CHAPTER - III
SYNTHESIS, CHARACTERIZATION AND DETERMINATION OF
THIRD ORDER NLO PROPERTIES OF
ETHYLENEDIAMINIUM DI (3-NITROPHENOLATE)

3.1 INTRODUCTION

Extensive research on organic functional group materials is ever in the ascend due to their interesting nonlinear optical effects which are extended to optical parametric amplifiers, optical parametric oscillators, Q-switched intracavity second harmonic devices, high optical damage threshold and other electro-optical applications [1–5]. Even though intensive efforts in this field have been taken for about thirty years, it is still very attractive to look for new nonlinear optical materials with various practical interests. At present, inorganic crystals such as lithium niobate and potassium dihydrogen phosphate (KDP) are generally used in nonlinear optical devices. The search is for new nonlinear optical materials applied to ultraviolet (UV), even vacuum ultraviolet (VUV) and far infrared (FIR) regions, as well as direct second harmonic generation (SHG) of diode laser [6]. Optical limiters for low power continuous wave (cw) lasers are also very important in applications such as prevention of optical damage to very sensitive sensors. For example, the human eye will be damaged permanently if exposed to a laser beam power of 1–5 mW for a few seconds. Information about the damage level of the sensor is necessary to determine the required limiting level of the device.
Crystal engineering is a rapidly developing interdisciplinary field with a wider scope for basic research and promising photonic applications as mentioned above [7, 8]. Organic crystals of nitrophenol family play a prominent role in nonlinear optical area due to their superior qualities such as high NLO coefficient, wide transparency windows, and extended thermal stability. Nitrophenol can form plenty of derivatives with bases due to the presence of phenolic –OH and one dimensional donor–acceptor π system. Growth and optical study of large numbers of nitrophenol family crystal have already been reported [9-12]. Recent literature shows that differentiation of functional groups and their changing positions in the phenyl ring results in a wide range of nonlinear coefficients. Especially mono-, di- and tri-substituted nitro-phenol and its salts have become important classes of NLO compounds, after the work of Long Liu et al., [13] on a series of phenol-ammonium salts. Based on his work, recently a new acentric system ethylenediaminium di (2-nitrophenolate) [EDA2NP] was identified to be an excellent second harmonic generation active material [14]. Impressed by the above facts in this chapter, a systematic approach on the synthesis, crystal growth and characterization of EDA3NP are presented. Also its second and third order NLO properties were estimated by Kurtz powder and Z-scan technique. In particular its possible use as a frequency converter to generate short wavelength (green) lasers and low power optical limiters to safeguard photosensitive components which are discussed in detail, in the forthcoming sections.
3.2 EXPERIMENT

3.2.1 Material Synthesis

The title compound was synthesized by following the procedures hinted by Long Liu et.al, [13]. The reaction scheme is depicted in scheme 3.1. Ethylenediamine (EDA) is a weak bronsted base that gains a proton in acidic solution and forms the salt of the respective acid. The reaction involves a proton transfer where a proton is transferred from the electron donor group of 3-nitrophenol to the electron acceptor group of EDA. The resultant product is ethylenediammonium di (3-nitrophenolate) (EDA3NP), in which the 3-nitrophenolate anion and ethylenediamine cation result from proton transfer.

In the typical procedure, the calculated amount of ethylenediamine (0.18 g, 2.90 mmol) was dissolved in methanol (5 ml) and 3-nitro phenol (1.00 g, 7.19 mmol) was thoroughly dissolved in methanol (50 ml) separately. The above solution was added together and the mixture was stirred for 3 hrs. The clear solution obtained was kept in air atmosphere at room temperature (30 °C) for 24 hours to evaporate parts of methanol. A crystalline yellowish brown salt were collected through filtration. The product was washed and dried at 40 °C for 12 h. The estimated yield was about 50 %.

