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Synthesis, Growth, structural and optical studies of organic nonlinear optical material- Piperazine-1,4-diium bis 2,4,6-trinitrophenolate.

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Abstract

Piperazine-1,4-diium bis 2,4,6-trinitrophenolate is one of the useful organic materials with nonlinear optical (NLO) and pharmaceutical applications. The material was grown by slow evaporation solution growth method at room temperature. The crystal system and lattice parameters were identified by single crystal XRD analysis. The grown material crystallizes in monoclinic system with P2₁/n space group. The main functional groups NH₂,NO₂,C-N,C=C, and phenolic 'O' atom were identified using FTIR analysis. The protons and carbons of grown crystal with various chemical environments were studied by ¹H and ¹³C NMR spectroscopy to confirm the molecular structure. The optical properties of the crystal were studied by UV-vis-NIR spectroscopy and the transmission 100% range starts from 532nm onwards. The optical band gap was measured as 2.63eV from the plot of $(\alpha hv)^2$ vs hv . The thermal stability was detected at 304.1°C using TG-DTA analysis. The dielectric studies of the sample were carried out at different temperatures in the frequency range from 50Hz to 5MHz to establish the dielectric nature of the crystal. Photoconductivity measurements were carried out on the grown crystal. The Second Harmonic Generation (SHG) of the crystal was tested to confirm the nonlinear optical property.

Keywords: Crystal structure, X-ray diffraction, Growth from solution, Single crystal growth, Organic compounds, Dielectric materials.

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1. Introduction

Second order non-linear optical (NLO) crystals are widely used to convert the frequency of coherent laser sources. Laser based imaging communications like remote sensing, optical data storage and optical computing, optoelectronics and counter measure systems require improved NLO materials to accomplish such conversion [1,2]. Organic crystals nowadays have been attracting much attention due to their superiority over the conventional inorganic substances for many applications. The advantages of organic materials over their inorganic counterparts are that they have high electronic susceptibility (χ), hyperpolarisability (β), facile modification through standard synthetic methods and relative ease of device processing [3]. Organic complexes were used in different pharmaceutical applications [4, 5] micro-emulsion and also organic semiconductors [6, 7].

Piperazine is the most important building block of recent drug discoveries [8].Picric acid derivatives are used in human therapy such as treatment of burns, antiseptic and astringent agent [9].Besides pharmaceutical applications, several complexes of picric acid with organic basic molecules exhibit nonlinear applications[10]. Donor-Acceptor groups in benzene derivatives produce high molecular nonlinearity. Picric acid has been studied for its ability to form salts which involve electrostatic forces, multiple hydrogen bonds of different strengths and π - π stacking interactions. Picric acid forms crystalline picrates with various organic compounds through ionic, hydrogen bonding and π - π interactions [11, 12]. It is known that picric acid acts not only as an electron acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions[13,14]. Many new organic crystals have been examined based on the predictive molecular engineering approach and have been shown to have potential applications in telecommunications and optical information processes [15]. Other advantages of organic compounds involve amenability for synthesis, multifunctional substitution, higher resistance to optical damage and maneuverability for device applications [16]. Molecular flexibility of organic

materials is an added advantage to enhance the nonlinear optical properties in a desired manner [17]. In addition, they have large structural diversity. By adopting molecular engineering methods in chemical synthesis one can easily refine the optical properties of organic molecules [18].

There is an increasing demand for single crystals to find applications in the development of technology and devices for their NLO property. Therefore, in the present investigation, the compound piperazine-1,4-diium bis 2,4,6-trinitrophenolate was grown first as a single crystal using slow evaporation technique. The growth of the crystal was followed by detailed characterization studies such as single crystal XRD study, UV-vis-NIR, FTIR and NMR spectral studies, thermal, dielectric, photoconductivity and SHG measurements to analyze structural property, transmission range, various functional modes, molecular structure, thermal stability, dielectric behavior, and photoconductivity and NLO property of the grown material.

2. Experimental Procedure

2.1. Material synthesis

Single crystals of Piperazine-1,4-diium bis 2,4,6-trinitrophenolate were grown by slow evaporation solution growth method at room temperature. Piperazine and Picric acid with 4:1 molar ratio were dissolved in deionized water to get a clear solution and the solution was stirred well for homogeneity. Initially the pH of the solution was measured near 5.0 using pH meter. By adding suitable amount of diluted Hydrochloric acid, the pH of the solution was decreased to 3.2 which is more than sufficient for the crystallization process. The resulting solution was filtered using a Whattman filter paper and the beaker containing the filtrate was kept in a dust free environment for crystallization.Fig.1 gives the reaction scheme for the formation of title compound. After a period of 20 days, yellow colour crystals of title compound were obtained. The purity of the synthesized crystal was improved considerably by repeating the recrystallization process three times. Fig.2 shows the as-grown single crystal of the title compound.

