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Synthesis, Crystal Growth and Characterization of Organic NLO Material: M-Nitroacetanilide

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Abstract

Single crystals of m-Nitroacetanilide (mNAa) were successfully grown by slow evaporation method at a constant temperature 40˚C from methanol solution. The solubility studies for mNAa were estimated. The cell dimensions were obtained by single crystal X-ray diffraction (XRD) study. The functional groups have been confirmed using Fourier transform infrared (FTIR) analysis. The placement of protons was identified from Nuclear Magnetic Resonance Spectroscopy (NMR) spectral analysis. UV-visible and fluorescence spectral analyses were carried out for the grown crystals. Thermo gravimetric analysis and differential thermal analysis were carried out to determine the thermal properties of the as grown crystal. The Second Harmonic Generation (SHG) efficiency of mNAa was also determined.

Keywords: Supersaturated Solution, X-Ray Diffraction, Single Crystal Growth, Organic Compounds, Nonlinear Optic Materials

1. Introduction

Nonlinear optical materials (NLO) have proven to be an interesting candidate for a number of applications such as second harmonic generation, frequency mixing, electro-optic modulation, etc. In recent years, organic NLO materials are attracting a great deal of attention for possible use in optical devices because of their large optical nonlinearity, low cut-off wavelengths, short response time and high laser damage thresholds [1]. Considerable work has been done in order to understand the microscopic origin of nonlinear behavior of organic materials [2-5]. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electrooptic effect and large second- or third-order hyperpolarizibilities compared to inorganic NLO materials [6]. Thus, there is much impetus to design and understand organic compounds for SHG applications.

To possess NLO property organic materials should contain highly conjugated π electron system affected by electron donor and acceptor groups. Hence in this class one such acetanilide derivatives, mNAa was taken under study which showed efficient NLO property. Some of the acetanilide derivatives such as Acetoacetanilide [7,8] and *p*-aminoacetanilide [9] were found to exhibit NLO properties. mNAa is a meta substituted aromatic compound with molecular formula $C_8H_8N_2O_3$. The molecular structure of mNAa, given in **Figure 1**, shows the charge transfer between electron acceptor (NO_2) and electron donor (NHCOR where R = CH_3) groups. This compound crystallizes in the monoclinic system in the chiral space group $P2_1$ with four independent molecules in the asymmetric unit. In this paper, we report the material synthesis, solubility, crystal growth, single crystal X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), optical, Fluorescence, thermal and NLO studies of mNAa.

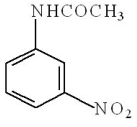


Figure 1. Molecular structure of mNAa.

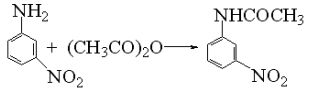
2. Experimental

2.1. Material Synthesis

The title compound was synthesized from analytical reagent (AR) mNA and acetic anhydride following the procedure given by Mahalakshmi *et al*. [10]. Required quantity of m-nitroaniline was dissolved in acetic anhydride at room temperature. The direct reaction between them as shown in the **Scheme 1** immediately yielded yellow colour compound. The precipitated product was filtered and dried using vacuum filtration. The material was repurified by recrystallization processes.

2.2. Solubility and Crystal Growth

The solubility of mNAa was determined using methanol, since methanol is found to be a suitable solvent to grow considerable size crystals. Recrystallized salt was dissolved in methanol and the solution was maintained at 30˚C in a constant temperature bath and stirred continuously to ensure homogenization of the solution. On reaching the saturation, the amount of the salt in the solution was analyzed gravimetrically. The same procedure was repeated for the temperatures 35˚C, 40˚C, 45˚C and 50˚C and results are shown in **Figure 2**. The mNAa exhibits good solubility and a positive solubility-temperature gradient in methanol. From the figure we understand that the solubility of mNAa is going saturated at higher temperatures.



Scheme 1. Reaction mechanism of m-Nitroacetanilide.