From the molecular structure of EDA3NP, one can infer that the main component of the material that provides enhanced NLO efficiency is due to its m-nitrophenol. The delocalization of the electronic cloud of the OH group is the cause for such enhanced NLO efficiency [15]. The basic nature of pyridine ring nitrogen, augmented by ethylene diamine grouping can attract proton from the phenolic OH group. This process leaves oxygen with a negative charge through which the above said electron delocalization can further be enhanced along with NLO property.
Figure 3.1 Reaction scheme for the synthesis of EDA3NP

3.2.2. Solubility and Crystal Growth

Selection of a suitable solvent is very definitive for the growth of good quality single crystals [16]. The equilibrium solubility and its temperature dependence are essential for solution growth. The data from the solubility curve will suffice so as to start growing fair quality single crystals [17]. The solubility of EDA3NP in methanol and ethanol was assessed as a function of temperature in the temperature range 30–50 °C. A thermostatically controlled vessel (100 ml) was filled with the solution of EDA3NP with some undissolved EDA3NP and stirred for 24 h. On the next day, a small amount of solution was pipetted out and the concentration of the solute was determined gravimetrically. Figure 3.2 shows the solubility curve of EDA3NP. From the obtained curve, one could infer that the title compound exhibits good solubility and a positive solubility temperature gradient (direct solubility) in both the solvents.

Single crystals of EDA3NP have been grown from saturated solution of the synthesized salt of EDA3NP by slow evaporation solution growth technique with ethanol and methanol as solvents at 30 °C by using a constant temperature bath.
Figure 3.2 Solubility curve of EDA3NP

Figure 3.3 As grown crystal of EDA3NP
Pale brownish yellow crystals have been obtained over a time span of 15–20 days (Figure 3.3). But the grown single crystals are found to be unstable at room temperature and this may be due to the strong hygroscopic nature of the material. Several attempts have been made to synthesize a single crystal of EDA3NP by varying the solvents and the growth conditions such as temperature and pH. But the result was observed to be the same and the instability of EDA3NP may be due to the meta position of nitrophenol.

The melting point of EDA3NP was measured as 88 °C by using a melting point apparatus (Model: Tempo PT 100–230 V) with the finely powdered sample. The sharp melting point confirms the good purity of the sample.

3.3. ELEMENTAL, STRUCTURAL AND THERMAL ANALYSES

3.3.1 Elemental Analysis

The microanalysis was carried out with powder samples derived from the grown crystals using CHN elemental analysis to confirm the elemental composition of the synthesized compound. The elemental analysis data of the compound is given in Table 3.1. The microanalysis reveals that the percentage of carbon, nitrogen and hydrogen are in good agreement with the computed values. The difference between the percentages of elements present is negligible and is within the experimental errors.

The computed values were calculated from the molecular formula C_{14}H_{18}N_4O_6. Based on the elemental composition identified, the molecular weight is estimated to be 338.32 g. Slight increase in the hydrogen value suggest the presence of water molecule in the synthesized compound.
Table 3.1 Elemental analysis data of EDA3NP

<table>
<thead>
<tr>
<th>Element</th>
<th>Experimental (%)</th>
<th>Computed (%)</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>46.40</td>
<td>47.19</td>
</tr>
<tr>
<td>N</td>
<td>15.65</td>
<td>15.72</td>
</tr>
<tr>
<td>H</td>
<td>5.50</td>
<td>5.66</td>
</tr>
</tbody>
</table>

3.3.2 Crystal Structural Analysis

As the title compound is highly hygroscopic in nature, the grown crystals are not stable in room temperature environment. Hence, single crystal XRD was not taken for EDA3NP. However, the powder sample was subjected to powder XRD analysis. The recorded PXRD pattern of the compound is depicted in Figure 3.4. Although the peaks could not be indexed as the system of crystallization is not known, the pattern is presented to understand the identity of the system. The pattern obtained is found to be different with the pattern of ethylenediamine and 3-nitrophenol available in literature. It is worthy to be mentioned that the peak positions of the sample are found to be at different positions when compared to its counter compounds such as EDA2NP and EDA4NP. The major peak appears at 22.6 and the d-spacing values are quite different from the other nitrophenolate derivatives. The sharp crystalline peaks in the recorded pattern confirm to the crystalline nature of the material.
Figure 3.4 Powder X-ray diffraction pattern of EDA3NP

