

## REVIEW

# A Review on the Non-Linear Optical Performance of Picric Acid based Crystals

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This review delves into the nonlinear optical characteristics of crystals derived from picric acid, providing a comprehensive analysis of their unique properties and potential applications in the realm of nonlinear optics. Picric acid, with its distinctive molecular structure, has been widely explored for its nonlinear optical behaviour, making it a fascinating subject for research and development. The review begins by elucidating the fundamental need and significance of crystal growth. The summary of preparation, spectral analysis and nonlinear optical characteristics and the significance of picric acid as a promising material in this domain is also discussed. The interpretation of nonlinear behaviour in optical properties of various compounds of picric acid is reviewed and discussed. The structural data of aminoacidic picrate crystals in the field of non-linear applications are reviewed. The conceptual background of nonlinear optical properties is well deliberated and used in order to have a better knowledge of the optical behaviour of the picrate crystals. UV-VIS spectroscopy and Second harmonic efficiency of picric acid compounds are also briefly discussed. In conclusion, this review provides a comprehensive overview of the nonlinear optical performance of picric acid-based crystals, offering valuable insights for researchers, scientists, and engineers working in the field of nonlinear optics.

Keywords: Non-Linear, Picric acid, Powder SHG, Optical property.

## **INTRODUCTION**

The significance of crystals in modern technology cannot be overstated. Substantial advances in the science and technology of crystal growth have resulted in huge advancements in a variety of industries that use crystal-based technologies. Progress in crystal growth is highly demanded due to recent advancements in the various fields including optics [1]. Crystals value has expanded beyond ornamentation to a variety of beneficial uses in optical, electrical and optoelectronic systems. Because the perfect crystals with appropriate size is required for a variety of other applications, crystal growth has evolved into a multidisciplinary field involving subjects from basic science as well as engineering.

Non-linear optics (NLO) studies are carried out by analyzing interactions of applied light energy in various materials, which will generate the new light waves with different physical features. Several industries required information technology as well as highly demands NLO materials. Non-linear optical (NLO) materials react non-linearly to the applied laser beam and new optical properties are observed in the output laser waves.

Because of their practical uses in harmonic frequency production, modulated waves, processing signals and laser advanced technology, the quest for novel materials having nonlinear property is an essential endeavour. Non-linear optical (NLO) crystals have several uses in telecommunications, including efficient signal processing and optical information storage systems. For different devices in the field of optoelectronics, the property of second harmonic generation and transparency are required in the NLO crystals [2-4].

A broad range of organic compounds with donor-acceptor groups are synthesized, mostly for the second order harmonic

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generation but also for third order non-linear optics. Acceptordonor groups are commonly added to organic crystals with conjugated configuration in order to make NLO materials with high hyperpolarizability property. Organics are substantially more advanced in NLO applications than inorganic materials. Most viable materials, particularly those used in high-power applications, are inorganic. Organic materials, on the other hand, are thought to be more structurally varied and so to hold greater long-term potential than inorganic materials. Organic solids offer a wide range of fascinating characteristics that are virtually always adjustable. Throughout the last three decades, a growing interest have been identified in these systems due to the discovery of novel features such as spin less conductivity, non-linear optical responses and superconductivity. Moreover, semiorganics are being investigated because they have features shared by both organic and inorganic materials [5,6].

Picric acid is similarly identified as picronitric acid, phenol trinitrate, carbazotic acid, trinitrophenol, melinite, 2-hydroxy-1,3,5-trinitrobenzene, pikrinsaure, acide picrique. Picric acid is a yellow crystalline, toxic, explosive substance that is commonly used in laboratories to identify activated chemicals. Picric acid is also utilized to make charge transfer complexes. Picric acid is primarily used in the explosive and dye industries. The addition of water results in the desensitize picric acid. The wetted product is far less responsive to shock than the dry acid. Picric acid reacts strongly with a broad variety of substances and rapidly generates picrate salts. Several of these compounds are more sensitive and vulnerable to stress than the acid itself.

The crystal structures demonstrate the picrate anion's unique capabilities as an adaptable counter-ion for cation complexation. A taxonomy of picrate cation interactions, as well as associated terminology, is offered from the literature. Since picrate is often used as a counter-ion in many complex networks and the separation and conveyance of alkali and alkaline earth metal atoms. The findings of this investigation and analysis of picrate flexible reactions have broad scientific and economic ramifications. The data presented here should also be considered for systems that use picrate as a counter ion and need much performance and discrimination towards a certain ion. The vast array of picrate cation association coordination and geometry possibilities may have a substantial impact on such systems.

Due of conformational constraints, the picrate is engaged in the oxygens in a few configurations. Experimental evidences for the nitro group's coordination ability to alkali metal atoms are known. Picrate is therefore a multifunctional mono/bi/tri edentulous ligand. It is found in alkali and alkaline metal atomic complexes including both natural and synthetic ion ophores. Another important aspect of nitro group is their capacity for creating coordination compounds with aromatic hydrocarbons, especially those conjugated with alkyl groups or expected to own electron-donating characteristics. Picric acid undergoes this action often and the complexes are frequently attractive crystalline solids that are useful for organic chemistry.

**Theory of non-linear optics:** The second order susceptibility  $\chi^{(2)}$  which discusses second harmonic generation in the non-centrosymmetric materials, The quadratic term responsi-

ble for third harmonic production, stimulated Raman scattering, phase conjugation and optical bistability is third order susceptibility. As a result, the induced polarization can double the fundamental frequency to produce second, third and even higher harmonics.

If the incident field is of sinusoidal nature of the form:

$$E = E_0 \cos \omega t$$

Then eqn. 3 can be written as:

 $P = \varepsilon_o \chi^{(1)} E_o \cos \omega t + \varepsilon_o \chi^{(2)} E_o^2 \cos^2 \omega t + \varepsilon_o \chi^{(3)} E_o^3 \cos^3 \omega t + \dots$ 

Using trigonometric relations:

$$P = \frac{1}{2} \varepsilon_o \chi^{(2)} E_o^2 + \varepsilon_o (\chi^{(1)} + \frac{3}{4} \chi^{(3)} E_o^2) E_o \cos \omega t + \frac{1}{2} \varepsilon_o \chi^{(2)} E_o^2 \cos 2\omega t + \frac{1}{4} \varepsilon_o \chi^{(3)} E_o^3 \cos 3\omega t + \dots$$

where the first term is constant and the second follows external polarization and is known as the first or basic harmonic of polarization, the third oscillates at a frequency of  $2\omega$  and is known as the second harmonic of polarization and the fourth is known as the third harmonic of polarization.

