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Structural, Theoretical and Experimental Properties of Meta Nitro Aniline (mNA)

Niranjana SR, Madhavan J and Victor Antony Raj M*.

Department of Physics, Loyola College, Chennai 600034, Tamil Nadu, India.

ABSTRACT

Organic Non Linear Optical single crystal of mNA are grown successfully by slow evaporation technique. Powder XRD analysis of the grown crystal confirms the crystalline nature of the crystals. Optical frequency absorption ability of the sample is analyzed by UV-Vis-NIR spectroscopic studies and optical band gap is obtained as 4.625 eV using Tauc's plot. FT-IR analysis of the grown crystal showed the functional groups exists in the grown crystal. Kurtz and perry technique is employed for Second Harmonic Generating (SHG) efficiency of the crystal and it is found as 30.4 times higher than KDP. HOMO-LUMO energy gap of mNA molecule is obtained as-0.13077 a.u .

Keywords: structural, theoretical, meta nitro aniline, mNA.

**Corresponding author*

INTRODUCTION

Today's industry has a strong demand for crystal species that are effective non-linear optical materials. Several practical applications such as lasers utilize such crystals. In general, organic nonlinear optical crystals have a better NLO capacity, with lower dielectric constants, than their inorganic counterparts [1]. The basic properties required for the applied use of NLO crystals are, that they have enough optical nonlinearity and are of sufficient size able to be subjected to mechanical processes such as crystal cutting and polishing at any angle. Many new organic crystals have been examined based on the predictive molecular engineering approach and have been shown to have potential applications. Molecular flexibility of organic materials is an added advantage to enhance the nonlinear optical properties in a desired manner. Molecules having large optical nonlinearity are likely to condense into a crystal with a noncentrosymmetric structure that gives rise to the non-quadratic NLO phenomenon. This is because a noncentrosymmetric structure is energetically more stable when compared to a centrosymmetric one. For example, meta nitro aniline (mNA), a typical organic NLO crystal, has a large optical nonlinearity and growing potential crystals are extremely useful for the enhancement of nonlinear optical devices [2]. Thus, the development of highly effective NLO crystals possessing large quadratic NLO properties and large dimensions are in need. In this article we present the growth, experimental and theoretical optical parameters of mNa a potential NLO material.

MATERIALS AND METHODS

Experimental

The saturated solution of mNA in acetone was prepared at 40°C. The purified mNA material were used for solubility studies and to grow bulk single crystals. Since mNA is less soluble in water, acetone was chosen as the solvent. The solubility of mNA was measured at 30, 35, 40, 45, 50, and 55°C by gravimetric method. It was found that solubility increased as the temperature increases. The solutions were filtered at the same temperature to avoid any insoluble impurities. Then, the solvent was allowed to evaporate, in order to obtain the maximum purification. The yielded material was further recrystallized twice before the growth is initiated. The purified salt is used to grow good optical quality bulk single crystals meta-nitro aniline. Figure.1 shows the photograph of as grown mNA single crystals. Grown crystals were characterized by Powder XRD studies, UV-Vis Spectral analysis, FT-IR analysis, Second Harmonic Efficiency studies, and HOMO-LUMO studies.

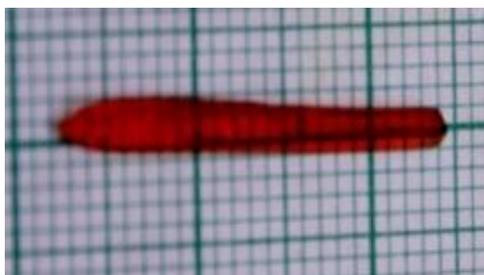


Figure.1. Photograph of as grown mNA single crystals

Computational details.

