International Journal of Interdisciplinary Innovative Research & Development (IJIIRD)

ISSN: 2456-236X

Vol. 10 Issue 01 | 2025

Computational Investigation of Nonlinear Optical Properties of Sulphamic Acid Using DFT and Multi-Model Polarizability Analysis

Shrikant Yadav[1,2], M. I. Baig[3].

[1] *Assistant Professor, Department of Physics, Yashwantrao Chavan College of Science Karad, Maharashtra, India.*

[2] *Research Scholar, Department of Physics, Prof Ram Meghe College of Engineering and Management, Badnera-Amravati, Maharashtra, India.*

[3] *Assistant Professor, Department of Physics, Prof Ram Meghe College of Engineering and Management, Badnera-Amravati, Maharashtra, India.*

DOI: 10.5281/zenodo.15740735

ABSTRACT

Pure sulphamic acid (SA) crystals were analyzed through a comprehensive computational approach to explore their structural and nonlinear optical (NLO) characteristics. Geometry optimization and thermal stability assessments were performed using Density Functional Theory (DFT), confirming the stability of the SA molecule. Dipole moment, quadrupole moment, and isotropic polarizability (α_s) were calculated to evaluate molecular polarization relevant to optical response. Electronic polarizability was estimated using multiple theoretical models, Penn model, Clausius–Mossotti relation, optical band gap analysis, and the Coupled Dipole Method, providing deeper insights into SA's dielectric and optical behavior. The findings reinforce the suitability of sulphamic acid as a stable and cost-effective candidate for photonic and optoelectronic device applications.

Keywords: - Density Functional Theory, Molecular polarization, Electronic polarizability, Nonlinear optics, Optoelectronics.

1. Introduction

Sulphamic acid (H_3NSO_3) is a structurally simple yet functionally significant inorganic compound with a wide range of industrial, nonlinear optical device fabrications, and analytical applications[1], [2]. It is known for its zwitterionic character in aqueous solutions, along with strong hydrogen bonding and thermal stability[3], [4], [5]. These properties, combined with its non-hygroscopic and mildly acidic nature, make sulphamic acid a valuable material in nonlinear optics and photonics applications [6], [7], [8]. Despite its broad practical usage, its molecular and electronic behavior at the quantum level remains underexplored, especially in the context of optical materials research.

In recent years, nonlinear optics (NLO) has become a rapidly advancing field due to its crucial role in developing ultrafast optical devices and next-generation photonic technologies. Materials exhibiting significant nonlinear optical properties are indispensable for a variety of advanced applications such as optical switching, frequency conversion, electro-optic modulation, laser safety devices, and high-density optical data storage [9], [10], [11] . A key requirement for such materials is their ability to respond nonlinearly to intense electromagnetic fields. Sulphamic acid, with its inherent zwitterionic structure and robust molecular framework, has shown potential as a nonlinear optical material[12], [13]. Its compatibility with crystal growth techniques and ability to incorporate dopants further enhance its relevance in NLO material development [3], [4].

Traditionally, the assessment of NLO properties has relied heavily on experimental synthesis and characterization. However, the emergence of computational chemistry, especially density functional theory (DFT), has revolutionized this approach. DFT offers a cost-effective and accurate method for probing the electronic structure, molecular geometry, frontier molecular orbitals (HOMO–LUMO), vibrational frequencies, and other key parameters such as dipole moment, polarizability, and first hyperpolarizability[14], [15], [16], [17]. These theoretical descriptors are directly linked to the NLO activity of a molecule and provide valuable insights into its potential performance in real-world applications. Computational studies, therefore, serve as a predictive and interpretive framework that complements experimental work, reducing trial-and-error and guiding the design of efficient NLO materials [15].