One of the most often used non-linear media techniques is the generation of second harmonic radiation, in which radiation at frequency is turned into radiation at frequency 2 $\omega$ . In general, this process occurs through virtual transitions, in which two photons are simultaneously destroyed and a single photon at 2 $\omega$  is created in a single quantum mechanical process. This approach can convert almost all of the incident fundamental energy into the second harmonic and it is frequently used in laboratories to create coherent optical light with wavelengths other than the fundamental of a fixed wavelength laser source. In most crystalline materials, the vectors P and E are not necessarily parallel, the co-efficient  $\chi$  must be treated as tensors, since the non-linear polarizability  $\chi^{(2)}$  depends on direction of propagation, polarization of electric field and orientation of the optics axis of the crystal.

The second order polarization can be represented by the equation:

$$P_i^{(2)} = \varepsilon_0 \Sigma \chi_{ijk}^{(2)} E_j E_k$$

where i, j, k represents co-ordinates x, y, z. If the molecule or crystal is centro-symmetric (*i.e.* crystal symmetric about a point) then  $\chi^{(2)} = 0$ . Therefore for non-centrosymmetric crystal, polarization can be related as:

$$\mathbf{P} = \varepsilon_{0} \boldsymbol{\chi}^{(1)} \mathbf{E} + \varepsilon_{0} \boldsymbol{\chi}^{(2)} \mathbf{E}^{2}$$

which passes second order linearity. Only crystal lack in inversion symmetry exhibit SHG.

In non-linear processes such as harmonic generation, sum and difference frequency generation and so on, phase matching is required for efficient frequency conversion (*i.e.* a suitable phase connection between the interacting waves is maintained throughout the propagation path). In order to get an effective non-linear interaction, the phase mismatch produced by medium dispersion should be close to zero, as shown by the relation:

$$\Delta K = \frac{4\pi}{\lambda}$$

The second harmonic conversion efficiency is a necessary requirement for selecting a non-linear optical crystal, frequency conversion procedure.

$$\eta = \frac{P^{2\omega}}{P^{\omega}} = 2 \left(\frac{\mu_o}{\varepsilon_o}\right)^{3/2} \frac{\omega^2 d^2 l^2 \sin^2(\Delta K 1/2)}{n^3 (\Delta K 1/2)^2} \frac{P^{\omega}}{A}$$

where  $\mu_o$ ,  $\epsilon_o$ , n,  $\omega$ , l, A and d are respectively the permeability of free space, permittivity of free space, index of refraction, angular frequency of fundamental wave, length of crystal, cross area of beam respectively in which

$$\Delta K = K^{2\omega} - 2K^{\omega}$$
$$K = \frac{2\pi}{\lambda}$$

The value of  $\eta$  is also affected by the phase mismatch of the interacting waves, the strength of the input laser beam, the crystal's refractive index and the direction of the incident beam with respect to the optical axis. The temperature range where high conversion efficiency may be attained is inversely related to crystal length. It is also affected by the temperature dependency of the refractive indices involved, which is given by:

$$\Delta T = \frac{0.44\lambda_{i}}{ld} \frac{(n_{o}^{2\omega} - n_{o}^{\omega})}{dT}$$

where  $\Delta T$  is full width at half maximum (FWHM) of the temperature range in which second harmonic generation is possible may be due to the ambient temperature variations or by absorption losses in the crystal.

The nitrophenol family of crystals has caught the attention of scientists over the last decade due to its high laser damage threshold, broad transparency windows and strong NLO coefficient [7-9]. Picric acid (2,4,6-trinitrophenol) was selected for this investigation because it has three electron withdrawing nitro groups, making it a good-acceptor for neutral carrier donor molecules. Picric acid has a stimulating -OH group and neutralizing nitro groups in its structure. Picric acid stands out among organic materials because of its proclivity to form salts or charge transfer molecular complexes with a wide range of organic molecules [10]. Picric acid derivatives are utilized in human medicine for things like burn treatment, antiseptics and astringents [11]. Charge transfer complexes are now very important since they may be used to have non-linear optical properties as well as electrical conductivities. The type of the associates engaged in the formation of bond influences charge transfer transiton in picrate complexes [12]. The metal derivatives of picric acid are useful in homoeopathic treatment and it exhibits an astonishing diversity in the bonding of metals. Most picric acid compounds exhibit significant second order NLO activity ( $\chi^2$ ) and promote acentric packing, resulting in high hyperpolarizability ( $\beta$ ). The extension of benzene derivatives has allowed for a rise in the amount of electrons and length of, resulting in a significant increase in hyperpolarizability value [13].

Picric acid not only acts as an acceptor in the production of various compounds, but it also acts as an acidic ligand in the synthesis of salts *via* specific electrostatic interactions. Due to these versatile properties of picric acid, we are encouraged to make an analyses review of various picrate crystals in different roles and its characterization studies were compared and tabulated.

Amino acid picrates: Recent precedent has drawn the attention of researchers to study of amino acid picrates. Significant attempts have been undertaken to mix amino acids into fascinating matrices to develop remarkable NLO materials that can compete with proven inorganic materials such as potassium dihydrogen phosphate (KDP), borates and niobates. The significance of amino acids in NLO applications stems from the fact that nearly all amino acids include an asymmetric carbon atom and crystallise in a non-centro symmetric space group. In solid form, many amino acids have a deprotonated group and a protonated group. Because of its dipolar orientation, it has various unique qualities, including chirality and the lack of strong conjugated bonds and a zwitterionic structure that increases crystal hardness [14]. The NLO properties have been enhanced due to the zwitterionic nature and broad transparency range of organic acid when combined with amino acid.

Despite the fact that picric acid is explosive in nature, we were driven to investigate the different amino acid picrates due to their critical uses. Picric acid, which forms crystalline picrates with amino acid such as L-alanine, can be thought of as the primary building block of more complicated amino acids, displaying significant non-linear properties. The structure and vibrational spectra of L-alanine and L-alaninium picrate were investigated, as well as the nucleation kinetics and hardness characteristics [15,16]. It also included-alaninium picrate [17, 18]. L-Aspararinium is a neutral amino acid containing the side-chain functional group carboxamide. Anitha et al. [19] determined the structure of L-aspararinium picrate crystal, whereas Liu et al. [20] investigated the growth and physical characteristics. Elleuch et al. [21] reported the comprehensive assignment of the vibrational bands. L-Arginine is thought to provide a variety of desirable biological qualities. In several enzymes, L-arginine has the guanidinium group as essential binding site for numerous hydrogen bond acceptors and has lately received a lot of attention. Martins et al. [22] present a spectroscopic and thermal study of rare-earth picrate complexes with L-arginine.