Quantum chemical Density Functional Theoretical (DFT) computations were performed using closed-shell Becke–Lee–Yang–Parr hybrid exchange–correlation three-parameter functional (B3LYP) in combination with 6-31G (d, p) basis set to derive the complete geometry optimizations, hyperpolarizability and HOMO-LUMO gap on isolated entities. The atom numbering scheme adopted in this study is given in Fig. 2. Above said task was achieved using Gaussian03W [3] program package, invoking gradient geometry optimization. The optimized geometries corresponding to the minimum potential energy surface have been obtained by solving self consistent field (SCF) equation iteratively. The absence of imaginary values of wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

Powder X-ray diffraction technique

The grown mNA sample was crushed as fine powder for X-ray diffraction studies. The recorded X-ray diffraction pattern of mNA is depicted in Figure 3. The recorded spectrum of the sample was taken at room temperature in a 2θ range of 10 to 50° using $\text{Cu K}\alpha$ radiation of wavelength 1.5418 \AA . It is confirmed that mNA belongs to orthorhombic crystal system, the unit cell parameters were found to be $a = 6.501 \text{ \AA}$, $b = 19.330 \text{ \AA}$ and $c = 5.082 \text{ \AA}$ with point group $mm2$, space group Pbc_21 . Sharp peaks in the XRD pattern reveals the high crystallinity of grown crystal.

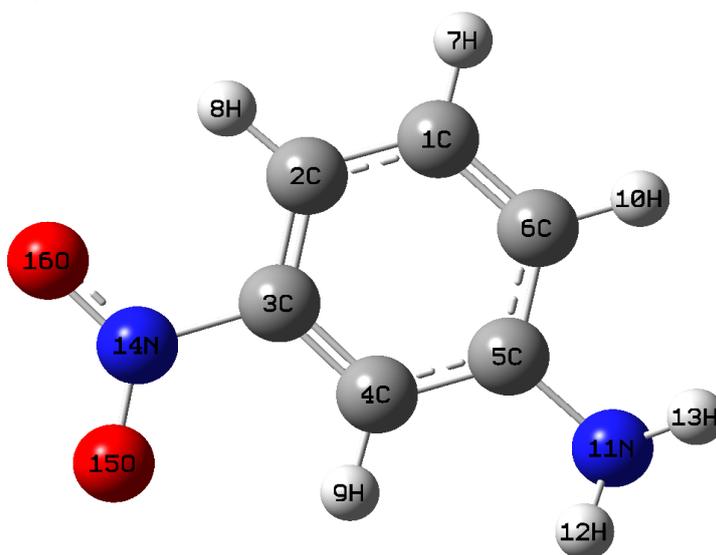


Figure 2: Atomic numbering adapted for ab initio computations of mNA molecule

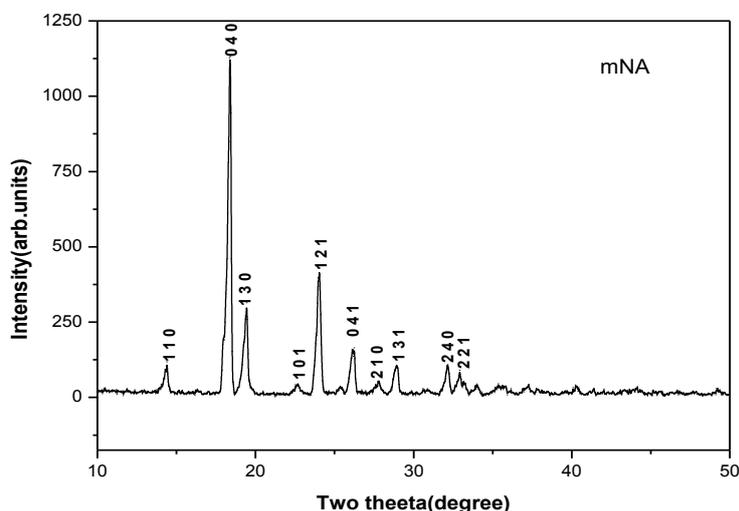


Figure 3L XRD pattern of mNA single crystal

Linear Optical Properties

The optical absorption plays an important role in identifying the potential of the NLO material. Materials having wide absorption window with reduced absorption around the fundamental and second harmonic wavelength are of greater utility for NLO applications. The optical absorption spectrum of mNA crystal has been recorded in the region 200-800 nm using Varian Cary 5E Model spectrophotometer. The UV-

Vis absorption spectrum of mNA single crystal is shown in Figure 4. The UV-Vis spectrum gives optical information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron in σ and π orbital from the ground state to higher energy states. The cut-off wavelength of mNA is found to be 317 nm. This reveals that the mNA crystal is highly suitable for second harmonic generation applications. The optical bandgap (E_g) could be estimated from the plots of $h\nu$ versus $(\alpha h\nu)^2$. A plot of $h\nu$ versus $(\alpha h\nu)^2$ was drawn (Fig. 5) and the optical band gap (E_g) value was obtained from the interception of the linear portion of the curve with X-axis. This gives the E_g value of 4.625 eV for metanitroaniline single crystal.