3.3.3 Molecular Structural Analyses

3.3.3.1 FTIR and Laser Raman Analyses

The recorded FTIR spectrum is shown in Figure 3.5(a). Vibrational spectroscopy is an important tool in understanding the chemical bonding. It also provides evidence for the charge transfer interaction between the donor and the acceptor groups through π-electron movement. It can be noted that the intermolecular hydrogen bonding network formed between hydrogen atoms of ethylenediamine of a cation and oxygen atoms of adjacent phenolate anions play an important role in achieving the desired molecular design [18]. The peak around 3200 cm\(^{-1}\) is assigned to intermolecular hydrogen bonding.
Figure 3.5 (a) FTIR and (b) Laser Raman spectra of EDA3NP
The peak at 3355 and 3194 cm\(^{-1}\) includes vibrations of N–H and C–H, and overtones and combination bands. In the overtone region, there is a prominent band near 1500 cm\(^{-1}\), due to combination of the asymmetrical NH\(_3^+\) bending vibration and the torsional oscillation of the NH\(_3^+\) group [19].

Asymmetrical and symmetrical bending vibrations of NH\(_3^+\) are seen at 1580 and 1506 cm\(^{-1}\). The rocking vibrations of C–H bond in phenol ring are assigned to the peaks ranges from 1100 to 1300 cm\(^{-1}\). The strong band at 1035 cm\(^{-1}\) is attributed to a C–N stretching vibrations. C–C–O symmetric stretching mode is observed as a very weak band at 870 cm\(^{-1}\). The band at 646 cm\(^{-1}\) arises due to the presence of stretching vibrations of C-C bond in the phenolic ring [20]. The torsional N–H oscillation of NH\(_3^+\) is obtained near 505 cm\(^{-1}\). From the recorded Raman spectrum (Figure 3.5(b)), the skeletal vibrations of N-O stretching and C-C stretching were mainly exhibited at 1496 cm\(^{-1}\). The strong vibration band at 1344 cm\(^{-1}\) corresponds to the C-H out of plane bending vibrations. The presence of various bands in both FTIR and Raman spectra confirms the formation of EDA3NP salt and picturizes the molecular structure.

### 3.3.3.2. FT-NMR Analysis

The \(^1\)H and \(^13\)C NMR were recorded using D\(_2\)O as solvent. Different functional groups have different characteristic chemical shifts, when compared to a given signal in an NMR spectrum having a reference table of chemical shifts and allowing the identification of functional groups in a molecule.

Hydrogen atoms attached to aromatic rings are mostly influenced by the induced ring current of the aromatic \(\pi\) electrons. \(^1\)H NMR spectra is given in Figure 3.6. Generally, the hydrogen atoms in aromatic rings appear in 6.5 ppm to 8.5 ppm range [21, 22]. The \(^1\)H NMR of EDA3NP shows four sets of peaks between 7.66 and 7.12 ppm. The signal splitting is caused by spin–spin coupling between adjacent nuclei. The doublet
obtained at 7.108, 7.112 and 7.129, 7.133 ppm represents the two protons in the C-H bond. The triplet signal obtained at 7.38, 7.36, 7.34 ppm is due to the C-H bond which has two protons. The singlet at 7.496 also represents the two protons in the ring. The other doublet signal at 7.485, 7.90 ppm is due to signal splitting of the H atom attached to the ring. The signal at $\delta = 3.0$ ppm is assigned to the D$_2$O solvent.