L-Glutamine side-chain is an amide generated by replacing the glutamic acid side-chain hydroxyl with an amine functional group, resulting in glutamic acid amide. Amalanathan et al. [23] investigated the interaction of charge transferring mechanism and tetrahedral properties of L-glutamine picrate. Glycine is the most basic amino acid, in addition it may combine with other chemical and inorganic components to produce a variety of new molecules. It crystallizes in three distinct forms, namely  $\alpha$ ,  $\beta$ ,  $\gamma$ . Meanwhile the glycine molecule may exist in a zwitterionic state, it can coordinate with positive, negative and neutral substances. Kai et al. [24] reported the crystal structure of glycine picrate (GP) whereas Devi et al. [25] presented a single crystal of GP produced by simultaneous slow evaporation and chilling process. Shakir et al. [26-28] produced and grew single crystals using a gradual cooling approach. A CuCl<sub>2</sub> doped GP, ferroelectricity in glycine picrate and development of glycine picrate by conventional and SR methods were reported by Thilagavathy & Ambujam [29].

There has been a lot of interest in mixing histidine with acids and salts to create new non-linear optical samples. Histidine

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compounds regularly fit in to non-centrosymmetric space groups, which is an important criteria for non-linear optical applications. A review of the literature finds that only a little amount of study on the different features of this complex has been documented. Rajarajan et al. [30] used slow evaporation to produce and construct a novel semi organic crystal PbNO<sub>3</sub> doped histidine picrate non-linear material. Ramasamy et al. [31] reported on the crystal formation, structure and characterization of L-isoleucine picrate. L-leucine L-leucinium picrate is a member of the vast organic NLO family, in which L-leucine L-leucinium works as a donor and picric acid as an acceptor of electrons. Anitha et al. [32] determined the crystal structure of this molecule. Bhagavannaraya et al. [33] investigated it using infrared technology. Guidara et al. [34] revealed detailed vibrational band allocations. L-Methionine is an essential amino acid that include sulphur and commonly found coordinated inside proteins due to its hydrophobic side chain. Anitha et al. [35] characterized the crystal structure, whereas Mary et al. [36] performed a vibrational spectrum study. Another work studied the chemical construction of DL-phenylalanine DLphenylalaninium picrate [37].

L-Proline is a common amino acid found in collagen besides unique among amino acids and Edwim et al. [38] investigated L-prolinium picrate using vibrational spectroscopy. Uma devi [39] and Anitha et al. [40] reported the growth and its characterization. Natarajan et al. [41] investigated the structural and spectroscopic properties of L-threoninium picrate. Petrosyana et al. [42] revisit the structure of L-tryptophan picrate and analyze its infrared spectrum. It is also noted that the detected infrared spectrum differs from the spectrum given in for the identical crystal. Gowri et al. [43] described the spectral, thermal and optical characteristics. Many papers on L-valinium picrate crystals have been published. L-valinium picrate infrared, NMR, vibrational spectrum and Raman spectroscopic experiments were discussed [44]. L-Valinium picrates, both pure and doped, were studied [45-49]. Growth and characterization of non-linear optical crystal L-valinium picrate have previously been described [50-54]. This research resulted in the notion of comparing and tabulating the XRD analysis, optical and SHG examinations of diverse amino picrate crystals. The crystal data for various amino picrates various in different roles and its characterization studies are summarized in Table-1.

	TABLE-1 CRYSTAL DATA FOR VARIOUS AMINO PICRATES								
S. No.	Amino picrates	Method	Crystal system	Lattice parameters (Å)	Space group	UV-cut off (nm)	S.H.G efficiency w.r.t. KDP	Ref.	
1	L-Alanine alaninium picrate	Slow evaporation	Monoclinic	a = 8.263(3) b = 7.515(2) c = 15.536(4)	<i>P</i> 2 <sub>1</sub> <i>P</i> 2 <sub>1</sub> <i>P</i> 2 <sub>1</sub>	**	1.47	[15]	
2	L-Alanine L-alaninium picrate monohydrate	Slow evaporation	Monoclinic	a = 8.268(2) b = 7.510(2) c = 15.540(3)	<i>P</i> 2 <sub>1</sub>	**	**	[16]	
3	β-Alanine β-alaninium picrate and DL- phenylalanine DL- phenylalaninium picrate	Slow evaporation	Triclinic	**	$P\overline{1}(C_i)$	**	**	[17]	
4	Di-β-Alaninium picrate	Slow evaporation	Triclinic	a = 4.5764(9) b = 12.060(2) c = 12.291(3)	ΡĪ	**	**	[18]	
5	L-Asparaginium picrate	Slow evaporation	Monoclinic	a = 10.367(4) b = 5.1611 (7) C = 13.120(3)	<i>P</i> 2 <sub>1</sub>	**	**	[19]	
6	L-Asparaginium picrate	Slow evaporation	**	LASP(Co <sup>2+</sup> ) a = 10.354 b = 5.155 c = 13.119	**	Characteristic absorption band-430 nm No absorption band-430nm and 1400nm	66	[20]	
7	L-asparaginium picrate	Slow evaporation	Monoclinic	a = 10.3608(2) b = 5.1506(1) c = 13.1189(2)	<i>P</i> 2 <sub>1</sub>	**	**	[21]	
8	Copper chloride doped glycine picrate	Slow evaporation	Monoclinic	a = 14.968 b = 6.722 c = 15.165	**	**	**	[27]	
9	Glycine picrate	Slow cooling method	Monoclinic	$\frac{PXRD}{a = 14.962}$ b = 6.722 c = 15.169	**	Absorption band 450	2.34	[26]	
10	Glycine picrate	Solution growth	Monoclinic	a = 14.9628(8) b = 6.7216(1) c = 15.1746(8)	**	400-1000nm	**	[25]	