3. Characterization techniques

The single crystal XRD data of the grown crystal was obtained using a Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer with MoKa(0.7107 Å) radiation at room temperature. The ORTEP view of the molecule was drawn at 50% probability thermal displacement ellipsoids with the atom numbering scheme. The crystal structure was solved by a direct method with the SHELXS-97 program[19,20]. The UV-vis-NIR spectrum was recorded in the range of 200-800nm using Perkin-Elmer Cary 5E spectrometer. The FT-IR spectrum of the title compund was obtained using JASCO FT-IR 410 spectrometer by the KBr pellet method. The ¹H and ¹³C NMR spectra of the title compound were recorded using DMSO as a solvent on a Brucker AVANCE III 500 MHz (AV 500) instrument at 23°C (300 MHz for ¹H NMR and 75 MHz for ¹³CNMR) to confirm the molecular structure. The TG-DTA of the title compound has been analysed by using a TGA Q50V20.13 Build 39 Perkin-Elmer Diamond TG-DTA instrument. A platinum crucible was used for heating the sample and analysis was carried out in an atmosphere of nitrogen at a heating rate of 10°C/min in the temperature range of 23-600°C. The dielectric property was studied using a HIOKI 3532-50 LCR HITESTER by varying the temperature in the frequency range from 50Hz to 5 MHz. Photoconductivity measurements were made on the grown crystal using KEITHLEY 485 picoammeter. The SHG efficiency of the grown crystal was determined with help of modified Kurtz and Perry technique using Nd:YAG laser with pulse repetition rate of 10Hz and wavelength 1064nm.

4. Results and Discussions

4.1. Single crystal XRD analysis

Single crystal X-ray measurements were made at 293 K using suitable data collection. In the single crystal XRD data collection, 9,494 reflections were recorded in the range of 2.68° to 24.99° of which 1887 reflections were unique reflections. The data reveal that the synthesized crystal belongs to the monoclinic crystal system with space group P2₁/n. The lattice parameters obtained are a=11.2650(2) Å, b=6.669 (10) Å, c=14.8880(3) Å, α =90°, β =106.98(10)° and γ =90°. The unit

cell volume is 1069.67(3) $Å^3$ and Z=2. The crystallographic data and structure refinement parameters are given in Table 1. Table 2 presents the crystallographic data of title compound and other picrate crystals for comparison. Since the grown crystal is a new compound (CCDC no.941605), the crystallographic data of this compound are different from those of other picrate crystals.

The title compound crystallizes in monoclinic system with space group P2₁/n. The asymmetric unit consists of one picrate anion and half piperazinium cation. The two halves of piperazinium cations are related through crystallographic centre of inversion. Fig.3 shows the ORTEP representation of the molecule with atom numbering scheme. The crystalline packing (Fig.4) shows that piperazinium cations are interposed between two centrosymmetric pairs of picrate anions. The anion pairs are hydrogen bonded (N-H...O) to the cations and the motif is connected to its b-translation equivalents to form a one dimensional hydrogen bonded chain parallel to b-axis.

The single crystal X-ray structure of the proton transfer complex of title compound shows the presence of protonated piperazine cation and deprotonated picrate anion for intermolecular hydrogen bonding associations as shown in ORTEP Fig.3 and also in Table 3.

The selected bond lengths and bond angles are presented in Table 4. The loss of a proton from picric acid is confirmed by the lengthening of the C-O bonds. The bond lengths and bond angles of the picrate anion show the characteristic values, with C6-C1=1.439(2) Å and C6-C5=1.4369(19) Å distances longer than the normal aromatic C-C values 1.40 Å. These differences are attributed to the loss of a hydroxyl proton at O7 which leads to the conversion from the neutral to the anionic state. The crystal packing diagram along Y-axis is shown in Fig.4.

The repulsive interactions of the deprotonated oxygen atom O7 with the electron withdrawing group NO₂ attached to the ortho positions of O7 are responsible for the shortening of the C1-C2=1.3692(19) Å andC4-C5=1.367(2) Å bonds. The repulsive interactions also have a role to play the significant differences in the internal C-C-C angles within the ring joining the NO₂

groups C6-C5-C4=124.58(13)° and C6-C1-C2=124.19(12)°.TheC5-C6-C1=112.03(12)° angle joining the deprotonated hydroxyl group is significantly smaller than the expected angle (120°). On comparison of bond lengths of C6-C1=1.439(2) Å,C6-C5=1.4369(19) Å,C1-C2=1.3692(19) Å, C4-C5=1.367(2) Å and C6-O7=1.2580(16) Å with normal bond lengths of C-C,C=C and C-O, it is found that the C6-C1,C6-C5(1.5 Å) have single bond character and C1-C2,C4-C5 (1.39 Å) have double bond character. The C-O (1.21 Å) also carries double bond character. This indicates that the crystal possesses more quinonoid character than benzenoid character.