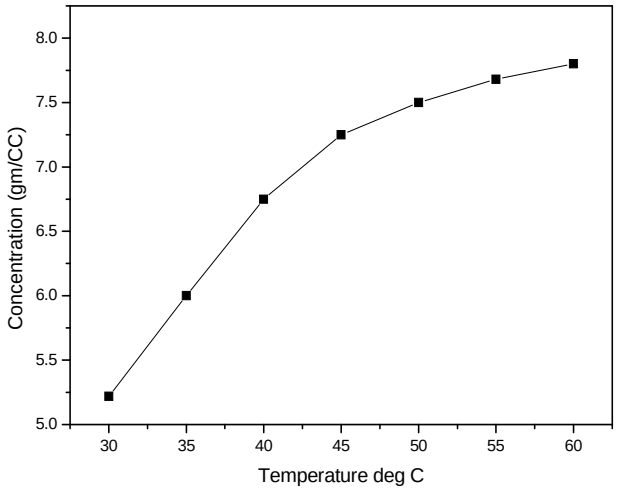


Figure 2. Solubility curve of mNAa.

Single crystals of mNAa were grown by slow evaporation growth technique using methanol as the solvent. About 250 ml of saturated solution was prepared at 40˚C and it was carefully filtered at the same temperature using Whatman filter paper of pore size 11 μm. The filtered solution was taken in a beaker and placed in a constant temperature bath maintained at 40˚C having an accuracy of ±0.01˚C. Optically good quality seed crystal of dimension 7 mm × 2 mm × 1 mm, obtained from slow evaporation method, was introduced into this solution. Crystal of dimension 10 mm × 4 mm ×3 mm was harvested in a growth period of two days using solvent evaporation method. The morphology of the harvested crystal was tetragonal bipyramid as shown in **Figure 3**.

3. Results and Discussions

3.1. Single Crystal X-Ray Diffraction

Single crystal XRD studies were carried out on the as grown mNAa crystal using Enraf-Nonius CAD-4 single crystal XRD reveals that mNAa belongs to monoclinic system. The unit cell parameters obtained are a = 9.7609 Å (9.767 Å), b = 13.3084 Å (13.298 Å), c = 13.3124 Å (13.272 Å), β = 103.15˚ (102.99˚) and cell volume is 1683.8 Å^3 (1679.8 Å^3). These values are in close agreement with the corresponding values given in parentheses reported by Mahalakshmi *et al*. [10].

3.2. Fourier Transform Infrared Spectroscopy

FTIR spectrum of the as grown crystals was recorded in the range 400 cm^{-1} - 4000 cm^{-1} at room temperature using JASCO 460 plus FTIR spectrometer. The sample was prepared following the pressed KBr pellet technique. The presence of functional groups of the sample, were identified from the spectrum as shown in **Figure 4**. The absorption at 3263 cm^{-1} is due to N-H stretching. The peak at 1674.10 cm^{-1} corresponds to C = O stretching vibration of carbonyl group. The presence of nitro group is confirmed by the peaks at 1556.88 cm^{-1} and 1599 cm^{-1}. The peaks at 1380 cm^{-1}, 1472.81 cm^{-1} and 1426.40 cm^{-1} are due to C = C stretching [11-13].

3.3. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectrum of mNAa was recorded using JEOL GS × 400 model FT-NMR spectrometer. mNAa crystal was powdered and dissolved in deuterated Dimethyl Sulfoxide (DMSO). FT-NMR spectrum recorded for mNAa is shown in **Figure 5**. A triplet at 7.5 ppm is due to aromatic proton. The singlet at 2.07 ppm is assigned to

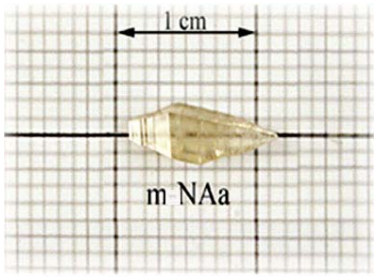


Figure 3. Photograph of as grown crystal.