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11	Glycine picrate	Sankaranarayannan and Ramasamy (SR) & Slow evaporative solution technique (SEST)	Monoclinic	a = 14.88 b = 6.69 c = 15.08	P2 <sub>1/</sub> a	90% transmission in entire visible region	2	[28]
12	Glycine picrate	Slow evaporation	Monoclinic	a = 14.968(3) b = 6.722(2) c = 15.165(3)	<i>P</i> 2 <sub>1/</sub> a	**	**	[24]
13	L-Isoleucinium picrate	Slow evaporation	Monoclinic	a = 9.970(3) b = 6.425(2) c = 12.871(4)	P2 <sub>1</sub>	440	16	[31]
14	L-Leucine L-leucinium picrate	Slow evaporation	Triclinic	a = 7.1470(5) b = 11.8540(8) c = 15.4560(1)	<i>P</i> 1	**	**	[32]
15	L-Leucine l-leucinium picrate	Slow evaporation	Triclinic	a = 7.129(2) b = 11.841(4) c = 15.409(6)	<i>P</i> 1	Characteristic absorption band360 and 422 Drastic reduction in absorption 80 and 900	1.5	[33]
16	L-Leucine L-leucinium picrate	Slow evaporation	Triclinic	a = 7.132(5) b = 11.799(9) c = 15.372(2)	<i>P</i> 1	**	**	[34]
17	DL-Methionine DL- methioninium picrate	Slow evaporation	Triclinic	a = 7.076(1) b = 12.102(1) c = 14.895(2)	PĪ	**	**	[35]
18	DL-Phenylalanine DL- phenylalaninium picrate	Slow evaporation	Triclinic	a = 7.333(3) b = 13.737(3) c = 15.381(6)	ΡĪ	**	**	[37]
19	L-Prolinium picrate	Temperature reduction method	Monoclinic	a = 10.901 b = 5.351 c = 12.466	**	480	52	[39]
20	L-Threoninium picrate	Slow evaporation	Monoclinic	a = 9.235(5) b = 6.265(5) c = 12.727(5)	P2 <sub>1</sub>	Absorption increases- 200and 356 Absence of absorption-450 and 1100	43	[41]
21	L-Tryptophanium picrate	Slow evaporation	Orthorhombic	a = 7.7745(7) b = 15.462(2) c = 31.088(3)	P212121	**	**	[42]
22	L-Tryptophanium picrate	Slow evaporation	Orthorhombic	a = 7.801 b = 15.481 c = 31.143	P212121	Transmission 5-1000 nm is app 95% Absence of absorption-450 and 1100	Very high output of 1.1 V with input laser power of 1.9 mJ/pulse compared to 9 mV of KDP	[43]
23 24	L-valinium picrate DL-valine DL-valinium	Slow evaporation Slow evaporation	Monoclinic Monoclinic	** **	$\frac{P2_1}{P2_{1/}n}$	** **	**	[44] [45]
25	L-Valinium picrate	Slow evaporative solution growth	Monoclinic	a = 9.96 b = 6.29 c = 12.65	**	425	56.5 (KDP) 8.96 (Urea)	[47]

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26	L-Valinium picrate (LVP) (pure)	Slow evaporation method	Monoclinic	a = 9.7 b = 6.29 c = 12.64		425	Intensity of output light observed- 1300 mV	[48]
	10 mol% Glycine mixed L-valinium picrate (10 GVP)		Orthorhombic	a = 9.22 b = 9.69 c = 19.06		460	Intensity of output light observed- 425 mV	
	50 mol% glycine mixed L-valinium picrate (50 GVP)		Monoclinic	a = 10.01 b = 6.31 c = 12.67		450	Intensity of output light observed- 1050 mV	
27	L-valinium picrate (LVP) (pure)	Slow evaporation	**	a = 10.021 b = 6.312 c = 12.711	**	Absence of absorption-470 and 900	60	[49]
	Ni-doped LVP			a = 9.980(3) b = 6.283(8) c = 12.671(4)			45	
28	L-Valinium picrate	Slow evaporation	Monoclinic	a = 9.96 b = 6.23 c = 12.64	**	470	**	[50]
29	L-Valinium picrate	Slow evaporation	Monoclinic	a = 9.96 b = 6.23 c = 12.64	<i>P</i> 2 <sub>1</sub>	470	57	[51]
30	L-Valinium picrate	Slow cooling solution growth	Monoclinic	a = 9.9707(2) b = 6.3137(3) c = 12.5910(8)	P2 <sub>1</sub>	**	Very high output of 1.3 V with input laser power of 1.9 mJ/pulse compared to 9mV of KDP	[52]
31	L-Valinium picrate	Slow evaporation	Monoclinic	a = 9.9770 b = 6.2394 c = 12.6420	**	480	60	[53]
32	L-Valinium picrate	Slow evaporative solution growth	Monoclinic	a = 9.2912 b = 6.3973 c = 12.5409	**	380	2	[54]
33	Glycine picrate	Slow cooling method	Monoclinic	a = 14.968 b = 6.722 c = 15.165	**	470	**	[55]
34	Triglycine sulpho- picrate(Tgspi)	Slow evaporation	Monoclinic	a = 5.214(2) b = 11.351(4) c = 10.658(13)	**	250	0.64	[56]
35	DL-Methionine DL- methioninium picrate	Slow evaporation	Triclinic	**	PĪ	**	**	[36]
36	L-Prolinium picrate	Slow evaporation	Monoclinic	a = 10.909 b = 5.352 c = 12.474	<i>P</i> 2 <sub>1</sub>	**	**	[40]
37	L-valinium picrate	Slow evaporation	Monoclinic	a = 9.9714(13) b = 6.2930(5) c = 12.6480(9)	<i>P</i> 2 <sub>1</sub>	**	**	[57]
**Nc	ot mentioned							

**Organic molecular systems:** Organic materials, in addition to amino acid picrates, have already been recognized as being of significant relevance among the materials causing NLO effects, notably the second harmonic generation (SHG), attributed to their chemical versatility to design and build various unique compounds [58]. Organic materials have also strong optical susceptibilities, inherent ultrafast response times and laser damage thresholds. Furthermore, due to their reduced cut off wavelengths and a large optical transparency window in the visible area, these materials are subject to substantial research. Organic compounds with high non-linear activity often have a -electron conjugated structure. The infrastructure for introducing the charge asymmetry necessary for second order non-linearity is provided by the donor and acceptor groups. Organic crystalline charge transfer (CT) connections have been used in both nanoemulsions and organic semiconductors. Nonlinear optical (NLO) applications may be found in several organic CT crystals composed of picric acid (donor) and organic acceptor (basic) molecules. Semiorganic NLO crystals have however piqued the interest of researchers because they have been recommended as a novel strategy for materials with remarkable unique properties that incorporate the properties from both inorganic and organic crystals, including such high damage threshold, less deliquescence and high non-linear coefficients [58,59].

The NLO activity has been investigated in a wide range of inorganic, organic and organometallic molecular systems. Dhanabal et al. and others examined the spectral characteristics and antimicrobial properties of 2-methylimidazolinium picrate, which forms a hydrogen bond between the hydrogen of the protonated nitrogen atom and the negatively charged oxygen atom [60]. The donor-acceptor energy would be relatively great in this case due to the hydrogen bonding that occurs between molecules. Basoglu et al. [61] theorized an ideal molecular structure, vibrational frequency and modes of free 8-hydroxyquinolinium picrate (8-HQP). Krishnakumar & Nagalakshmi [62] produced 8-HQP, which possesses donor acceptor molecular system. They have also conducted experimental research on its vibrational spectroscopic characteristics. Sudharsana et al. [63] explored the theoretical and experimental research of 2,5-dichloroanilinium picrate.