Table 5 shows the torsional angles data for the grown crystal. The torsion angles of O3-N2-C5-C6, O1-N1-C1-C6 are found to be 34.5(2) ° and 25.1(2) ° respectively. From the torsion angles data, it has been found that the ortho nitro groups are commonly involved in hydrogen bonding interactions.

The twist angles of the three nitro groups attached to the benzene ring are[O2-N1-O1=122.75(13) °], [O3-N2-O4=123.46(14) °], and [O6-N3-O5=123.16(13) °]. The twisting nature of the nitro groups in picrate ions shows that the ortho nitro groups are away from the plane of the benzene ring, possibly as a result of steric hindrance with the phenolic group at C6.

The packing of molecules in the crystal lattice is determined by conventional and unconventional C-H...O hydrogen bonds. In addition to the conventional hydrogen bonds, the short C-H...O intermolecular contacts between C4-H4 or C5-H5 and nitro group are also observed. This is an important feature in all- aromatic picrate complexes [23].

4.2. FTIR analysis

The FTIR spectrum of the title compound is shown in Fig.5. The characteristic absorption bands were recorded in the spectral range 4000-400 cm⁻¹ in order to confirm the presence of functional groups in the crystal. The presence of NO₂, N-H and C-H is confirmed with the assigned wavenumbers from the spectrum. The 3318 cm⁻¹ and 3068 cm⁻¹ absorption peaks are due to N-H asymmetric and symmetric stretching vibrations. The absorption peaks at 3068 cm⁻¹ and 2841 cm⁻¹ are due to C-H asymmetric and symmetric stretching vibrations. The presence of peaks

corresponding to 1624 cm⁻¹ and 1273 cm⁻¹ are due to C=C stretching vibrations and the presence of phenolic 'O' atoms. The peaks at 1436 cm⁻¹ and 1321 cm⁻¹are due to asymmetric and symmetric stretching vibrations of the nitro group. The lower peaks at 848 cm⁻¹ and 787cm⁻¹ are due to deformation and wagging of nitro groups respectively while 615 cm⁻¹ and 589 cm⁻¹ are due to rocking vibration of nitro group. The observed spectral data and their assignments for title compound are tabulated in Table 6. The functional groups of the grown material are thus identified.

4.3. NMR spectroscopy

The ¹H NMR and ¹³C NMR spectral analyses are the two important analytical techniques used to study the molecular structure of title compound. Fig..6a shows the structure of title compound with different number of protons and carbon chemical environments involved in the structure.

4.3.1. ¹H NMR spectrum

Fig.6b shows the recorded ¹H NMR spectrum of grown crystal which shows five different signals due to five distinct proton environments including solvent signal. The peaks at δ 2.3ppm corresponds to solvent peaks. The normal peak corresponding to CH₂ (C7 and C8) protons will lie in the region of δ 4-5ppm. Since CH₂ is shielded due to NH₂⁺ proton CH₂ proton has increased its absorbing power of the higher order magnetic field for the precessional motion of the nucleus. The energy difference caused shifts the peak signal from δ 4-5ppm to δ 2.5ppm. Hence, the shifting of the peak signal towards lower value confirms the shielding effect.

The signal at δ 6.8ppm assigned to NH₂⁺ protons in piperazine are deshielded due to the decreasing absorbing powers of the applied magnetic field by N and O atoms. As a result, δ value is increased from 2-3ppm to 6.8ppm. Hence the signal at δ 6.8ppm confirms the deshielding effect of N and O atoms on NH₂⁺ proton. The peak at δ 7.5ppm is due to the aromatic protons in the picrate moiety of the crystal having the same kind of chemical environment attached with C2 and

C4 carbon atoms. The peak at 9.961ppm reveals the interaction between picric acid and piperazine which leads to desheilding of phenolic proton in picric acid.