The recorded $^{13}$C NMR spectrum using D$_2$O as solvent is given in Figure 3.7. The presence of signal at 111.1 [111.6] and 112.6 [111.7] ppm is attributed to the C-N environment in aromatic carbons. The chemically equivalent aromatic carbons (C=C) are confirmed by the absorption peak found at 124.2 [124.9] ppm. The signals at $\delta = 130.1$ [130.1] and 148.9 [149.1] ppm represent the C-H environment in aromatic carbons. The signal at $\delta = 161.2$ [163] ppm represent the C-O environment in aromatic carbons. All the values given in the square bracket corresponds to the literature value of the title compound and it agrees very well with each other [13].

The signal at 39 ppm is attributed to the D$_2$O solvent and aliphatic C-H groups signal do not appear because of solvent effect with D$_2$O. The $^1$H and $^{13}$C NMR confirm the presence of various functional groups present in the structure of the compound. As no other peaks are observed, the synthesized compound is identified as a pure material with no association of any by product.
Figure 3.6 $^1$H NMR spectrum of EDA3NP

Figure 3.7 $^{13}$C NMR spectrum of EDA3NP
3.3.4 Thermal Analysis

EDA3NP sample weighing 3.430 mg was taken for measurement and the obtained TG-DTA curve is illustrated in Figure 3.8. Careful examination of the TGA curve of EDA3NP exhibits weight losses in two stages. The first stage of decomposition takes place for the sample before 100 °C. There is a gradual weight loss of about 3 % which shows that the synthesized material has traces of physically adsorbed water molecules. The second decomposition occurs in the temperature range of 130 and 220 °C with a major weight loss of 94% (3.2 mg). This weight loss is attributed to the decomposition of meta nitro phenol molecules from the structure of the compound [22].

It exactly matches with an endothermic peak at 202.45 °C in DTA curve which is assigned as the decomposition point of EDA3NP. A gradual weight loss of 2% starts at 220 °C and it continues up to 302 °C and leaves a final residue of 1%.

The recorded DSC curve is shown in Figure 3.9. The DSC pattern clearly shows a sharp endothermic peak at 88.4 °C without any weight loss corresponding to the melting point of the material. A small endothermic peak occurring at about 64.63 °C is assigned to secondary absorbed water or weakly entrapped lattice water. The final decomposition starts around 200 °C at where the material loses its complete weight due to the dissociation of carbon network [23].
Figure 3.8 TG-DTA curve of EDA3NP

Figure 3.9 DSC curve of EDA3NP
3.4 LINEAR OPTICAL ANALYSIS

The UV–Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron in the $\sigma$ and $\pi$ orbital from ground state to higher energy state. The UV–Vis–NIR spectrum of EDA3NP is shown in Figure 3.10. When absorption is monitored from shorter wavelength to longer wavelength, the enhanced absorption is observed between 200 nm and 400 nm. The material shows a very strong absorption in the UV region. The absorption maxima peaks are found to be at 214, 231, 272 nm with absorbance of 3.644, 3.489 and 2.248 respectively. The material shows gradual decrease in absorbance beyond 333 nm (0.846) and it almost becomes zero (0.2) at 400 nm.

Figure 3.10 UV-Vis Absorbance spectrum of EDA3NP
The cutoff wavelength of EDA3NP is found to be 400 nm and the sample has maximum transmission up to 96 %. The optical window is found to be 400–1500 nm. This is mainly due to the presence of 3-nitrophenol. In general, the absorption peaks of benzene are mainly around 200 nm. However, when it comes to 3-nitrophenol, which has a hydroxyl group and a meta-substituent of nitro group, the absorption peaks are strongly red shifted [24]. The conjugated groups enhance the \( \pi-\pi^* \) transition of 3-nitrophenol.

There is low absorption at the fundamental wavelength (1064 nm) of the Nd:YAG laser which contributes to its resistance in laser induced damage. Further, there is very little absorption at the wavelength of 532 nm, which can improve the second harmonic output. The characteristic absorption band is observed at 333 nm and hence the crystal is expected to be transparent to all the UV–Visible–NIR radiation in between these wavelengths. The material with low absorbance and wide optical window range makes it valuable for applications that require blue–green light. This enabled in arriving at a perceptible conclusion that the material can be a better entrant for nonlinear optical applications. The linear refractive index is evaluated theoretically using the reflectance data for the wavelength of interest and found to be 1.37 @ 532 nm.