Obulichetty & Saravanabharathi [64] emphasised the photoluminescence of crystalline benzimidazolium picrates are controlled by supramolecular structure. This exhibit  $\pi$ - $\pi$  stacking involving the cation (benzimidazolium) and anion (picrate), as well as n-interaction and extended networks of hydrogen bonds in the solid state. As an antifungal agent, imidazole, an aromatic heterocyclic alkaloid, is found in commercial pharmaceutical goods. As a cationic unit, the asymmetric unit includes two imidazole molecules, one picrate ion and one water molecule. The molecules in the crystal are linked by N-H...O, N-H..N and O-H-O hydrogen bonds and imidazolium picrate was synthesized using a gradual cooling approach [65]. Imidazoleimidazolinium picrate monohydrate (IIP) crystals were grown by Vivek & Murugakoothan [66,67] using slow evaporation and Sankaranarayanan-Ramasamy (SR) method, with the author claiming that the SR method grown unidirectional IIP crystals have higher transmittance and hardness values than conventional method grown IIP crystals. Amalanathan et al. [68] carried out analysis of the molecular structure and vibrational spectra of napthalene picrate using DFT calculations. Their structural, thermal, optical properties given by Chandramohan et al. [69] in which the formation of the complex during the reaction of napthalene with picric acid is firmly proven via manifestation of major donor and acceptor bands in the resulting compound.

Anandha Babu *et al.* [70] studied the structural, thermal, linear and non-linear optical characteristics of dimethylamm-

onium picrate (DMAP) formed by slow evaporation technique, while Magesh et al. [71] explored the same compound DMAP utilizing slow evaporation solution growth and Sankaranarayanan-Ramasamy (SR) method. It is found that crystal created using the SR approach has more perfection and the transmission is almost 14% higher than crystal grown using the usual slow evaporation method. Protonation of the pyridine ring nitrogen atom enhances the hydrogen bonding contact between picric acid and picolinic acid during complex formation. Picric acid's interaction with a heterocyclic molecule (picolinic acid) has been studied and a crystalline complex of picolinum picrate monohydrate (PPM) has been produced [72]. Dhanabal et al. [73,74] studied the spectral, thermal and optical properties of crystals of 4-dimethylaminopyridinium picrate and discovered that benzotriazolinium picrate is a promising NLO candidate because of the inclusion of the donor and acceptor group in the molecule, which provides infrastructure to consider introducing charge imbalance. This charge unbalance is required by SHG features.

Mohana Priyadarshini *et al.* [75,76] studied the synthesis, structure and characterization of *m*-toluidinium picrate and *o*-toluidinium picrate. It is reported that N–H…O and C–H…O are responsible for crystalline cohesion. A three-dimensional network is formed by the ions and hydrogen bonds. Intermole-cular hydrogen bonding between the nitrogen of *p*-toluidine and the phenolate ion of picric acid results in the formation of *p*-toluidinium picrate. Dhanabal *et al.* [77-79] studied the synthesis, structural, thermal and non-linear optical characterization of 4-hydroxytetramethylpiperazinium picrate crystals, as well as the antimicrobial activity of 4-piperidinium carboxyl-amide picrate and 3,5-dimethylpyrrazolinium picrate against various bacteria and fungi species.

Sethuram *et al.* [80,81] reported the synthesis and characterization of a 2D network of intermolecular N–H···O and C– H···O hydrogen bonds in 2-aminomethylpyridinium picrate crystal. Jegannathan *et al.* [83] reported the vibrational spectra of nico-tinium picrate, which belongs to the space group  $P_1/c$ and contains nicotinium as a cation and picrate as an anion. Bindya *et al.* [84] examined the crystal structure of amitriptylinium picrate, which revealed that donors from amitriptyline and acceptors from picrate form intermolecular C–H···O hydrogen bonds and N–H···O salts bridges.

Ma *et al.* [85] synthesized dinitroazetidinium picrate and investigated its thermal behaviour using DSC and TG-DTA methods. The first exothermic thermal decomposition reaction's kinetic model function and kinetic parameters were determined. This is very important in determining thermal stability in nonisothermal conditions and in determining the compatibility of energetic materials. The energy transfer mechanism in the complex was accelerated by overlapping the donor's emission and acceptor's absorption spectrums. Based on the luminous feature of the Eu(III) ion and its prospective applications, the Eu(III) complex with tetraethylene glycol (EO4) and picrate anion (Pic) serving as ligands crystallizes in triclinic with space group  $P\overline{1}$  [86]. Additionally, picrate complexes of Nd(III) and Eu(III) with 2-azacyclononanone produced by slow evaporation form in monoclinic with space group  $P2_1/n$  [87]. According to Naseema *et al.* [88] urea and picric acid on reaction form urea picrate *via* the charge transfer process, with urea acting as the electron donor and picric acid acting as the acceptor species in the intermolecular charge transfer complex with a cutoff wavelength of 450 nm. There is no light absorption at 532 nm and it has been suggested that urea picrate might be used in optical device applications such as optical limiters. Shanthi *et al.* [89] identified *N*,*N*-dimethylurea picrate (MDUP) crystal to be a non-linear optical and ferroelectric material and it is one of the organic crystals with excellent optical characteristics when compared to urea. Anandha Babu *et al.* [90] discovered a strong hydrogen bond between the –OH group of picric acid and the dimethylammonium cation. Inside the DMUP molecule, three intramolecular hydrogen bonds exist.

Picric acid and 2',6'-dimethoxyflavone are bound by hydrogen bonds formed the -OH bonding. Moreover, this hydrogen creates an intermolecular hydrogen connection with the *ortho*-nitro group's O atom. Lago *et al.* [91] reported a stacking interaction between the benzopyrone component of flavones and picric acid. Chantooni Jr. & Britton *et al.* [92] examined the X-ray crystal structure of 1:1 dimethylpicric acid-acenaphthene complex, in which the molecules are arranged in stacks of alternating picric acid and acenaphthene molecules. Rajarajan *et al.* [93] reported the slow evaporation method to yield a high crystallinity diphenylamine picrate crystal with a UV cutoff of less than 300 nm. SHG measurements suggest that a material with an input of 6.1 mV mj/pulse and an output of 8 mV mj/pulse in comparison to KDP (6.8 mV) is a promising material for NLO characteristics.

Vesta *et al.* [94] reported trinitrophenol methyl *p*-hydroxybenzoate (TNMPHB) belongs to the centric crystal class and has a high value of hyperpolarizabilities. Gowri *et al.* [95] created an adenosinium picrate crystal in which adenosine works as the donor and picric acid as the electron acceptor, providing the molecule with the ground state charge asymmetry essential for second-order non-linearity. Rajarajan *et al.* [96-97] investigated acetamide-picrate and succinic-picrate crystals doped with copper sulphate and discovered that both crystals have an absorption spectrum results in desirable for NLO crystals.