This study presents a detailed quantum chemical investigation of sulphamic acid using DFT methods. The focus is on geometry optimization, thermal property evaluation, and the computation of electronic parameters essential for understanding NLO behavior. The dipole moment and quadrupole moment are analyzed to provide insight into the molecule's charge distribution and electrostatic profile. In addition, isotropic polarizability (α_5) and electronic polarizability are computed using both direct DFT-derived methods and various theoretical models. These include the plasma energy ($\hbar\omega P$), Penn gap energy (E_P), Fermi energy (E_F), and polarizability estimates based on the Penn model (α_1), Clausius–Mossotti relation (α_2), optical band gap method (α_3), and Coupled Dipole Method (α_4). This multi-faceted approach enables a comprehensive understanding of the dielectric and optical response behavior of sulphamic acid.

The results of this work contribute to the fundamental knowledge of sulphamic acid's molecular and optical properties and establish a computational basis for evaluating its viability as a material for nonlinear optical and photonic device applications.

2. Results and Discussion

2.1 Powder XRD analysis

The PXRD pattern of pure sulphamic acid (SA) crystals displays distinct, intense peaks indicative of excellent crystallinity and phase purity. The narrow full width at half maximum (FWHM) values reflect superior crystal quality, which is critical for optoelectronic performance. Using FullProf software for Rietveld refinement, and referencing structural data from the Crystallography Open Database (COD ID: 1538448), the lattice parameters and atomic coordinates were precisely refined. The low residuals and strong agreement factors confirm the accuracy of the structural model, supporting the high-quality crystalline nature of SA for potential use in advanced optical and electronic applications.

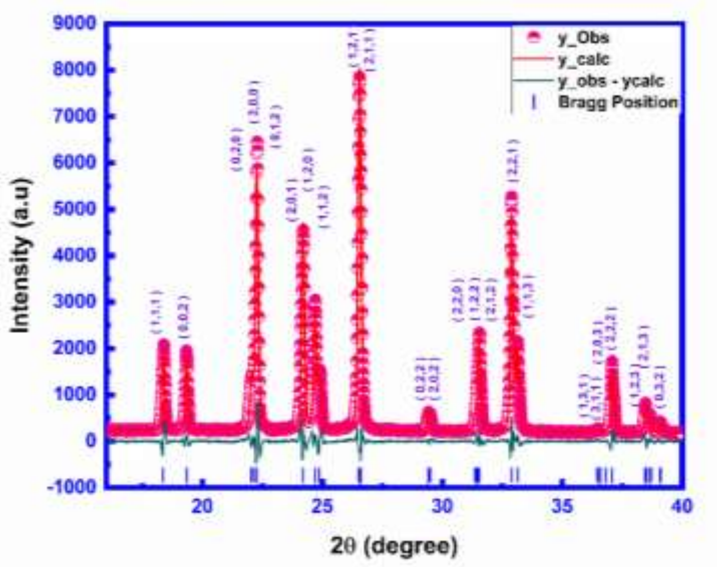


Fig -1: Refinement of SA

The powder XRD data for pure SA, along with refined structural parameters, are summarized in Table 1. The results show excellent agreement with reported cell parameters, confirming the reproducibility and precision of the crystal growth method. The high consistency between experimental and reference data validates the phase purity and structural integrity of the SA crystals, supporting their suitability for functional applications.

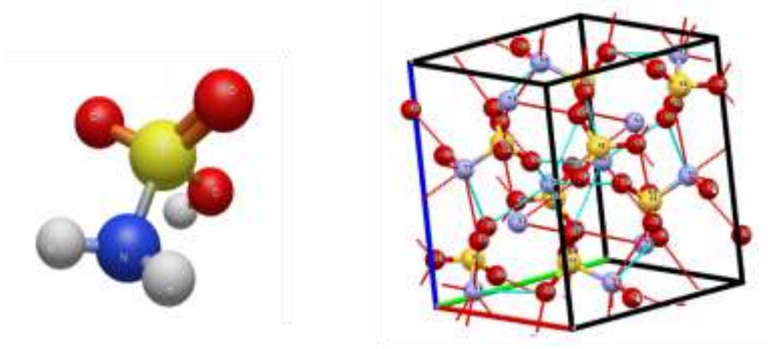
Table 1. Powder XRD data for pure SA.