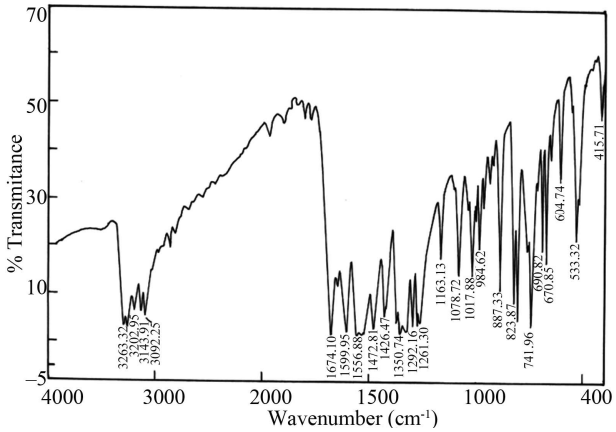


Figure 4. FTIR spectrum of mNAa.

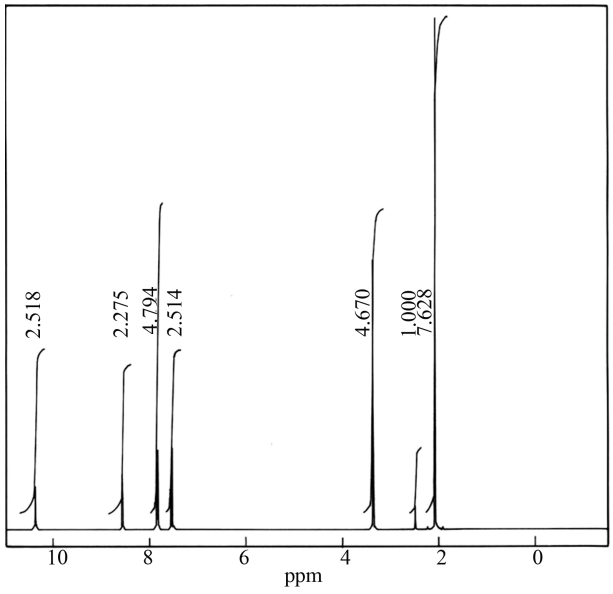


Figure 5. NMR spectrum of mNAa.

CH_3 proton. Singlet at 3.37 ppm is due to NH. A singlet at 10.39 ppm is due to NH proton [12].

3.4. UV-Vis Studies

Optical transmittance spectrum of mNAa single crystal was recorded in the region 200 nm - 1100 nm using SHIMADZU 1601 UV-Vis spectrophotometer. The maximum transmittance is about 61% for mNAa crystal of 3 mm thickness. UV-Vis transmission spectrum presented in **Figure 6** shows that the crystal has good transparency in the range 340 nm - 1100 nm, which indicates that this crystal can be employed in the NLO applications in the entire visible and IR region. The absence of the absorption in the visible region is the necessity for this compound as it is to be exploited for NLO applications in the room temperature.

3.5. Fluorescence Studies

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability [14]. Fluorescence finds wide application in the branches of biochemistry and medicine. It is also used as lighting in fluorescent lamps, Light Emitting Diode (LED) lamps etc. The excitation and emission spectra for mNAa recorded using FP-6500 Spectrofluorometer shown in **Figure 7**. The emission spectrum was measured in the range 350 nm - 600 nm. It is observed that the compound was excited at 340 nm and the corresponding emission was observed at 409 nm. The compound mNAa fluoresces due to the carbonyl chromophore [15].

3.6. NLo Studies

A preliminary study of the powder SHG conversion efficiency was carried using Kurtz and Perry powder technique [16]. Q-switched Nd:YAG laser (QUANTA RAY ICR 11) of wavelength 1064 nm with an input power of 5 mJ and pulses of 8 ns with the repetition rate of 10 Hz was used. The crystalline sample of mNAa was pow-

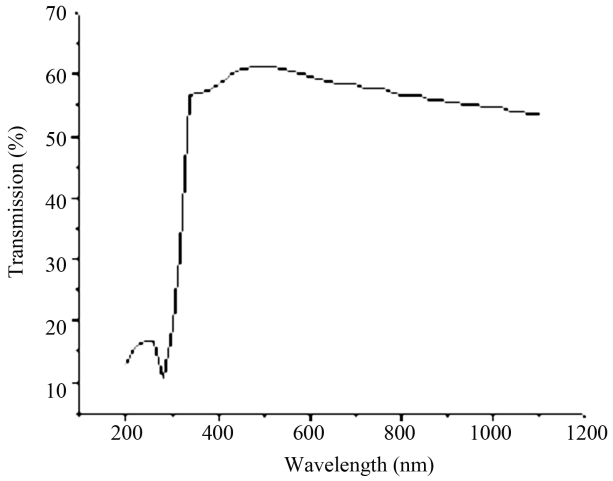


Figure 6. UV-Vis spectrum of mNAa.