4.3.2. ¹³ C NMR spectrum

Fig.6c shows the ¹³C NMR spectrum of the title compound. The appearance of 6 distinct carbon signals in the spectrum including the solvent peak unambiguously confirms the molecular structure of the title compound. The signal at δ 150.88 ppm has been assigned to the C6 aromatic carbon (C-O) atom in the picrate ion. The signal at δ 133.76ppm is assigned to C5 and C1 carbon attached to nitrogen atoms (C-N) in the picrate moiety having same carbon environments and the δ 144.31ppm corresponds to C3 while δ 124.58ppm corresponds to C2 and C4 aromatic carbon atoms of picrate anion. The signal at δ 121.50 ppm shows C7 and C8 of piperazinium cation. The solvent peaks are shown at δ 40.08 ppm. It is concluded that the spectrum provides the useful information about the various types of carbon atoms involved in the molecular structure of the title compound.

4.4 UV-vis- NIR spectral analysis

The UV-vis-NIR absorption spectrum of the grown crystal was recorded in the wavelength range of 200-800 nm (Fig.7a). The higher intensity of the absorption band observed in the UV region may be due to conjugated systems present in the grown material. The absorption is very low near infrared region and the entire visible region with cut-off wavelength 240nm. However,100% transmission is observed from 532nm onwards. The optical band gap (Eg) was evaluated using Tauc's relation given by

$$\alpha hv = A(E_g - hv)^2 \tag{1}$$

where α is the absorption coefficient, A is a constant, E_g is the optical band gap, h is the Planck constant and v is the frequency of the incident photons. The value of band gap energy was

estimated from the graph between $(\alpha hv)^2$ and hv (Fig.7b) by extrapolating the linear portion of the curve to zero absorption. The optical band gap was measured as 2.63 eV. The higher value of optical band gap suggests that material is dielectric in nature. Only the dielectric material will have wide transparency. The material with wide transparency is required for the fabrication of optical devices.

4.5. Thermal analysis

The Thermogravimetric (TG) and Differential thermal analysis (DTA) were carried out in the nitrogen atmosphere at a heating rate of 10°C min ⁻¹ from 0 °C to 600 °C. It is observed from TG curve that the weight loss is negligible (0.70%) at 166°C and the major weight loss starts from 304.1°C onwards. This observation which is confirmed by the endothermic peak of DTA analysis at 304.1°C.

Even though the weight loss starts at 166°C, the major weight loss occurs from 304.1 °C onwards. Hence, the crystal can be used in devices with more thermal stability up to 304.1 °C. The weight loss at 166°C is due to evaporation of solvent molecules. The decomposition at 600 °C gives a residue of 21.90% and this is due to the carbon residue. The sharpness of the peak shows the good degree of crystalline quality of the crystal [26, 27]. The title compound has fairly high melting point. Table.7 shows the comparison of thermal stability (melting point) of the grown crystal with that of other picrate crystals.

4.6 Dielectric studies

The dielectric constant and dielectric loss were measured in the frequency range from 50 Hz to 5 MHz at various temperatures. Good quality crystal was selected for dielectric studies. The surface of the sample was coated with silver for good electrical contact. The dielectric constant and dielectric loss were calculated using the formula,

Dielectric constant $\varepsilon' = Cd/A\varepsilon_o$ (2)

and

Dielectric loss $\tan \delta = \varepsilon_r D$

(3)

where C is the capacitance, d is the thickness, A is the area of the crystal and D is the dissipation factor.

The plots of dielectric constant versus frequency and dielectric loss versus frequency are shown in Figs.9a and 9b at 323 K, 373 K and 423 K. From the graph, the dielectric constant is found to decrease with increase in frequency. The large values of dielectric constant at low frequencies are due to the presence of space charge polarization [35]. The decrease in the value of dielectric constant with frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the AC electric field applied beyond a certain critical frequency [36]. The very low value of dielectric constant at higher frequencies is important for the fabrication of ferroelectric, photonic and electro-optic devices [37]. The low values of dielectric constant and dielectric loss at high frequencies suggest that grown crystal contains minimum density of defects with high optical quality [38].

4.7 AC conductivity studies

The AC conductivity of grown crystal was evaluated using the formula

$$\sigma_{ac} = 2\pi f \varepsilon_{o} \varepsilon_{r} \tan \delta \tag{4}$$

where ε_{o} is the permittivity of the dielectric constant, ε_{r} is the dielectric constant, f is the frequency of ac applied and tand is the dielectric loss. Fig.10a shows the variation of ac conductivity with frequency. The ac conductivity is zero up to 1MHz and starts increasing from 1 MHz onwards. This is due to the fact that the relaxation time of charge carriers is not matching with the time period of the applied ac field up to 1 MHz and so the conductivity of the material is almost zero. The variation of ac conductivity with temperature follows the Arrhenius plot as

$$\sigma_{ac} = \sigma_0 exp(-E_a/kT)$$
(5)

where E_a is the activation energy, k is the Boltzmann constant and T is the temperature (in kelvin). Fig.10b shows the plot of $\ln \sigma_{ac}$ versus temperature. As the temperature is increased, the ac conductivity is found to increase. When the temperature is increased, the thermal energy sufficiently increases to enhance the movement of charge carriers for increasing the ac conductivity. The slope of the plot gives the activation energy required to aid the conduction process for the charge carriers. The value is found to be 0.1795 eV and the lower value of activation energy establishes that the grown crystal contains less number of defects.