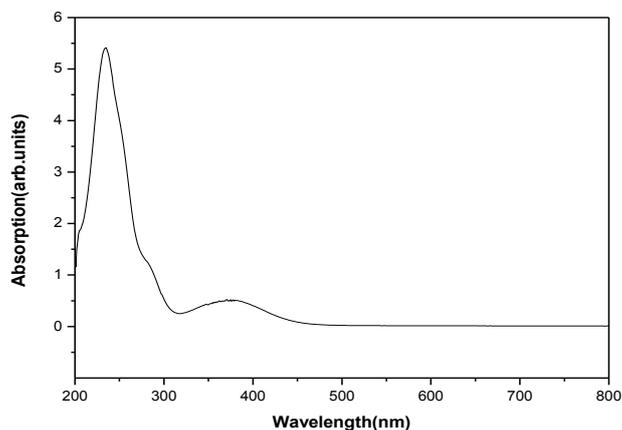


Figure 4: Optical absorption spectra of mNA single crystal

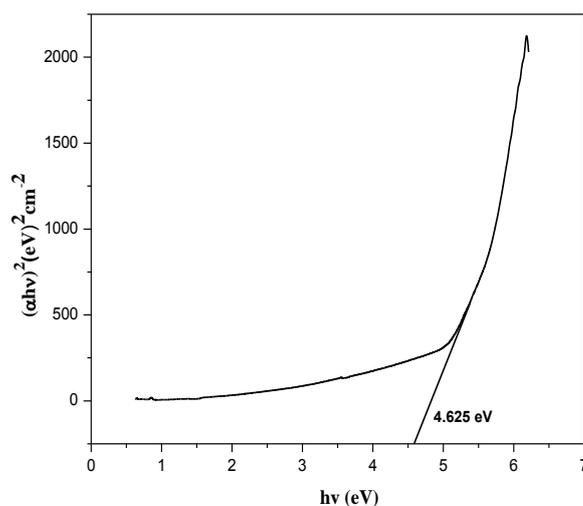


Figure5: Optical band gap of mNA crystal

FT- IR spectra

The main objective of the vibrational analysis is to find vibrational modes connected with specific molecular structures of the compound. FT-IR spectrum of the mNA crystal was recorded in the range 500 cm^{-1} to 4000 cm^{-1} , using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. Obtained FT-IR spectra of the sample is shown in figure.6

NH₂ Vibrations

The NH₂ asymmetric stretching vibrations[4] give rise to a strong band in the region $3390\pm 60\text{ cm}^{-1}$ and the symmetric NH₂ stretching is observed as weak band in the region $3210\pm 60\text{ cm}^{-1}$. NH₂ asymmetric and

symmetric stretching vibration is at 3431 and 3329 cm^{-1} respectively in the recorded spectrum of mNA crystal. The rocking/twisting mode of NH_2 is expected in the region $1195 \pm 90\text{ cm}^{-1}$ in IR spectrum. A strong peak obtained at 1089 cm^{-1} in mNA exhibits the presence of NH_2 rocking/twisting mode of vibration. The wagging mode of NH_2 is expected in the region $840 \pm 55\text{ cm}^{-1}$. The candidate material mNA exhibits this NH_2 wagging vibration at 868 cm^{-1} . Bellamy L.J 1975 suggested that the NH_2 scissoring mode lies in the region $1529\text{--}1650\text{ cm}^{-1}$ [5]. Baran E.J et al (2007) reported the NH_2 scissoring, exists at 1680 cm^{-1} and 1664 cm^{-1} for some organic complexes [6]. In accordance with above literature data, in our present study of mNA the NH_2 scissoring mode vibrations occurred at 1624 cm^{-1} . The presence of a strong absorption peaks at 1348 cm^{-1} (NH_3^+ symmetric deformation), 1264 cm^{-1} (NH_3^+ rocking mode) and at 2926 cm^{-1} (NH_3^+ asymmetric stretching) confirmed the protonation of the molecule.