Crystal data	SA [12] (Reported SXRD)	SA (Present work)	SA (From COD) ID: 1538448
a (Å)	8.0943	8.07066	8.07
b (Å)	8.0667	8.10957	8.11
c (Å)	9.2589	9.23906	9.25

α	90°	90°	90°
β	90°	90°	90°
γ	90°	90°	90°
Volume (Å^3)	603	604.6926	605.79
System	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca

2.2 Molecular Geometry Optimisation

The ground-state molecular geometry of sulphamic acid (SA) was optimized using density functional theory (DFT) with the B3LYP hybrid functional and the 6-11G(d,p) basis set, as implemented in ORCA 5.0. This level of theory provides an accurate balance between computational efficiency and electronic structure prediction, particularly for hydrogen bonding and zwitterionic systems. The optimization process converged to a stable minimum-energy configuration, confirmed by the absence of imaginary frequencies in vibrational analysis. The Optimised Geometry and packing fraction of Sulphamic acid is shown in Figure 2.



a) b)

Fig -2: a) Optimized molecular geometry of SA b) Packing of SA

2.3 Computational Thermal Analysis

The thermal analysis of Sulphamic acid (H_3NSO_3) was conducted using Density Functional Theory (DFT) with the B3LYP functional, offering valuable insights into its thermodynamic stability and energetic variations under different temperature and pressure conditions. The computed thermochemical parameters internal energy (U), enthalpy (H), entropy (S), and Gibbs free energy (G) provide a comprehensive description of the material's thermal behavior[18]. These parameters are critical for understanding the thermodynamic stability and reactivity of Sulphamic acid under varying environmental conditions. The internal energy remains relatively constant across different pressures at a given temperature, indicating the robustness of the electronic structure under external perturbations. This suggests that the molecular framework of Sulphamic acid is resilient to changes in pressure, which is a desirable property for materials used in high-pressure applications. Enthalpy, calculated as $H = U + k_BT$, exhibits minimal variations with pressure, further reinforcing the system's thermodynamic stability. Entropy, which accounts for vibrational, rotational, and translational contributions, increases with temperature, reflecting the expected rise in molecular motion and disorder[19], [20]. The variation of entropy with temperature at different pressures is illustrated in Figure 3.

Further, a slight decrease in entropy with increasing pressure suggests a reduction in molecular freedom, which could influence the material's optical and structural properties. This behavior aligns with the principles of statistical thermodynamics, where increased pressure typically restricts molecular motion, leading to lower entropy. The Gibbs free energy, derived from $G = H - T \cdot S$, decreases with increasing temperature, indicating enhanced thermodynamic feasibility at rising temperatures.

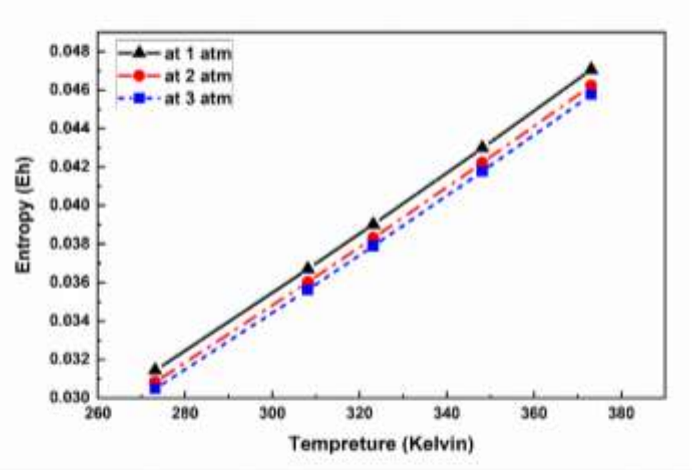


Fig -3: Computational Thermal Analysis of SA by using B3LYP Functionals.

