

Growth and Characterization of 4 –Bromo 2-nitro Aniline a New Nonlinear Optical Organic Crystal

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Abstract

The single crystals of organic nonlinear optical material 4 – Bromo 2-nitro aniline were grown by solvent evaporation technique using ethanol as solvent. The grown crystals were characterized by IR, NMR and mass spectroscopy. The crystal shows high second harmonic generation conversion efficiency.

Keywords: A1. Optoelectronics; A2. recrystallized; B1. evaporation technique; B2. powder technique.

Introduction

Optoelectronics has stimulated the search for highly nonlinear organic crystals for efficient signal processing [1-3]. In recent years, organic NLO materials have been the subjects of intensive study because of their advantages in comparison with currently used inorganic materials [4]. Also an extremely large number of organic compounds with non localized Π - electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the inorganic optical materials.[5]. The crystal with high NLO property is the interest of research due to its wide application including the photonics. In this paper, the crystal growth of a new organic Non Linear Optical (NLO) crystal - 4-bromo 2- nitro aniline is reported. The grown crystals are characterized for their chemical composition and also are tested for its SHG conversion efficiency.

Experimental Procedure

Synthesis and Crystal growth

m-nitro acetanilide shows very weak SHG conversion property i.e; 0.037 times that of urea. As the presence of bromine increases the SHG property of the organic compound [6] we tried to synthesize 4-bromo m-nitro acetanilide by the following procedure.

Calculated amount of acetanilide is dissolved in the calculated amount of glacial acetic acid and is stirred well in a conical flask. To this calculated amount of bromine in glacial acetic acid is added slowly drop wise along with constant stirring. Precipitate formed is 4-bromo acetanilide(M.P is 167deg.C). Calculated amount of recrystallized 4-bromo acetanilide is taken in a conical flask and to this nitrating mixture is added keeping the temperature below 10°C. Pour the reaction mixture on to 250g of crushed ice with vigorous stirring.

The precipitate formed is filtered dried and recrystallized with ethanol. The melting point of the compound formed is found to be 112°C. To confirm the formation of compound the elemental analysis was carried out and the spectral analysis indicates the formation of 4-bromo 2-nitroaniline rather than the 4-bromo m-nitroaniline which we tried for.

Good quality crystals of the title compound are grown by slow evaporation technique [7-9] using ethanol as the solvent. Laboratory grown crystals of 4-bromo 2-nitroaniline is shown in fig.1.

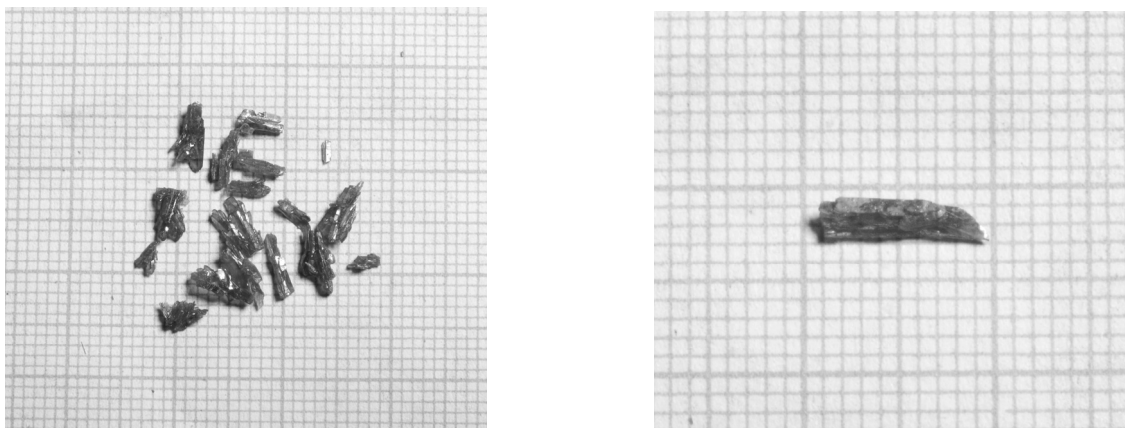
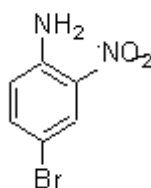