O-H Vibrations.

The O–H group gives rise to three vibrations (stretching, in-plane bending and out-of-plane bending vibrations). The O–H group vibrations are likely to be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. The hydroxyl stretching vibrations are generally observed in the region around 3500 cm^{-1} [7]. In the case of the un-substituted phenols it has been shown that the frequency of O–H stretching vibration in the gas phase is 3657 cm^{-1} [8]. In our case a strong FT-IR bands at 3093 , and 3075 cm^{-1} are assigned to O–H stretching vibrations. The reason for the blue shift may be due to solid phase of the material. The O–H in-plane bending vibration in the phenols, in general lies in the region $1150\text{--}1250\text{ cm}^{-1}$ and is not much affected due to hydrogen bonding unlike to stretching and out-of-plane bending frequencies. The weak band in FT-IR spectrum at 1163 cm^{-1} is assigned to O–H in plane bending vibration. The O–H out-of-plane bending mode for the free molecule lies below 300 cm^{-1} and it is beyond the infrared spectral range of the present investigation. However, for the associated molecule the O–H out-of-plane bending mode lies in the region $517\text{--}710\text{ cm}^{-1}$ in both intermolecular and intramolecular associations, the frequency is at a higher value than in free O–H [9]. In our present investigation a strong band observed in FT-IR spectrum at 669 cm^{-1} is assigned to O–H out-of-plane bending vibration.

C-N Vibrations

The C-N ring stretching vibration bands occur in the region $1650 - 1500\text{ cm}^{-1}$ [10]. mNA molecule exhibits this vibration in IR spectrum at 1582 cm^{-1} . C–N stretching absorption is usually assigned in the region $1382\text{--}1266\text{ cm}^{-1}$ [11]. In our present work, the band observed at 1264 cm^{-1} in FT-IR spectrum has been assigned to C–N stretching vibration for mNA. Frequency band observed at 735 cm^{-1} by FT-IR analysis is assigned to C-N out plane bending and band at 817 cm^{-1} is due to C-N in plane deformation for mNA single crystals.

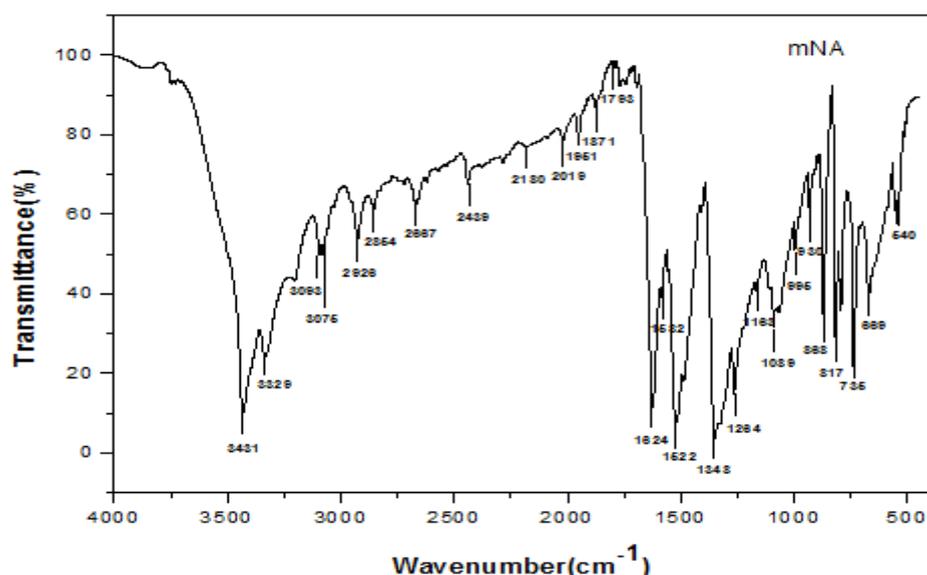


Figure 6: FT-IR spectrum of mNA single crystal

NLO studies

The nonlinear optical property of the grown mNA single crystal was tested by passing the output of Nd: YAG Quanta ray laser with pulse energy emitting 1064 nm, generating about 6 mJ / pulse. The SHG efficiency of mNA was determined by Kurtz and Perry powder technique [12]. Microcrystalline material of KDP was used as a reference for comparison with mNA for Second Harmonic Generation experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 92 mW and 2.8 W, respectively were obtained for KDP and mNA samples. Thus, the SHG efficiency of mNA is 30.4 times higher than KDP.