Muthu et al. [98,99] reported the crystal structure of (chloro) tris(thiourea-kS)cadmium(II) picrate (CTTCP), in which the precursor picric acid crystallizes in the non-centrosymmetric space group Pca21, while the complex crystallises in the centrosymmetric space group P1. The FTIR and single XRD measurements verified the product generation and the structure of tetrakis(thiourea) zinc(II) picrate (TTZP) was investigated. Because of their biological activity and non-linear optical features, thiosemicarbazones have recently sparked a lot of interest in co-ordination chemistry. Santhakumari et al. [100] studied the synthesis, growth, optical and antibacterial properties of thiosemicarbazide cadmium(II) picrate (TSCPACD) crystal, which has a stronger antifungal impact. The addition of carbonyl and the metal atom results in a rise in antifungal activity. In this study, various crystals of organic, semi-organic and charge transfer derivatives of picric acid were presented. These included the cocrystals of picric acid/acetophenone, ortho-nitroaniline with picric acid (ONAP) using two different methods, dimethyl ammonium picrate (DMAP), paracetamol-picric acid (PP), Lhistidine di picrate, benzimidazole benzimidazolium picrate, 4-nitroaniline-picric acid (2/1), potassium hydrogen phthalate picrate (KHPP), 6-methylbenzotriazolinium picrate crystal, picric acid doped ADP single crystals and pure and picric acidadded KDP crystals [101-113]. The study compared and summarized the structure determination, UV-visible absorption and second and third harmonic generation investigations of several picrate crystals. The crystal data for various organic picrates in different roles and its characterization studies are summarized in Table-2.

	TABLE-2 CRYSTAL DATA OF VARIOUS ORGANIC PICRATE CRYSTALS								
S. No.	Picrate crystals	Method	Crystal system	Lattice parameters (Å)	Space group	UV-cut off (nm)	Non-linear property- S.H.G efficiency w.r.t. KDP/THG	Ref.	
1	2-Methylimida- zolinium picrate	Slow evaporative solution growth	Monoclinic	a = 17.360(13) b = 11.8172(14) c = 14.734(7)	C2/c	380	S.H.G efficiency -2	[60]	
2	8-Hydroxyquino- linium picrate	Slow evaporative solution growth	Monoclinic	a = 8.26 b = 9.25 c = 19.90	P2 <sub>1/c</sub>	230	Can be used as third harmonic generator of Nd: YAG laser to produce nearly 354.6nm	[62]	
3	2,5- Dichloroanilinium picrate	Slow evaporative solution growth	Monoclinic	**	**	Absorption around: 210 and 357 nm Completely transparent: 470 and 1100 nm	S.H.G efficiency -0.8	[63]	
4	2-Methyl benzimidazolium picrates	Slow evaporation	Monoclinic	a = 9.147(5) b = 13.916(5) c = 11.961(5)	<i>P</i> 2 <sub>1/</sub> n	Two absorption maxima one at 369 nm and other at 412 nm	**	[64]	
5	Imidazolium picrate (IP)	Slow cooling solution growth	Orthorhombic	a = 8.944(2) b = 13.496(5) c = 20.195(7)	P bca	No absorption between 520 nm and 800 nm Absorption between 470 nm and 520 nm	**	[65]	

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6	Imidazole- imidazolinium picrate monohydrate	Slow evaporation and slow cooling method	Orthorhombic	a = 3.8180(1) b = 20.8160(8) c = 21.4420(8)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	69% transmission in entire visible region	S.H.G efficiency 3.6	[66]
7	Imidazole- imidazolinium picrate monohydrate(IIP)	Sankaranarayanan -Ramasamy(SR)	Orthorhombic	a = 3.818 b = 20.816 c = 21.442	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	76% transmission in entire visible region Lower cutoff -378	S.H.G efficiency 3.6	[67]
8	Napthalene picrate	Slow evaporative solution growth	Monoclinic	a = 16.248(5) b = 6.871(2) c = 14.306(5)	P2 <sub>1/</sub> a	Absorption maxima at 380 nm No significant absorption at 532 nm	SHG nature verified through preliminary NLO testing which attributes to the noncentrosymmetry nature	[69]
9	Dimethylammonium picrate (DMAP)	Slow evaporation	Orthorhombic	a = 9.995(3) b = 11.119(8) c = 21.326(7)	Pca2 <sub>1</sub>	500	S.H.G efficiency 2	[70]
10	Dimethylammonium picrate (DMAP)	Slow evaporation solution growth (SEST) and Sankaranarayanan -Ramasamy (SR)	**	**	**	Transmittance of SEST and SR method grown crystal were 36% and 50% Lower cutoff: 493	**	[71]
11	Picolinum picrate monohydrate (PPM)	Slow evaporation solution growth	Monoclinic	a = 5.4091(5) b = 9.9414(9)	<i>P</i> 2 <sub>1/</sub> n	nm 50% transparency Lower cutoff-	**	[72]
12	4-Dimethylamino- pyridinium picrate	Slow evaporation solution growth	Monoclinic	c = 27.511(2) a = 15.3432 b = 12.4239 c = 15.7860	**	4 /4nm Strong Absorption at 280 and 379nm No absorption between 480 and 900 nm Lower cutoff: 370 nm	S.H.G efficiency 32	[73]
13	Benzotriazolinium picrate	Slow evaporation solution growth	Monoclinic	a = 9.2349(8) b = 11.9272(11) c = 12.8848(12)	<i>P</i> 2 <sub>1/</sub> c	Strong absorption at 370 nm No absorption between 470 and 900 nm	S.H.G efficiency 2	[74]
14	M-Toluidinium picrate	Slow solvent evaporative solution growth	Monoclinic	a = 12.3595(5) b = 16.9012(6) c = 7.4301(3)	P2 <sub>1/</sub> c	98% transmission between 510 and 1100 nm Lower cutoff: 488	**	[75]
15	<i>o</i> -Toluidinium picrate	Slow solvent evaporative solution growth	Monoclinic	a = 11.6475(2) b = 16.763(5) c = 7.5702(4)	<i>P</i> 2 <sub>1/</sub> c	nm 97% Transmission between 500 and 1100nm Lower cutoff: 488 nm	**	[76]
16	<i>p</i> -Toluidinium picrate	Slow evaporation solution growth	monoclinic	a = 12.9304(6) b = 15.7176(7) c = 7.5103(4)	<i>P</i> 2 <sub>1</sub> /c	440 nm Absorption is minimum 440-800 nm	Very weak SHG signal is observed by internal stress	[77]
17	4-Piperidinium carboxylamide picrate	Slow evaporation solution growth	**	<u>PXRD</u> a = 13.3410 b = 13.6714 c = 8.4473	**	Absorption at 378 nm No absorption between 400 and 900 nm	**	[79]
18	3,5-Dimethylpyrra- zolinium picrate	Slow evaporation solution growth	Monoclinic	a = 8.1001(4) b = 6.0482(3) c = 14.7037(8)	P2 <sub>1/</sub> c	Absorption at 265 and 380 nm Absence of absorption 480 and 900 nm	Emission of green light confirms SHG	[80]
19	2-Aminomethyl- pyridinium picrate (2-ampp)	Slow evaporation solution growth	Monoclinic	a = 34.812(4) b = 4.5943(19) c = 21.464(3)	C2/c	360	S.H.G efficiency 2	[81]
20	Benzamide picric acid (1:1) adduct	Slow evaporation solution growth	Monoclinic	a = 7.8644(3) b = 7.0664(3) c = 25.6580(10)	<i>P</i> 2 <sub>1/</sub> c	356	**	[82]
21	Amitriptylinium picrate	Slow evaporation solution growth	Triclinic	a = 10.0649(11) b = 11.0187(12) c = 12.0352(13)	$P\overline{1}$	**	**	[83]
22	3,3- Dinitroazetidinium picrate (DNAZ > PA)	Slow evaporation	Orthorhombic	a = 0.7655(1) b = 0.8962(2) c = 2.0507(4)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	**	**	[84]