The decrease in Gibbs free energy with temperature also implies that the compound becomes more thermodynamically favorable for reactions or phase transitions as temperature rises[20], [21]. The thermal stability and consistent thermodynamic parameters of Sulphamic acid highlight its potential for nonlinear optical applications and photonic device fabrication.

2.4 Electronic polarizability (α*) for Pure SA.

The electronic polarizability (α*) is a fundamental parameter that describes the response of a material's electron cloud to an external electric field. It plays a crucial role in determining the nonlinear optical properties of the material[22], [23]. A material's electronic polarizability (α*) is directly influenced by its dielectric constant. The valence electron plasma energy ($\hbar\omega$p), Penn gap (Ep), and Fermi energy (Ef) also depend on the material's dielectric constant. The density of SA is calculated using the formula:

$$\rho = \frac{M*Z}{N_A*V} \qquad \ldots(1)$$

where: M=97.10 g/mol (molecular weight of SA(H_3NSO_3)), Z=4 (number of molecules per unit cell for SA), N_A=6.022 × 10^{23} mol^{-1} (Avogadro's number), V = 603 × 10^{-24} cm^3 (volume of the unit cell). Crystal density is found to be 2.14 g/cm^3. The valence electron plasma energy is calculated as:

$$\hbar\omega_P = 28.8\left(\frac{Z'*\rho}{M}\right)^{1/2} \qquad \ldots(2)$$

where Z′=32 (total number of valence electrons in SA: H=3, N=5, S=6, O=18). The Penn gap and Fermi energy are calculated using:

$$E_P = \frac{\hbar\omega_P}{\sqrt{\epsilon'-1}} \qquad \ldots(3)$$

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \qquad \ldots(4)$$

where ϵ'=18.23 (dielectric constant of SA).
The electronic polarizability is calculated using the Penn model [22], [23] as,

$$\alpha_1 = \left[\frac{\hbar\omega_P{}^2 * S_0}{(\hbar\omega_P{}^2 * S_0)+3\,E_P^2}\right] * \frac{M}{\rho} * 0.396 * 10^{-24}\ \mathrm{cm}^3 \qquad \ldots(5)$$

where S_0 is a constant calculated as:

$$S_0 = 1 - \frac{E_P}{4E_F} + \frac{1}{3}\left(\frac{E_P}{4E_F}\right) \qquad \ldots.(6)$$

Similarly, we can calculate the electronic polarizability (α2) using the Clausius-Mossotti relation as

$$\alpha_2 = \frac{3M}{4\pi N_A}\left[\frac{\epsilon_0-1}{\epsilon_0+2}\right] \qquad \ldots(7)$$

The electronic polarizability is also calculated using the optical band gap energy (Eg=5.19 eV for SA):

$$\alpha_3 = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] * \frac{M}{P} * 0.396 * 10^{-24}\ \mathrm{cm}^3 \qquad (8)$$

Renne and Nijboer introduced the coupled dipole method (CDM) to analyze the electronic polarizability of materials, as

$$\alpha_4 = \frac{Z' * e}{m_e * \omega_0^2}\left[\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right] \qquad \ldots(9)$$

Where Z'=32 (total valence electrons), e =1.602×10^{-19} C (electron charge), m_e = 9.1×10^{-28} g (electron mass), ω_0=2πf rad/s (frequency at 100 KHz). The electronic polarizability values at different temperatures are given in Table 2.

Table No.2 Comparison of Electronic Polarizability and Related Parameters

Parameters	Values for SA	Values of KDP Crystal [22]
Plasma energy ($\hbar\omega_P$)	24.14 eV	17.33 eV
Penn gap energy (E_P)	5.82 eV	2.39 eV
Fermi energy (E_F)	31.68 eV	12.02 eV
Electronic polarizability (α_1) (Penn analysis)	1.525×10^{-23} cm^3	2.14×10^{-23} cm^3
Electronic polarizability (α_2) (Clausius-Mossotti)	1.533×10^{-23} cm^3	2.18×10^{-23} cm^3
Electronic polarizability (α_3) (Optical band gap)	7.89×10^{-24} cm^3	–
Electronic polarizability (α_4) (CDM)	2.285×10^{-23} cm^3	–