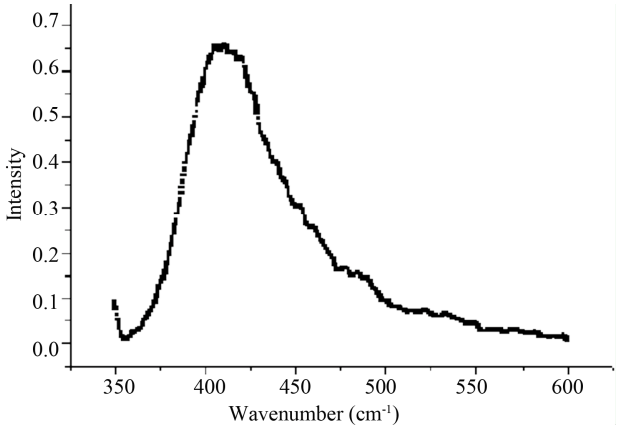


Figure 7. Emission spectrum of mNAa.

dered to a particle size of ≈ 125 μm. When the powder sample of mNAa was illuminated with this laser source emission of green light was observed. In order to determine the efficiency of mNAa, a sample of parent compound mNA, which is also found to be an important material in the research field of nonlinear optics [17] was powdered to the same particle size and hence was used as reference material. The SHG conversion efficiency of mNAa is found to be 0.1 times that of mNA.

3.7. Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out for mNAa and spectra are shown in **Figure 8**. They were recorded using a simultaneous thermal analyzer PL-STA 1500 in nitrogen atmosphere for temperature range 20˚C to 800˚C at a heating rate of 20˚C/min. The sharp endothermic peak in DTA at 148˚C indicates the melting point of the crystal. The melting point measured directly using TEMPO melting point apparatus was 149˚C. There is no exothermic or endothermic peak below this endotherm. This illustrates the absence of any absorbed water in the crystal sample. It also shows the absence of any isomorphic transition. The material exhibits single sharp weight loss starting at 215˚C and below this temperature no significant weight loss is observed. The sharpness of the peaks indicates a good degree of crystallinity of the sample.

4. Conclusions

A single crystal of mNAa, an organic NLO material, was grown by solvent evaporation method from methanol solution. The single crystal X-ray analysis revealed that the crystal belongs to monoclinic system. The functional groups were identified using FT-IR spectroscopic technique. NMR spectral analysis were carried out to identify

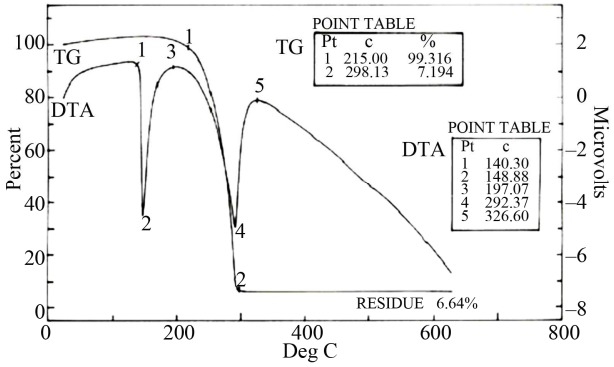


Figure 8. TGA-DTA curves of mNAa.

the position of protons. The optical properties such as UV-Vis in transmittance mode and second harmonic generation (SHG) conversion efficiency were investigated to explore the nonlinear optical characteristics of the above crystal. In addition, the thermal properties of the mNAa crystal were studied with TG analysis.

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