3.5 NONLINEAR OPTICAL ANALYSIS

3.5.1 SHG Test

The grown specimen of EDA3NP was subjected to a Kurtz powder test [25-27] using a Q-switched, mode locked Nd:YAG laser of 1064 nm with the frequency 10 Hz and a pulse width of 8 ns (spot radius of 1 mm). The input laser beam was directed on the crystal powder. The emitted light was passed through an IR filter and was measured by means of a photomultiplier tube and oscilloscope assembly. When a laser of 1064 nm was radiated directly on the powder, a green light beam of double frequency 532 nm was observed thus, indicating that EDA3NP possesses second harmonic generation behaviour.
The SHG efficiency of the EDA3NP sample was evaluated by taking the microcrystalline powder of KDP as the reference material. The SHG efficiency results show a signal output of 14 mV with input laser power of 5.5 mJ/pulse when compared to 44 mV of KDP. Relative powder SHG efficiency of EDA3NP is only 0.3 times than that of KDP.

3.5.2 Z-Scan Analysis

The transmittance through the aperture as a function of the distance between the sample and the beam waist is called Z-scan curve. The Z-scan technique offers a useful path to probe both the nonlinear refractive index and the nonlinear absorption coefficient of a sample. The nonlinear refractive index of EDA3NP was determined by the closed Z-scan method developed by Sheik-Bahae et al. [28] where a linearly polarized Gaussian beam from a diode-pumped Nd:YAG laser of wavelength 532 nm was used as the excitation source for the Z-scan technique. The Gaussian profiled laser beam was focused on a 1 mm cuvette containing the 1mM concentration EDA3NP solution by lens, \( f = 3.5 \) cm to produce a beam waist \( \omega_0 \) of 15.35 \( \mu \)m. As the sample is scanned through the beam, the far field profile shows intensity variation across the beam profile, which is recorded through an aperture. Open aperture Z-scan was performed on the material in order to probe the nonlinear absorption mechanisms. Also, the experiment was repeated with pure solvent (ethanol) to measure its contribution and no significant feature was observed for ethanol in either the open or the closed Z-scan traces.

Figure 3.11 gives the nonlinear pattern obtained for closed and open aperture of Z -scan in EDA3NP in ethanol at a concentration 1 mM. The curve 3.11 (a), shows the normalized transmittance obtained from the closed Z-scan experiment as a function of axis distance Z measured from the focal point. The peak followed by a valley- normalized transmittance obtained from the closed aperture Z -scan data indicates that the sign of the refraction nonlinearity is negative, i.e., self-defocusing occurs. The self-defocusing effect
is due to the local variations in the refractive index with temperature [29]. Table 3.2 summarizes the values of the nonlinear refractive indices, the nonlinear absorption coefficients, and the third-order susceptibilities of EDA3NP in liquid media following the theory developed by Sheik Bahae et al. [28].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>EDA3NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonlinear refractive index (n&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>-3.99 x 10&lt;sup&gt;-8&lt;/sup&gt; cm²/W</td>
</tr>
<tr>
<td>Nonlinear absorption coefficient (β)</td>
<td>-6.11 x 10&lt;sup&gt;-3&lt;/sup&gt; cm/W</td>
</tr>
<tr>
<td>Real part of the third-order</td>
<td>1.89 x 10&lt;sup&gt;-6&lt;/sup&gt; esu</td>
</tr>
<tr>
<td>susceptibility [Re(χ&lt;sup&gt;3&lt;/sup&gt;)]</td>
<td></td>
</tr>
<tr>
<td>Imaginary part of the third-order</td>
<td>1.23 x 10&lt;sup&gt;-6&lt;/sup&gt; esu</td>
</tr>
<tr>
<td>susceptibility [Im(χ&lt;sup&gt;3&lt;/sup&gt;)]</td>
<td></td>
</tr>
<tr>
<td>Third-order nonlinear optical</td>
<td>2.25 x 10&lt;sup&gt;-6&lt;/sup&gt; esu</td>
</tr>
<tr>
<td>susceptibility (χ&lt;sup&gt;3&lt;/sup&gt;)</td>
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In curve 3.11 (b), the pattern from open aperture refers to the saturable absorption. Although from Figure 3.10, it can be inferred that, the material shows a small linear absorption (0.2) at 532 nm, it has strong non linear which is evident from the peak pattern signature [30]. Since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of n<sub>2</sub> is less straightforward. Hence to obtain pure and effective n<sub>2</sub> the closed aperture transmittance is divided with its corresponding open aperture transmittance. The ratio of closed-aperture transmittance to the corresponding open-aperture transmittance is shown in Figure 3.11 (c).
Figure 3.11 (a) Closed aperture pattern, (b) Open aperture pattern, (c) Ratio of closed aperture to open aperture transmittance pattern of Z-Scan and (d) Optical limiting pattern of EDA3NP
3.5.3 Optical Limiting Studies