To understand the electronic properties computationally, a DFT approach has been taken, and electronic properties like dipole moment (μ_{tot}), quadrupole moment, and isotropic polarizability were calculated using TD-DFT functionals. Calculated values of all components and their resultants of dipole moment and polarizability are given in Table 3 [where 1 a.u. = 1.4818×10^{-25} cm³]. The respective value of μ_{tot} is found to be **2.3 times higher** than urea [μ_{Urea}=0.5402 a.u.][24]. Hence, the computational analysis suggests that the studied molecule (SA) exhibits significant dipole moment and polarizability, making it a potential candidate for nonlinear optical (NLO) applications.

Table No.3 Electronic property calculation by using DFT

Property	Magnitude (a.u.)	Isotropic Value (cm³)
Dipole Moment	1.55258	-
Quadrupole Moment	-26.70480	-
Isotropic Polarizability α_5	39.04749	5.786×10^{-24} cm^3

The electronic polarizability of the SA molecule, calculated using different theoretical approaches, shows remarkable consistency and highly promising values. Excellent agreement between analytical equations and DFT-based calculations underscores the robustness of the computational models and the molecule's well-defined electronic structure. The high polarizability values highlight the SA molecule's exceptional ability to undergo electronic distortion under an applied electric field, a critical property for nonlinear optical (NLO) materials.

This strong electronic response positions the SA molecule as a highly promising candidate for advanced NLO applications, such as optical switching and frequency doubling. The consistency across methods reinforces confidence in these predictions, showcasing their potential for real-world optoelectronic devices. The balanced and robust electronic distribution further suggests efficient interaction with light and external fields, making it ideal for next-generation NLO technologies.

3. Conclusion

A comprehensive computational investigation of pure sulphamic acid (SA) was performed using Density Functional Theory (DFT) to explore its structural, electronic, and optical characteristics pertinent to nonlinear optical (NLO) applications. The optimized molecular geometry and thermodynamic parameters confirm the intrinsic stability of the molecule. The calculated dipole moment, quadrupole moment, and isotropic polarizability (α_5) indicate strong intermolecular interactions and notable polarization, which are favorable traits for optical switching and modulation. Also, electronic polarizability was evaluated through multiple theoretical frameworks, including the Penn model, Clausius–Mossotti relation, optical band gap method, and coupled dipole method, providing a multidimensional perspective on SA's dielectric and optical response. These results collectively establish sulphamic acid as a structurally stable, electronically active, and computationally validated candidate for future use in photonic and optoelectronic device applications.

4. REFERENCES

[1] C. P. Sahana, P. R. Deepthi, M. Challa, P. M. Kumar, A. Sukhdev, and J. Shanthi, “Exploring the Influence of FeSO4 on the Structural and Thermal Properties of Sulphamic Acid Single Crystals,” *Iranian Journal of Science*, vol. 47, no. 1, pp. 275–283, Feb. 2023, doi: 10.1007/S40995-022-01407-1/METRICS.

[2] L. Anandaraj and L. Jothi, “Investigation on synthesis, growth, optical, mechanical, dielectric and third order non linear optical properties of cadmium chloride monohydrate doped sulphamic acid crystals for nonlinear optical device fabrications,” *J Mol Struct*, vol. 1250, p. 131672, Feb. 2022, doi: 10.1016/J.MOLSTRUC.2021.131672.

[3] R. Valluvan, K. Selvaraju, and S. Kumararaman, “Growth and characterization of sulphamic acid single crystals: A nonlinear optical material,” *Mater Chem Phys*, vol. 97, no. 1, pp. 81–84, May 2006, doi: 10.1016/J.MATCHEMPHYS.2005.07.063.

[4] N. Indumathi, S. Senthil, M. V. A. Raj, E. Chinnasamy, and K. Deepa, “Synthesis, growth, vibrational analysis, hardness studies and theoretical calculations on inorganic NLO sulphamic acid lithium chloride single crystal,” *Mater Today Proc*, vol. 50, pp. 2636–2639, Jan. 2022, doi: 10.1016/J.MATPR.2020.07.591.