4.8 Photoconductivity studies

The photoconductivity measurements were carried out for the grown crystal using Keithley 485 picoammeter. Initially, the sample was kept away from any other radiations. Dark current was measured by connecting the sample in series with a DC power supply and picoammeter. Electrical contacts were made on the sample using silver paint. The photocurrent for the same sample was measured by exposing it to the radiation from a halogen lamp containing iodine vapor by focusing a spot of light on the sample with the help of a convex lens. The applied field was increased from 100 to 4000 V/cm and the corresponding photo current was recorded. The photo current and dark current were plotted as a function of the applied field. Fig.11 shows the variation of both the dark current and photo current of the sample with applied voltage. From the Fig.11, both the dark and photocurrent are seen to increase linearly with the applied field. The photocurrent is found to be less than the dark current for every applied electric field. This phenomenon is known as negative photoconductivity. However, the negative photoconductivity in this case may be due to the reduction of the number of charge carriers and their lifetime in the presence of radiation[39][40].

In Stockman model, a two level scheme is proposed to explain negative photoconductivity in semiconductors and the details are reported [41]. For a negative photoconductor, forbidden gap holds two energy levels in which one is placed between the Fermi level and the conduction band while the other is located close to the valence band. The second state contains traps

(recombination centres) to capture electrons and holes [42]. As a result, the number of mobile charge carriers is reduced giving rise to negative photoconductivity..

Even though, the present material shows negative photoconductivity, it is capable of inducing dipoles due to intense incident radiation to reveal the nonlinear behavior of the material. It is found that the material shows SHG efficiency comparable with that of standard KDP material.

4.9 SHG efficiency measurements

The SHG efficiency of the grown crystal was measured by modified Kurtz and Perry technique using Nd: YAG laser with pulse repetition rate of 10Hz and wavelength 1064 nm. The sample was ground well and tightly packed in a micro capillary tube. The relative SHG efficiency of the grown crystal was measured by comparing the SHG output with the help of a standard KDP (Potassium dihydrogen phosphate) sample of same particle size. The relative efficiency was found to be 0.8 times that of standard KDP. SHG was confirmed by the emission of green radiation (532nm) from the crystal. On a molecular scale the extent of charge transfer (CT) across the NLO Chromophore determines the level of SHG efficiency. Even though the grown crystal belongs to centrosymmetric group, it exhibits considerable amount of NLO behavior. .Rieckoff et al [43], Ghazaryan et al[44], Shakir et al [45] and Dhanabal et al[32] have studied the SHG efficiency of some centrosymmetric crystals R,S-Serine, diglycine picrate ,glycine picrate and 2-methylimidazolinium picrate crystals.

In the grown crystal, the strong proton donor picric acid transfers a proton to the strong proton acceptor piperazine. Intermolecular hydrogen bonding is formed between the hydrogen of the protonated nitrogen atom of piperazine and the negatively charged oxygen atom of the picrate anion. In the present case, the donor–acceptor strength is considerably high due to the intermolecular hydrogen bonding. The NLO behaviour of the title compound may be due to the presence of intermolecular hydrogen bonding. This indicates that the synthesized title compound can be used as a better NLO material.

5. Conclusion

Single crystals of Piperazine-1,4-diium bis 2,4,6-trinitrophenolate were synthesized and crystallized using piperazine and picric acid as starting materials by slow evaporation method. The structure of the grown crystal was solved using SHELXS-97 program. It is observed from the crystallographic data that the grown crystal belongs to monoclinic system with P2₁/n space group. The high value of optical band gap and the wide transmission range were ascertained using UV-vis-NIR spectrum. The presence of various functional groups and protons and carbon atoms of various chemical environment present in the grown crystal was confirmed by FT-IR and NMR spectral analysis. Thermal studies reveal that the grown crystal is thermally stable up to 304.1°C. Dielectric studies establish the dielectric behaviour of the grown crystal which is important for the study of NLO property. The crystal possesses SHG efficiency 0.8 times than that of KDP. Hence, the grown single crystal is one of the useful organic crystals with NLO applications.

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Crystallographic data of Piperazinium picrate has been deposited with the Cambridge Crystallographic Data Centre [CCDC No.941605]. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 0 1223 336 033; email: <u>deposit@ccdc.cam.ac.uk</u>].