Figure 3.11 (d) shows the optical limiting behavior of EDA3NP solution. For incident energy less than 36 mW, the output varies linearly according to Beer’s law and above this; the output saturates and becomes a plateau. The threshold value is 36 mW and the corresponding output value gets clamped at 7.91 mW. This verifies that the samples are good candidates for optical limiting at 532 nm cw lasers. Thus EDA3NP with strong nonlinear response and self-defocusing behavior is a potential candidate for the protection of optical sensors such as night vision devices.

The nonlinearity in this case being of thermal origin, the value of the nonlinear refractive index depends on the sample concentration. The optical limiting threshold can be improved by changing the operational parameters such as sample concentration, aperture size and the focal length of the lens. Thus the optical arrangement can be modified according to the requirements of the dynamic range and field of view of the sensor [30, 31].

3.6 CONCLUSION

An organic material, EDA3NP was synthesized for second and third order NLO applications and single crystals were grown by slow evaporation technique. Molecular structural confirmation was carried out by FTIR, FT-NMR and Raman studies. It can be noted from the FTIR that the intermolecular hydrogen bonding network formed between hydrogen atoms of ethylenediamine of a cation and oxygen atoms of adjacent phenolate anions play an important role to achieve the desire molecular design. The $^1$H and $^{13}$C NMR confirm the presence of various functional groups in the structure of the compound. As no other peaks are observed, the synthesized compound is a pure material. The DSC pattern clearly shows a sharp endothermic peak at 88.4 °C without any weight loss which corresponds to the melting point of the material. DTA curve shows that the
decomposition point of EDA3NP is 202.45 °C. The material with wide optical window range (400–1500 nm) makes it valuable for applications that require blue–green light. This enable in arriving at made us to come to a perceptible conclusion that the material can be a better entrant for nonlinear optical applications.

EDA3NP was characterized with negative nonlinear refraction and saturable absorption behavior by employing the Z-scan technique and by using cw excitation at 532 nm. They possessed high nonlinearities which are primarily thermal in nature. In solution form, its nonlinear refractive index, nonlinear absorption coefficient and third-order nonlinear optical susceptibility were recorded as – 3.99 x 10⁻⁸ cm² W⁻¹, - 6.11 x 10⁻³ cm W⁻¹ and 2.25 x 10⁻⁶ esu respectively. EDA3NP possess low optical limiting thresholds in the range of 36 mW, with the output clamped at 7.91 mW. Thus the material could be efficiently used as optical limiters by utilizing their high refractive nonlinearity and judicious aperture based design in low power cw regime. By Kurtz powder technique, the efficiency of EDA3NP was found to be only 0.3 times that of KDP. The optical limiting behavior of EDA3NP indicates that this material is a potential candidate for the protection of optical sensors.

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