[5] M. I. Baig, M. Anis, M. D. Shirsat, H. H. Somaily, and S. S. Hussaini, “Exploring linear-nonlinear optical, dielectric and microscopic traits of sulphamic acid crystal exploiting Zn2+ for photonic device applications,” *Journal of Materials Science: Materials in Electronics*, vol. 32, no. 12, pp. 16445–16455, Jun. 2021, doi: 10.1007/s10854-021-06197-7.

[6] J. Arumugam, M. Selvapandiyan, S. Chandran, M. Srinivasan, and P. Ramasamy, “Crystal growth, optical, thermal, laser damage threshold, photoconductivity and third-order nonlinear optical studies of KCl doped sulphamic acid single crystals,” *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 8, pp. 6084–6096, Apr. 2020, doi: 10.1007/S10854-020-03161-9/METRICS.

[7] J. Arumugam, M. Selvapandiyan, S. Chandran, M. Srinivasan, and P. Ramasamy, “Effect of MgSO4 on sulphamic acid single crystals and their structural, optical, mechanical, thermal and third order nonlinear optical studies,” *Mater Chem Phys*, vol. 242, p. 122479, Feb. 2020, doi: 10.1016/J.MATCHEMPHYS.2019.122479.

[8] M. I. Baig, M. Anis, M. D. Shirsat, H. H. Somaily, and S. S. Hussaini, “Exploring linear-nonlinear optical, dielectric and microscopic traits of sulphamic acid crystal exploiting Zn2+ for photonic device applications,” *Journal of Materials Science: Materials in Electronics*, vol. 32, no. 12, pp. 16445–16455, Jun. 2021, doi: 10.1007/s10854-021-06197-7.

[9] P. Anandan, G. Parthipan, T. Saravanan, R. Mohan Kumar, G. Bhagavannarayana, and R. Jayavel, “Crystal growth, structural and optical characterization of a semi-organic single crystal for frequency conversionapplications,” *Physica B Condens Matter*, vol. 405, no. 24, pp. 4951–4956, Dec. 2010, doi: 10.1016/j.physb.2010.09.042.

[10] Y. Shang *et al.*, “Nonlinear optical inorganic sulfates: The improvement of the phase matching ability driven by the structural modulation,” *Coord Chem Rev*, vol. 494, p. 215345, Nov. 2023, doi: 10.1016/J.CCR.2023.215345.

[11] A. E. De Barr, “The applications of single crystals,” *Contemp Phys*, vol. 2, no. 6, pp. 409–422, Aug. 1961, doi: 10.1080/00107516108205288.

[12] R. Kumar *et al.*, “Sulphamic acid: potential single crystal for nonlinear optical applications,” *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 17, pp. 14271–14278, Sep. 2020, doi: 10.1007/S10854-020-03983-7/METRICS.

[13] R. Ramesh Babu, K. Sethuraman, N. Vijayan, R. Gopalakrishnan, and P. Ramasamy, “Dielectric and structural studies on sulphamic acid (SA) single crystal,” *Mater Lett*, vol. 61, no. 16, pp. 3480–3485, Jun. 2007, doi: 10.1016/J.MATLET.2006.11.111.

[14] P. K. M. Lokhande, D. S. Patil, M. M. Kadam, and N. Sekar, “Theoretical Investigation of Optical and Nonlinear Optical (NLO) Properties of 3-Azabenzanthrone Analogues : DFT and TD-DFT Approach.,” *ChemistrySelect*, vol. 4, no. 34, pp. 10033–10045, Sep. 2019, doi: 10.1002/SLCT.201901681.

[15] M. Bursch, J. M. Mewes, A. Hansen, and S. Grimme, “Best-Practice DFT Protocols for Basic Molecular Computational Chemistry**,” *Angewandte Chemie - International Edition*, vol. 61, no. 42, Oct. 2022, doi: 10.1002/ANIE.202205735.