28	picrate	Slow evaporation	Wonoennie	a = 11.097(8) b = 6.825(2) c = 11.128(6)		440
29	1,3-Dimethylurea dimethylurea dimethylammonium picrate (DMUP)	Slow evaporation solution growth	Orthorhombic	a = 14.288(4) b = 17.023(5) c = 6.8268(13)	Cmc2 <sub>1</sub>	520
30	2'6'- Dimethoxyflavone with picric acid	Slow evaporation	Monoclinic	a = 15.100(5) b = 7.624(3) c = 39.997(15)	P2 <sub>1/</sub> c	**
31	Dimethylpicric acid- acenaphthene (DMPA)	Slow evaporation	Orthorhombic	a = 7.3685(1) b = 15.4159(1) c = 16.1296(3)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	**
32	Trinitrophenol methyl p- hydroxybenzoate (TNMPHB)	Slow evaporation	triclinic	a = 8.0012(3) b = 8.2454(3) c = 13.2364(5)	ΡĪ	Max absorbance: 200-340 nm Slight increased absorption: 500- 800 nm Below 500 nm: sharp increase absorption
33	Adenosinium picrate	Slow evaporation	Orthorhombic	a = 8.776 b = 33.013 c = 6.728	$P2_{1}2_{1}2_{1}$	365
34	Acetamide-Picrate doped with CuSO <sub>4</sub>	Slow evaporation	Monoclinic	a = 5.10 b = 5.59 c = 11.06	**	260
35	Succinic-oicrate doped with CuSO <sub>4</sub>	Slow evaporation	**	**	**	Below 300 nm (260 nm)
36	(Chloro)tris(thiourea- kS)cadmium(II) picrate (CTTCP)	Slow evaporation	Triclinic	a = 7.4632(3) b = 7.9567(3) c = 17.4885(7)	<i>P</i> -1	507
37	<i>tetrakis</i> (Thiourea) zinc(II) picrate (TTZP)	Slow evaporation	Triclinic	a = 6.8333(5) b = 12.6011(10) c = 18.3423(14)	ΡĪ	290
38	Thiosemicarbazide cadmium(II) picrate (TSCPACD)	Slow evaporation	Triclinic	a = 5.3496(3) b = 11.0788(6) c = 15.0049(8)	<i>P</i> -1	300
39	Cocrystal of picric acid/ acetophenone	Solvent evaporation	Monoclinic	a = 8.494(18) b = 17.41(4)	P21/c	**

Monoclinic

Monoclinic

Orthorhombic

Monoclinic

c = 10.18(2)

Cc

Cc.

Pca21

P21/c

a = 10.366

b = 15.139c = 14.091

a = 10.4

b = 15.29

c = 14.97a = 9.212(3) Å

\*\*

b = 18.821(5) Å

c = 9.795(2) Å

Vertical

Bridgman

technique

Dimethyl ammonium Slow evaporation

Slow evaporation

Slow evaporation

40

41

42

43

Orthonitroaniline

with picric acid (ONAP)

Orthonitroaniline

Picric acid crystal

picrate (DMAP)

with picric acid

(ONÂP)

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[89]

[90]

[91]

[92]

[94]

[95]

[96]

[97]

[98]

S.H.G efficiency

Output are 26mv and 1.2 V for KDP

\*\*

\*\*

\*\*

S.H.G efficiency

Input power(6.1mv

Input power(6.1mv

\*\*

0.25

mj/pulse) w.r.t KDP(6.8 mv) Output (8.8 mv mj/pulse)

mj/pulse) w.r.t KDP(6.8 mv) Output (9.0 mv mj/pulse) \*\*

and DMUP

1.045

[99] [100] \*\* \*\* [101] 528 \*\* [102] 508 \*\* [103] S.H.G efficiency [104] Lower cut-off wavelength at 430 0.83 nm, the crystal is found to be transparent n the 508-900 nm Optical band gap -4.90 eV 460 nm Third order [105] harmonic Band gap - 2.4 eV generation- Z scan Self focusing nature Non-linear refractive index n2-  $4.98 \times 10^{-2}$ cm<sup>2</sup>/W Non-linear absorption coefficient  $\beta$  - 0.4 × 10-4 cm/W Third-order NLO Susceptibility  $\chi$  (3-)  $8.26 \times 10^{-6}$  esu