Figure 1

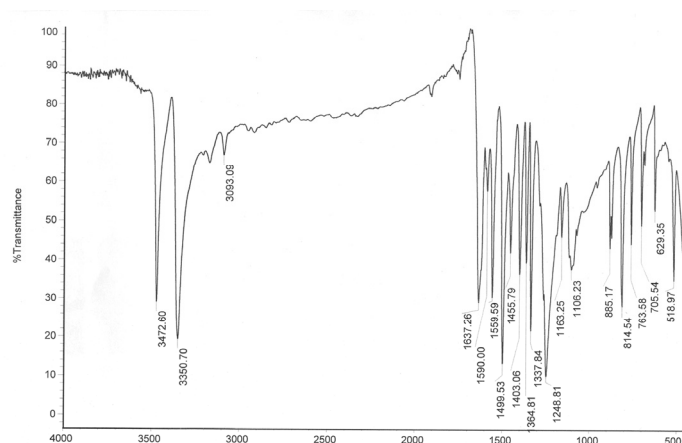
The schematic diagram of the title compound is shown in fig2.

**Figure 2**

Crystal characterization

IR spectrum

In order to qualitatively analyze the presence of functional groups in 4-bromo 2-nitroaniline Fourier Transformation Infrared (FTIR) was recorded 500 to 4000 cm^{-1} using the Thermo Nicolet, Avatar 370 spectrometer. The sample used was in pellet form in KBr phase. The characteristic absorption peaks are observed in the range from 500 to 4000 cm^{-1} is shown in fig. 3. The peak due to aromatic H is at 3093 cm^{-1} . The peak at 3472 is due to NH₂.

**Figure 3**

Mass and NMR spectra

The mass [10] and NMR spectra of 4-bromo 2-nitroaniline is carried out. The FAB mass spectra were recorded on a JEOL SX 102.DA-6000 Mass Spectrometer/Data system using (6kV,10mA) as the FAB gas. The accelerating voltage was 10kV and the spectra were recorded at room temperature. m – Nitrobenzyl alcohol (NBA) was used as the matrix.

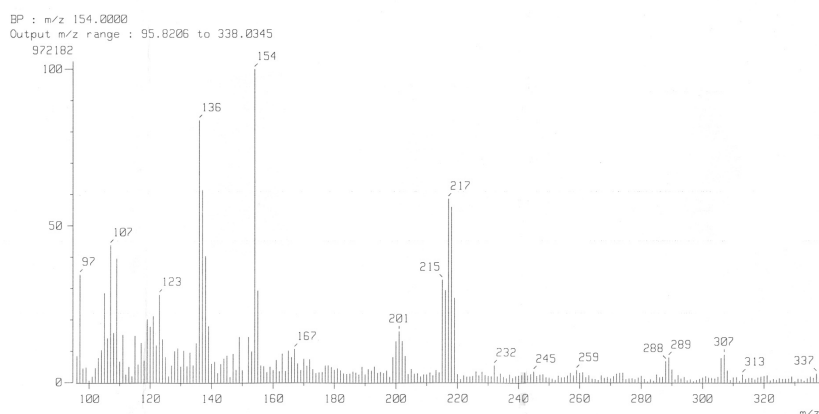


Figure 4

In the above mass spectrum (fig.4.) the peak at $m/z = 136$ and the base peak at $m/z = 154$ is the matrix peaks since *m*-Nitrobenzyl alcohol was used as matrix, The peak at $m/z = 217$ corresponds to the molecular ion of $[(NO_2)(C_6H_3)-NH_2 - Br]^+$ along with protonated molecular ion..