HOMO-LUMO Analysis

The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule. We obtained a plot of the frontier molecular orbital of the first and last molecules of each group (HOMO and LUMO) to analyze the main atomic contributions for these orbitals. The energy gap between HOMO and LUMO characterizes the molecular chemical stability and it is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. Relatively large LUMO–HOMO energy gap of the studied molecule indicates that it can be considered as kinetically stable. In addition, energy of the HOMO is directly related to the ionization potential, while energy of the LUMO is directly related to the electron affinity. The features of the HOMO and LUMO calculated by DFT/ B3LYP/6-31G (d, p) can be seen in Fig.7. The energy gaps are largely responsible for the chemical and spectroscopic properties of the molecules [13]. According to the calculation the energy band gap (ΔE) of the molecule is about -0.13077 a.u.

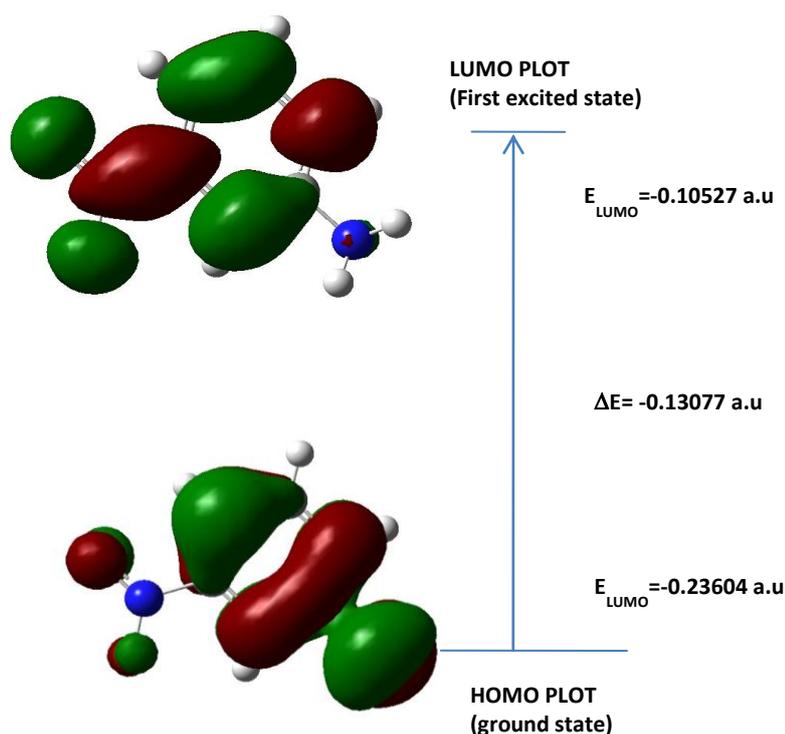


Figure 7 : HOMO – LUMO plot of mNA molecule

CONCLUSION

Good quality single crystals of mNA are grown successfully by slow evaporation technique. The crystalline nature of the crystals are confirmed by Powder XRD analysis. Full Width at Half maximum value obtained from High Resolution XRD studies showed the high crystalline quality of the as grown single crystal.

UV-Vis-NIR spectroscopic studies is employed to understand the Optical frequency absorption ability of the as grown sample. Optical band gap mNa is obtained as 4.625 eV using Tauc's plot. FT-IR analysis of the grown crystal showed the functional groups present in the crystal. Second Harmonic Generating (SHG) efficiency of the crystal is found as 28 times higher than KDP. HOMO-LUMO energy gap of mNA molecule is obtained as 0.13077 a.u .

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