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44	Paracetamol-picric acid (PP) cocrystals	Slow evaporation	Monoclinic	a = 7.2859(7) Å b = 14.0565(11) Å c = 15.5572(12) Å	P21/c	Lower cut-off wavelength ~491 nm Band gap energy- 2.35 eV	Third order harmonic generation- Z scan Self defocusing nature Non-linear refractive index n2- 7.35 × 10 <sup>-8</sup> cm <sup>2</sup> /W Non-linear absorption coefficient $\beta$ - 0.10 × 10 <sup>4</sup> cm/W Third-order NLO Susceptibility $\chi$ (3) 2.37 × 10 <sup>6</sup> esu	[104]
45	Benzimidazole benzimidazolium picrate	Solution growth method	Triclinic	a = 12.8293(4) Å, b = 11.2817(4) Å, c = 14.5416(5) Å,	<i>P</i> -1.	**	**	[107]
46	L-Histidine di picrate	Solution growth method	Monoclinic	a = 6.6065(1)Å b = 25.7004(2)Å c = 7.9629(2)Å	P21	**	S.H.G efficiency 3.44	[108]
47	4-Nitroaniline-picric acid (2/1)	Solution growth method	Orthorhombic	a = 23.43(7) b = 9.291(2) c = 10.45(4)	<i>P</i> bcn	**	SHG-Exhibits a green light showing the presence of SHG property.	[109]
48	Picric acid doped ADP single crystals	Slow solvent evaporation	Tetragonal	Sample a = b (Å) c (Å) Pure ADP 7.505 7.550 0.4 PIC 7.519 7.565 0.6 PIC 7.502 7.565	**	**	Third order harmonic generation- Z scan Self focusing nature	[110]
49	Pure and picric acid- added KDP crystals	Slow evaporation	Tetragonal	a = c = 7.40 Å, b = 7.01 Å	I42d	**	S.H.G efficiency 1.21	[111]
50	Potassium hydrogen phthalate picrate (KHPP)	Solution growth	Monoclinic	a = 5.08 Å, b = 14.33 Å c = 9.62 Å	**	The lower cutoff wavelength –282 nm Band-gap energy 4.83 eV	S.H.G efficiency 1.72	[112]
51 **No	6-Methylbenzo- triazolinium picrate crystal	Slow evaporation	Orthorhombic	a = 19.6453Å, b = 8.5439 Å, c = 4.1946 Å	P212121	The absorption peaks observed at 240 and 280 nm are due to electronic transitions. There is no absorption between 300 and 1200 nm	S.H.G efficiency was found to be twice than that of KDP	[113]

Significance of non-linear optical crystals in second and third harmonic generation: In the field of non-linear optics and photonic applications, the development of effective and innovative non-linear optical (NLO) crystals is of great importance. These crystals are in high demand due to their potential value in developing optoelectronic and modern photonic devices. To ensure optimal performance, these materials must possess certain fundamental properties such as wide transparency in the visible range, a high laser damage threshold, a large phase matching angle, fast non-linear optical response, high chemical and thermal stability, excellent NLO properties, non-toxicity, large birefringence, low optical absorption and ease of device production. The modified Kurtz-Perry powder method, using second harmonic generation (SHG), is typically used to probe the quality of these materials. Additionally, non-centrosymmetric crystals are particularly suitable for second harmonic production and frequency converter device applications due to their high phase match.

Third harmonic generation (THG) is a non-linear optical phenomenon that has numerous applications in various scientific areas such as interfacial studies, sub-wavelength light manipulation and high sensitivity bio-molecular detection. This phenomenon involves the use of an optical frequency multiplier to triple the frequency of a light source, which interacts with a non-linear optical material to produce a photon with higher frequency and shorter wavelength. Potassium dihydrogen phosphate (KDP) is a popular material used in optical frequency multipliers for this purpose. To measure the third-order nonlinear susceptibility, Z-scan analysis is employed, which allows for efficient determination of the non-linear refractive index (n2) with its sign and magnitude. This technique is highly regarded and widely used for gaining knowledge about non-linear optical properties in solids, liquids and thin films, such as the non-linear absorption coefficient ( $\beta$ ) and the third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ). The study and practical interest in non-linear optical (NLO) processes in crystals through thirdorder NLO susceptibility  $\chi^{(3)}$  is vast due to its applications in diverse optical systems, optical information processing and optical functional devices. The generation of optical harmonics, such as THG in crystals, has provided valuable information on the NLO characteristics of materials, particularly in determining the cubic susceptibility  $\chi^{(3)}$ . Third harmonic generation (THG) has several applications, including the production of high power laser sources and non-linear microscopy [114-120].

**Applications of picric acid:** Picric acid crystals are known for their exceptional second and third order non-linear optical properties, making them highly desirable in the field of nonlinear optics. These crystals exhibit frequency doubling generation, which is crucial in converting laser beams of one frequency into two lower power frequencies and are therefore widely used in optical fibre communications systems, laser displays, optical switching and harmonic generation in nonlinear optical imaging and microscopy. Picric acid is also a valuable material in the production of non-linear optical waveguides and fibres. Additionally, picric acid crystals have been used to generate terahertz radiation, which is vital in the medical imaging, spectroscopy and security applications.

Picric acid finds several applications in medicine, including its use as a histology and bacteriology dye and an antiseptic. It is also used as a catalyst in pharmaceuticals and food processing and for chemical analysis in the chemical industry. Picric acid is employed in photography as a developing agent for producing high-resolution images and in the textile industry as a dye and an antistatic agent. Industrial laboratories use picric acid to detect the presence of metals and evaluate their strength [121-124].

#### Conclusion

The materials possessing non-linear optical properties, which finds potential applications in various fields including large data of processing and transmission, have fascinated numerous interests in recent digital years. Extensive study over the last decade has shown that the highest degree of optical nonlinearity is obtained from the organic crystals than their inorganic materials. As a result, organic non-linear optical materials are currently intensively studied. Moreover, organic materials feature significant non-linearity, structural variety, or flexibility, as well as quick reaction in electro-optic effects. The organic materials also have the benefit of being able to have their qualities adjusted by altering the molecular structure through molecular engineering and chemical synthesis. Because substantial hyperpolarizability in molecular level is the foundation of strong second harmonic generation (SHG). The organic compounds with extended conjugation electronic configuration that often display big values are unquestionably potential molecules for NLO materials. The substantial value of the initial hyperpolarizability, is connected with intramolecular charge transfer caused by electron migration from electron source to electron acceptor groups with the help of conjugated framework of the molecule. Recently, research into amino acid picrates has piqued the interest of scientists. Picric acid with donor-acceptor configuration (COO<sup>-</sup> and NH<sub>2</sub><sup>+</sup>) is highly suitable material for NLO applications. Picric acid creates crystalline picrates of several

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organic compounds due to its Lewis acid behaviour. Besides, it functions as a better acidic ligand in salt production via specialized electrostatic or hydrogen bonding interactions. Picric acid recognized for its lower cutoff wavelength, high optical quality with transparency in UV region, suitably big non-linear coefficient and excellent SHG efficiency, emerged from the comparative investigation. The derivatives prepared form picric acid are intriguing options subsequently the phenolic OH presence promotes salt formation with diverse base organic compounds. Because of the proton transfer, the conjugated base produced has higher molecular hyperpolarizability. By the interaction due to hydrogen bonds, the different organic sub-networks produce noncentrosymmetry system in the crystal and improve stability in thermal and mechanical behaviours. Centrosymmetric nature of the system plays major role and the nature of the partners has a profound influence on the acceptor-donor electron bonding in the molecules. As a result, this study provides an aerial survey of amino picrates as well as different picrate crystals, with characterization investigations contrasted and summarized.

### **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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