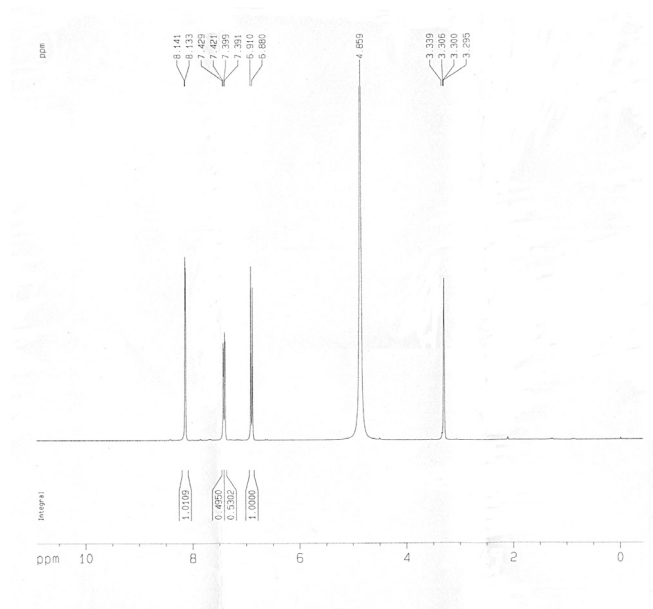


Figure 5

The formation of the compound is further confirmed by the 1H -NMR(300 MHz $CH_3 OD$) spectra given in fig 5. 1H NMR is carried out by DSX – 300/AMX-

400/DRX-500/AV500 NMR spectrometer. The signal due to aromatic protons appeared at $\delta = 6.88- 6.91(\text{d}, 1\text{H } J=9\text{Hz})$, $7.39-7.42(\text{dd}, 1\text{H}, J= 2.4 \text{ Hz and } 1\text{Hz})$ and $8.13-8.14(\text{d}, 1\text{H}, 2.4 \text{ Hz})$

Results and discussion

Conversion efficiency

The SHG intensity of the crystals using the powder technique was developed by Kurtz and Perry[11] The crystal was powdered and densely packed in a capillary. An Nd: YAG laser beam of wavelength 1064 nm, pulse width 8ns and repetition rate 10 Hz was made to fall normally on the sample in the capillary tube. The second harmonic signal was detected by a photo multiplier tube (here used is Hamamatsu R2059) and displayed on a storage oscilloscope Tektronix (TDS 3052B). The SHG conversion of the newly grown crystal was found to 1.2 times that of Urea. The SHG conversion efficiency of some standard organic compounds are given in the table.1 below, the values of which can be compared with that of laboratory grown new crystal 4-bromo 2-nitroaniline. We can see that m-nitro aniline shows very good SHG efficiency which can be attributed to its π electron conjugate system. o-nitro aniline and m-nitro acetanilide shows week SHG conversion efficiency. This marked decrease in the SHG property may be attributed to the cancellation of molecular electric dipole moment partly, because of the approximate opposite orientation of the molecules in unit cell of the crystal.

Table 1: Conversion efficiency of some standard organic compounds.

| Name of the Compound | SHG efficiency (Urea = 1) |
|---|---------------------------|
| m-nitro aniline | 7.4U |
| O-nitro aniline | Weak |
| m-nitro acetanilide | 0.037 U |
| 4-bromo acetanilide | weak |
| 4-bromo 2nitro aniline (Title Compound) | 1.2U |

The already reported research reveals that bromine attached to the benzene ring strengthens the donor acceptor group which is responsible for SHG conversion efficiency of the material [12-15]. This may be the reason for good SHG conversion efficiency exhibited by 4-bromo 2nitro aniline (Title Compound).

Conclusion

Single crystals of 4-bromo 2-nitroaniline were grown from ethanol using slow evaporation technique. Formation of the compound was confirmed by the elemental chemical analysis like FTIR, Mass and NMR spectra. The powder SHG

measurements using Kurtz technique indicates that SHG of 4-bromo 2-nitroaniline is 1.2 times that of urea, thus making it a promising NLO material in the future. The table.1 of SHG conversion indicates that the substitution of bromine to the o-nitro aniline increases its SHG conversion efficiency substantially and is the matter of interest in research.

Acknowledgements

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