Figure captions

Fig.1 Reaction scheme of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.2 As grown single crystal of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.3 ORTEP diagram of the Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.4 The packing of the molecules, viewed along 'b' axis

Fig.5 FT-IR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.6a Structure of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

6b¹H NMR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

6c¹³C NMR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.7a UV- visible-NIR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

7b Plot of $(\alpha hv)^2$ versus photon energy

Fig.8 TGA and DTA curve of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Fig.9aVariation of dielectric constant of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

crystal as a function of frequency at different temperatures.

9b Variation of dielectric loss of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

crystal as a function of frequency at different temperatures.

Fig. 10a Plot of ac conductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate versus frequency.

10bPlot of ac conductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate versus temperature.

Fig .11 Field dependent photoconductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate single crystal



Fig.1. Reaction scheme of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate



Fig.2.Grown single crystal of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate



Fig.3. ORTEP diagram of the Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate





Fig.5. FT-IR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate .



Fig.6 (a) Structure of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate





Fig.6 (c) ¹³C NMR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate



Fig.7. (a) UV- visible-NIR spectrum of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate



Fig.7.(b) Plot of $(\alpha hv)^2$ versus photon energy

A



Fig.8. TGA and DTA curve of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate



Fig.9.(a) Variation of dielectric constant of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

crystal as a function of frequency at different temperatures.



Fig.9. (b) Variation of dielectric loss of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

crystal as a function of frequency at different temperatures



Fig.10.(a) Plot of AC conductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate versus frequency.



Fig.10. (b) Plot of AC conductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate versus temperature.



Fig 11. Field dependent photoconductivity of Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate single crystal

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Table 1. Crystallographic data and structure refinement parameters for Piperazine-1, 4-diium bis

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Formula weight Formula weight Temperature Wavelength Unit cell dimensions $C_{16} \Pi_{16} V_8 O_{14}$ 544.37 293(2) K 0.71073 Å Monoclinic, P ₂ 1/n $a = 11.2650(2) Å$; $\alpha = 90 \text{ deg.}$ $b = 6.66900(10) Å; \beta = 106.9890(10) \text{ deg.}$
Torinina weight 344.37 Temperature $293(2)$ KWavelength 0.71073 ÅCrystal system, space groupMonoclinic, P ₂ 1/nUnit cell dimensions $a = 11.2650(2)$ Å; $a = 90$ deg. $b = 6.66900(10)$ Å; $B = 106.9890(10)$ deg
Temperature $253(2)$ KWavelength 0.71073 ÅCrystal system, space groupMonoclinic, P_21/n Unit cell dimensions $a = 11.2650(2)$ Å; $a = 90$ deg. $b = 6.66900(10)$ Å; $B = 106.9890(10)$ deg
Wavelength 0.71075 A Crystal system, space groupMonoclinic, $P_2 1/n$ Unit cell dimensions $a = 11.2650(2) \text{ Å}$; $\alpha = 90 \text{ deg.}$ $b = 6.66900(10) \text{ Å}$; $\beta = 106.9890(10) \text{ deg.}$
Unit cell dimensions $a = 11.2650(2) \text{ Å}; \alpha = 90 \text{ deg.}$ $b = 6.66900(10) \text{ Å}; \beta = 106.9890(10) \text{ deg.}$
$a = 11.2050(2) \text{ A}, \ a = 90 \text{ deg}.$ $b = 6.66900(10) \text{ Å} \cdot \text{B} = 106.9890(10) \text{ deg}$
$n = n$ nogen i i i Δr $n = 1$ i n g g g i i i i n hen Δr
0 = 0.0000(10) A, p = 100.000(10) deg.
$c = 14.8880(3) \text{ Å}$; $\gamma = 90 \text{ deg.}$
Volume 1069.67(3) Å ³
Z 2
Calculated density 1.690 Mg/m ³
Absorption coefficient(μ) 0.151 mm ⁻¹
F(000) 560
Crystal size 0.35 x 0.30 x 0.30 mm
Theta range for data collection2.68 to 24.99 deg.
Reflections collected / unique $9494 / 1887 [R(int) = 0.0239]$
Completeness to theta 24.99 - 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9958 and 0.9257
Refinement method Full-matrix least-squares on F ²
Data / restraints / parameters 1887 / 3 / 181
Goodness-of-fit on F ² 1.057
Final R indices $R1 = 0.0331$, wR2 = 0.0890
R indices (all data) $R1 = 0.0372, wR2 = 0.0925$
Extinction coefficient 0.069(4)
Limiting indices -13<=h<=13, -7<=k<=7, -17<=l<=17
Identification code shelx1
CCDC No. 941605

Table 2. Comparison of crystallographic data of title compound with other piperazine picrate

crystals.