[16] M. K. Parte, P. K. Vishwakarma, P. S. Jaget, and R. C. Maurya, “Synthesis, spectral, FMOs and NLO properties based on DFT calculations of dioxidomolybdenum(VI) complex,” *https://doi.org/10.1080/00958972.2021.1880574*, vol. 74, no. 4–6, pp. 584–597, 2021, doi: 10.1080/00958972.2021.1880574.

[17] G. Rajasekar, M. K. Dhatchaiyini, and A. Bhaskaran, “Crystal growth, structural, optical, laser damage threshold, mechanical and DFT studies on a new metal-organic framework: Potassium boro (hemi) fumarate,” *J Mol Struct*, vol. 1230, p. 129663, Apr. 2021, doi: 10.1016/J.MOLSTRUC.2020.129663.

[18] Y. B. Shankar Rao, M. V. S. Prasad, N. Udaya Sri, and V. Veeraiah, “Vibrational (FT-IR, FT-Raman) and UV–Visible spectroscopic studies, HOMO–LUMO, NBO, NLO and MEP analysis of Benzyl (imino (1H-pyrazol-1-yl) methyl) carbamate using DFT calculaions,” *J Mol Struct*, vol. 1108, pp. 567–582, Mar. 2016, doi: 10.1016/J.MOLSTRUC.2015.12.008.

[19] N. Issaoui *et al.*, “Combined experimental and theoretical studies on the molecular structures, spectroscopy, and inhibitor activity of 3-(2-thienyl)acrylic acid through AIM, NBO,FT-IR, FT-Raman, UV and HOMO-LUMO analyses, and molecular docking,” *J Mol Struct*, vol. 1130, pp. 659–668, Feb. 2017, doi: 10.1016/J.MOLSTRUC.2016.11.019.

[20] V. Balachandran, A. Janaki, and A. Nataraj, “Theoretical investigations on molecular structure, vibrational spectra, HOMO, LUMO, NBO analysis and hyperpolarizability calculations of thiophene-2-carbohydrazide,” *Spectrochim Acta A Mol Biomol Spectrosc*, vol. 118, pp. 321–330, 2014, doi: 10.1016/j.saa.2013.08.091.

[21] K. Rajalakshmi, S. Gunasekaran, and S. Kumaresan, “Vibrational assignment, HOMO–LUMO and NBO analysis of (2S)-2-[(2-{[(2S)-1-hydroxybutan-2-yl]amino}ethyl)amino]butan-1-ol by density functional theory,” *Spectrochim Acta A Mol Biomol Spectrosc*, vol. 130, pp. 466–479, Sep. 2014, doi: 10.1016/J.SAA.2014.04.025.

[22] P. Karuppasamy, M. Senthil Pandian, P. Ramasamy, and S. Verma, “Crystal growth, structural, optical, thermal, mechanical, laser damage threshold and electrical properties of triphenylphosphine oxide 4-nitrophenol (TP4N) single crystals for nonlinear optical applications,” *Opt Mater (Amst)*, vol. 79, pp. 152–171, May 2018, doi: 10.1016/J.OPTMAT.2018.03.041.

[23] P. Karuppasamy, T. Kamalesh, M. Senthil Pandian, P. Ramasamy, V. Sunil, and A. K. Chaudhary, “Bulk crystal growth, crystalline perfection and optical homogeneities of 2AP4N single crystals for second and third order frequency conversion and terahertz (THz) device applications,” *Opt Mater (Amst)*, vol. 118, p. 111261, Aug. 2021, doi: 10.1016/J.OPTMAT.2021.111261.

[24] H. A. S. Al-Shamiri *et al.*, “Experimental and theoretical studies of linear and non-linear optical properties of novel fused-triazine derivatives for advanced technological applications,” *Sci Rep*, vol. 12, no. 1, p. 19937, Dec. 2022, doi: 10.1038/S41598-022-22311-Z.