Energy, E(RB3LYP)	−3302.288669	Hartree
Dipole Moment (μ)	4.956	Debye
Polarizability (α)	200.494	a.u.
First Hyperpolarizability (β)	6863.884	a.u.

Conclusion

In the present study, the BONS compound was synthesized and grown as good quality single crystals using a slow evaporation technique. Single-crystal and powder X-ray diffraction analyses confirmed the excellent crystallinity of the material and determined its non-centrosymmetric orthorhombic structure, which is an essential pre-requisite for second-order nonlinear optical activity. The characteristic functional groups were identified from FTIR spectroscopy, and the molecular structure along with different proton environments was well confirmed from 1H NMR analysis. Optical transparency studies revealed a wide transmission window with a lower cut-off wavelength at 405 nm. This confirms suitability for visible and near infrared optical applications of the BONS compound. The thermal stability of the grown crystals was established by TG/DTA analysis. It exhibited stability up to its melting point without any phase transition, and the integrity of the molecule was further confirmed by high-resolution mass spectrometry. Mechanical characterization carried out using Vickers microhardness shows that the hardness number increases as the applied load increases, following the RISE pattern, thus reflecting sufficient mechanical strength to endure device fabrication. LDT was assessed as 254.78 MW cm^{-2} and demonstrated that the material can bear high-power laser irradiation. Photoluminescence studies showed strong green light emission centered at 515.44 nm, further confirming its optoelectronic potential.

Experimentally, the nonlinear optical efficiency of BONS had been confirmed through the Kurtz–Perry powder SHG technique; it shows that this material exhibits an SHG efficiency approximately 69 times greater than that of KDP, indicating its extremely strong second-order nonlinear response. The experimental observation has been strongly supported by DFT calculations, which give a relatively high dipole moment (4.956 Debye), large mean polarizability (200.494 a.u.), and a remarkably high first hyperpolarizability (6863.884 a.u.). The energy gap between the HOMO and LUMO was observed to be moderate along with a favorable quantum reactivity descriptor for efficient intramolecular charge transfer within the π-conjugated framework. This good agreement between the experimental SHG measurement and theoretical prediction confirms the idea that enhanced NLO performance in BONS originates due to its non-centrosymmetric crystal structure, extended π-conjugation, and strong donor–acceptor interaction. Conclusion: Overall, combined experimental and computational results provide BONS as a highly promising organic nonlinear optical crystal for frequency conversion, photonic, and optoelectronic device applications.

References

1. S. Shi, C. Lin, G. Yang, L. Cao, B. Li, T. Yan, M. Luo and N. Ye, A2Bi2 (SeO3) 3F2 (A= K and Rb): Excellent Mid-Infrared Nonlinear Optical Materials with Both Strong SHG Responses and Large Band Gaps, Chem. Mater., 2020, 32(18), 7958–7964, DOI: 10.1021/acs.chemmater.0c02837.
2. J. Quertinmont, P. Beaujean, J. Stiennon, Y. Aidibi, P. Leriche, V. Rodriguez, L. Sanguinet and B. Champagne, Combining Benzazolo-Oxazolidine Twins toward Multi State Nonlinear Optical Switches, J. Phys. Chem. B, 2021, 125(15), 3918–3931, DOI: 10.1021/acs.jpcb.1c01962.
3. J. Naeem, R. Bano, K. Ayub, T. Mahmood, S. Tabassum, A. Arooj and M. A. Gilani, Assessment of Alkali and Alkaline Earth Metals Doped Cubanes as High Performance Nonlinear Optical Materials by First Principles Study, J. Sci.:Adv. Mater. Devices, 2022, 7(3), 100457, DOI: 10.1016/j.jsamd.2022.100457.
4. R. Bano, M. Asghar, K. Ayub, T. Mahmood, J. Iqbal, S. Tabassum, R. Zakaria and M. A. Gilani, A Theoretical Perspective on Strategies for the Fabrication of High Performance Nonlinear Optical Materials, Front. Mater., 2021, 8, 532, DOI: 10.3389/fmats.2021.783239.
5. 20 R. Bano, K. Ayub, T. Mahmood, M. Arshad, A. Sharif, S. Tabassum and M. A. Gilani, Mixed Superalkalis Are a Better Choice than Pure, Dalton Trans., 2022, 51, 8437– 8453, DOI: 10.1039/d2dt00321j.
6. A. Ahsin and K. Ayub, Superalkali-Based Earthides Li3O@ [12-Crown-4] M (Where M= Li, Na, and K) with Remarkable Static and Dynamic NLO Properties; A DFT Study, Mater. Sci. Semicond. Process., 2022, 138, 106254, DOI: 10.1016/j.mssp.2021.106254.
7. A. Ahsan and K. Ayub, Adamanzane Based Alkaline Earthides with Excellent Nonlinear Optical Response and Ultraviolet Transparency, Opt. Laser Technol., 2020, 129(April), 106298, DOI: 10.1016/j.optlastec.2020.106298.
8. A. Azadi and H. R. Shamlouei, Feasibility of Using the Anode Functionalized with Calix [4] Pyridine in Lithium and Sodium Atom/Ion Batteries: DFT Study, Comput. Theor. Chem, 2021, 1202, 113332, DOI: 10.1016/ j.comptc.2021.113332.
9. L. M. G. Abegao, R. D. Fonseca, F. A. Santos, J. J. Rodrigues, K. Kamada, C. R. Mendonça, S. Piguel and L. De Boni, First Molecular Electronic Hyperpolarizability of Series of p Conjugated Oxazole Dyes in Solution: An Experimental and Theoretical Study, RSC Adv., 2019, 9(45), 26476–26482, DOI: 10.1039/C9RA05246A.
10. R. Dennington; T. Keith and J. Millam. GaussView, Version 6.1.1. Semichem Inc., Shawnee Mission, KS. 2019. 37 D.-F. WANG and Y.-D. WU, A Theoretical Comparison of Conformational Features of Calix [4] Aromatics, J. Theor. Comput. Chem., 2004, 3(01), 51–68, DOI: 10.1142/ S0219633604000908.
11. M. F. Asif, R. Bano, R. Farooq, S. Muhammad, T. Mahmood, K. Ayub, S. Tabassum and M. A. Gilani, Shedding Light on the Second Order Nonlinear Optical Responses of Commercially Available Acidic Azo Dyes for Laser Applications, Dyes Pigm., 2022, 202, 110284, DOI: 10.1016/ j.dyepig.2022.110284.
12. F. Ullah, K. Ayub and T. Mahmood, Remarkable Second and Third Order Nonlinear Optical Properties of Organometallic C6Li6–M3O Electrides, New J. Chem., 2020, 44(23), 9822– 9829, DOI: 10.1039/D0NJ01670E.
13. N. Kosar, L. Zari, K. Ayub, M. A. Gilani and T. Mahmood, Static, Dynamic Nonlinear Optical (NLO) Response and Electride Characteristics of Superalkalis Doped Star like C6S6Li6, Surf. Interfaces, 2022, 31, 102044, DOI: 10.1016/ j.surfin.2022.102044.
14. R. Bano, M. Arshad, T. Mahmood, K. Ayub, A. Sharif, S. Tabassum and M. A. Gilani, Superalkali (Li2F, Li3F) Doped Al12N12 Electrides with Enhanced Static, Dynamic Nonlinear Optical Responses and Refractive Indices, Mater. Sci. Semicond. Process., 2022, 143, 106518, DOI: 10.1016/ j.mssp.2022.106518.
15. R. Bano, K. Ayub, T. Mahmood, M. Arshad, A. Sharif, S. Tabassum and M. A. Gilani, Diamondoid as