Crystal name	Title compound	1,4 diium picrate	1-Methylpiperaziine-1,4-

		piperazine (1/2/1) [21]	diium dipicrate[22]
Molecular Formula	$C_{16}H_{16}N_8 O_{14}$	$C_{14}H_{24}N_7O_7$	$C_{11}H_{16}N_5O_7$
Molecular weight	544.37	630.50	558.39
System	Monoclinic, $P_2 1/n$	Triclinic, P 1	Triclinic ,P 1
Unit cell dimension	a = 11.2650(2) Å;	a = 7.7150(6) Å;	a = 8.2001(12) Å;
	$\alpha = 90 \text{ deg.}$	$\alpha = 98 \text{ deg}$	$\alpha = 89 \text{deg.}$
	b = 6.66900(10)Å	b = 8.8658(6) Å;	b = 10.1780(15) Å;
	$\beta = 106.9890(10) \text{deg}$	$\beta = 98 \text{ deg}$	β=78deg
	c = 14.8880(3) Å	c = 11.3024(8) Å;	c = 13.7399(18) Å ;
	$\gamma = 90 \text{ deg.}$	$\gamma = 109 \text{ deg.}$	$\gamma = 81 \text{deg.}$
Cell volume	1069.67(3) Å ³	649.62(8) Å ³	1109.6(3) Å ³
Z	2	1	4
μ	0.151 mm^{-1}	0.14mm ⁻¹	0.15mm ⁻¹
Solvents	Water	Methanol	Methanol

Table 3.Bond lengths [A] and angles [deg] of Hydrogen atom for Piperazine-1, 4-diium bis

	2,4,6-trinit	rophenolate		
D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
N(4)-H(4B)O(7)	0.892(13)	1.987(15)	2.7872(16)	148.5(15)
N(4)-H(4B)O(1)	0.892(13)	2.419(15)	3.0823(17)	131.3(13)
N(4)-H(4A)O(7)#2	0.865(14)	1.949(15)	2.7349(16)	150.5(16)
N(4)-H(4A)O(3)#2	0.865(14)	2.471(15)	3.1444(19)	135.2(15)

Figl for " Table 4. Selected bond lengths [Å] and angles [deg] for Piperazine-1, 4-diium bis 2,4,6trinitrophenolate

Atoms	\mathbf{I} and \mathbf{I}	Atoms	Angles in deg
Atoms	Length (A)	Atoms	Aligies III deg
C(1)-C(2)	1.3692(19)	C(4)-C(5)-N(2)	116.38(12)
C(1)-C(6)	1.439(2)	C(6)-C(5)-N(2)	118.99(12)
C(1)-N(1)	1.4576(18)	O(7)-C(6)-C(5)	123.57(13)
C(2)-C(3)	1.382(2)	O(7)-C(6)-C(1)	124.40(13)
C(2)-H(2)	0.93	C(5)-C(6)-C(1)	112.03(12)
C(3)-C(4)	1.377(2)	N(4)-C(7)-C(8)#1	110.78(12)
C(3)-N(3)	1.4457(18)	N(4)-C(7)-H(7A)	109.5
C(4)-C(5)	1.367(2)	C(2)-C(1)-C(6)	124.19(12)

C(4)-H(4)	0.93	C(2)-C(1)-N(1)	116.33(12)
C(5)-C(6)	1.4369(19)	C(6)-C(1)-N(1)	119.48(12)
C(5)-N(2)	1.4555(18)	C(1)-C(2)-C(3)	118.95(13)
C(6)-O(7)	1.2580(16)	C(1)-C(2)-H(2)	120.5
C(7)-N(4)	1.483(2)	C(3)-C(2)-H(2)	120.5
C(7)-C(8)#1	1.509(2)	C(4)-C(3)-C(2)	121.30(13)
C(7)-H(7A)	0.97	C(4)-C(3)-N(3)	119.40(12)
C(7)-H(7B)	0.97	C(2)-C(3)-N(3)	119.27(13)
C(8)-N(4)	1.4808(19)	H(8A)-C(8)-H(8B)	108.1
C(8)-C(7)#1	1.509(2)	O(2)-N(1)-O(1)	122.75(13)
C(8)-H(8A)	0.97	O(2)-N(1)-C(1)	117.98(13)
C(8)-H(8B)	0.97	O(1)-N(1)-C(1)	119.24(12)
N(1)-O(2)	1.2148(17)	O(3)-N(2)-O(4)	123.46(14)
N(1)-O(1)	1.2198(17)	O(3)-N(2)-C(5)	119.35(13)
N(2)-O(3)	1.2191(18)	O(4)-N(2)-C(5)	117.17(13)
N(2)-O(4)	1.2193(18)	O(6)-N(3)-O(5)	123.16(13)
N(3)-O(6)	1.2158(17)	O(6)-N(3)-C(3)	118.76(13)
N(3)-O(5)	1.2273(17)	O(5)-N(3)-C(3)	118.08(13)
N(4)-H(4B)	0.892(13)	C(8)-N(4)-C(7)	112.22(12)
N(4)-H(4A)	0.865(14)	C(8)-N(4)-H(4B)	110.0(11)
C(5)-C(4)-C(3)	118.84(13)	C(7)-N(4)-H(4B)	108.7(10)
C(5)-C(4)-H(4)	120.6	C(8)-N(4)-H(4A)	110.8(12)
C(3)-C(4)-H(4)	120.6	C(7)-N(4)-H(4A)	108.6(12)
C(4)-C(5)-C(6)	124.58(13)	H(4B)-N(4)-H(4A)	106.4(14)

Atoms	Angles in deg	Atoms	Angles in deg
C(6)-C(1)-C(2)-C(3)	3.4(2)	N(1)-C(1)-C(6)-C(5)	178.53(12)
C(1)-C(2)-C(3)-N(3)	176.08(12)	C(6)-C(1)-N(1)-O(2)	156.72(14)
C(3)-C(4)-C(5)-C(6)	3.1(2)	C(2)-C(1)-N(1)-O(1)	155.02(14)
C(4)-C(5)-C(6)-O(7)	177.78(13)	C(4)-C(5)-N(2)-O(3)	147.91(15)
N(2)-C(5)-C(6)-O(7)	0.4(2)	C(6)-C(5)-N(2)-O(4)	146.78(15)
C(2)-C(1)-C(6)-O(7)	178.88(13)	C(2)-C(3)-N(3)-O(6)	3.1(2)
C(7)#1-C(8)-N(4)-C(7)	55.88(17)	C(4)-C(3)-N(3)-O(5)	1.48(19)

Table 5. Torsion angles for Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate .

Table.6. Spectral data and their assignments for Piperazine-1, 4-diium bis 2,4,6-trinitrophenolate

Frequency Cm ⁻¹	Assignments
3318 cm^{-1} and 3068 cm^{-1}	N-H asymmetric stretching and
	symmetric stretching vibration
$2841 \text{ cm}^{-1} \text{ and } 2788 \text{ cm}^{-1}$	C-H asymmetric stretching and
	symmetric stretching vibration
2193cm ⁻¹	C-N stretching vibration
1624 cm^{-1} and 1546 cm^{-1}	C=C stretching vibrations
1273 cm^{-1}	phenolic 'O' atom

$1436 \text{ cm}^{-1} \text{ and } 1321 \text{ cm}^{-1}$	asymmetric and symmetric stretching
	vibration of the nitro
1080 cm^{-1}	C-O stretching vibration
914 cm ⁻¹ and 985 cm ⁻¹	C-H out of plane bending vibration
744 cm ⁻¹ and 713 cm ⁻¹	out of plane bending vibration for
848 cm ⁻¹	NO_2 deformation
	Q-*
787cm ⁻¹	NO ₂ wagging
659 cm^{-1}	C-C out of plane ring deformation
$615 \text{ cm}^{-1} \text{ and } 589 \text{ cm}^{-1}$	Rocking vibration of nitro group[24,25].

Table .7. Meltings points compared with other picrate crystals.

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Compond	Melting point
LLLP[28]	186
DMUP[29]	124
TTZP[30]	200
2APP[31]	229
MIMP[32]	248
DMAP[33]	261
LPP[25]	250
TMPP[34]	128
Title compound	304

Highlights:

- Growth of good quality organic single crystal of Piperazine-1,4-diium bis 2,4,6-trinitrophenolate using water as a solvent.
- Determination of cell parameters and unit cell dimensions of Piperazine-1,4-diium bis 2,4,6trinitrophenolate crystal by single crystal X-ray diffraction method.
- Chemical and molecular structure establishment by FTIR and NMR spectroscopy and thermal stability studies by TG/DTA method.
- Determination of Optical properties of Piperazine-1,4-diium bis 2,4,6-trinitrophenolate by UV- visible spectroscopy.
- SHG (second harmonic generation) efficiency of Piperazine-1,4-diium bis 2,4,6-trinitrophenolate crystal were determined by Kurtz and Perry technique.

MAS