Potential Nonlinear Optical Material by Superalkali Doping: A First
16. Principles Study, Diamond Relat. Mater., 2023, 135(March), 109826, DOI: 10.1016/j.diamond.2023.109826.
17. W. Sun, D. Wu, Y. Li and Z. Li, Novel Earthides with Considerably Large First Theoretical Study on Superalkali (Li3) in Ammonia: Hyperpolarizabilities, Dalt. Trans., 2024, 43, 486–494, DOI: 10.1039/c3dt51559a.
18. T. Lu and Q. Chen, Interaction Region Indicator: A Simple Real Space Function Clearly Revealing Both Chemical Bonds and Weak Interactions, Chem.:Methods, 2021, 1(5), 231–239, DOI: 10.1002/cmtd.202100007.
19. A. Ahsan and K. Ayub, Extremely Large Nonlinear Optical Response and Excellent Electronic Stability of True Alkaline Earthides Based on Hexaammine Complexant, J. Mol. Liq., 2020, 297, 111899.
20. X. Li, Y. Zhang and J. Lu, Remarkably Enhanced First Hyperpolarizability and Nonlinear Refractive Index of Novel Graphdiyne-Based Materials for Promising Optoelectronic Applications: A First-Principles Study, Appl. Surf. Sci., 2019, 2020(512), 145544, DOI: 10.1016/ j.apsusc.2020.145544.
21. Chao H, Ye BH, Zhang QL, Ji LN (1999) A luminescent pH sensor based on a diruthenium(II) complex: "off-on-off" switching via the protonation/deprotonation of an imidazole-containing ligand. Inorg Chem Commun 2:338–340
22. Pujar MA, Bharamgoudar TD (2020) Cobalt(II), nickel(II) and copper(II) complexes of bidentate biN-[2-(4-hydroxyphenyl)ethyl]decanamide s. Transition Met Chem 13:423–425
23. Abbas, M. A., Mahar, J., Hameed, N., & Rasool, M. S. (2025). DFT-Guided Design of a Low-Band-Gap Pyrazoline Scaffold: The Critical Role of a Para-Nitro Substituent. *Multidisciplinary Surgical Research Annals*, *3*(3), 461-503.
24. Abbas, M. A., Mahar, J., Rasool, M. S., Khan, M. J., & Khan, M. Z. (2025). The Dual Therapeutic Promise of Quinoa: Exploring Antidiabetic and Antioxidant Effects through Experimental and Computational Models. *Multidisciplinary Surgical Research Annals*, *3*(3), 504-544.
25. Abbas, M. A., Mahar, J., Khan, M. J., Rasool, M. S., & Khan, M. Z. (2025). IN SILICO INVESTIGATION OF 3, 6-DIPHENYL-[1, 2, 4] TRIAZOLO [3, 4-B][1, 3, 4] THIADIAZOLE DERIVATIVES AS EGFR MODULATORS FOR LUNG CANCER TREATMENT. *The Cancer Research Review*, *4*(2), 243-308.
26. Abbas, M. A. (2025). Advanced Synthesis and Multifunctional Characterization of Neodymium-Doped $Ba_2NiCoFe_{28-x}O_{46}$ X-Type Hexagonal Ferrites: A Comprehensive Study of Structural, Morphological, and Electromagnetic Properties. *Sch Acad J Biosci*, *8*, 1213-1227.