Optics and Laser Technology 103 (2018) 291–299

Contents lists available at ScienceDirect

Optics and Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Full length article

Spectroscopic and quantum chemical perspectives on 2-amino 5-methylpyridinium 4-nitrobenzoate – An organic single crystals for optoelectronics device applications

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ARTICLE INFO

Article history:
Received 13 June 2017
Received in revised form 19 January 2018
Accepted 21 January 2018

Keywords:
Solution growth
Nonlinear optics
Dielectric
DFT calculations

ABSTRACT

In this work, an optical quality single crystals of 2-amino 5-methylpyridinium 4-nitrobenzoate (2A5MPNB) were grown by slow evaporation solution growth technique using methanol as a solvent. The phases and functional groups of 2A5MPNB have been confirmed through powder X-ray diffraction and Fourier transform infrared (FTIR) studies, respectively. The optical transmittance window and the lower cut-off wavelength of the 2A5MPNB have been identified by UV–Vis–NIR studies. Dielectric and photoconductivity studies were also performed for the grown crystals. In order to analyze the mechanical strength Vickers hardness studies were taken for the grown crystal. The thermal behaviour was investigated by TG/DTA studies. NLO and laser damage properties were explored using Nd:YAG laser. Moreover, the quantum chemical calculations on 2A5MPNB have been performed by density functional theory (DFT) calculations using the B3LYP method with 6–311++G(d,p) basis set. The predicted first hyperpolarizability is found to be 14.45 times greater than that of urea and suggests that the title compound could be an attractive material for nonlinear optical applications.

1. Introduction

In this modern era, organic nonlinear optical (NLO) materials have acquired importance with the rapid development in the field of optoelectronics and advent of a large number of devices utilizing solid state laser sources. Since the advent of the laser in the 1960s, the application of nonlinear optics in optoelectronic and photonic devices grasped the attention of nonlinear optical materials. Especially, organic nonlinear optical materials exhibiting second harmonic generation are in great demand, due to their applications in optical switching, optical limiting, two-photon laser scanning microscopy, eye and sensor protection, optical signal reshaping and stabilizing fast fluctuations of laser power [1–6]. In recent years, the demand for optically active organic crystals has increased due to useful applications in the field of terahertz wave generation, photonics and electro-optics. The electronic susceptibilities of organic NLO materials are several orders of magnitude higher than those of inorganic materials. Furthermore, organic materials demonstrate the flexibility of molecular design and ease of device fabrication [7]. Polar and chiral organic molecules with π-electron conjugated moieties substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end have increased asymmetric electronic distribution in both the ground and excited states; thus, their second order polarizability is increased. Hence, these molecules are expected to be leading candidates for fundamental and applied investigations.

Pyridine and acid (base-acid) are one of the promising pairs to form non-centrosymmetric crystalline arrangement and also they exhibit high NLO efficiency. Previously many efficient pyridinium-acid based crystals were grown and their properties were reported [8–11]. In this direction, Madhukar Hemamalini and Hoong-Kun Fun have reported [12] the crystal structure of 2-amino 5-methylpyridinium 4-nitrobenzoate. As this molecule crystallizes with the non-centrosymmetric crystal structure, we focused our interest towards the systematic studies on 2A5MPNB and the results obtained are discussed in detail. The studies here are reported for the first time in literature, to the best of our knowledge.

The present work is aimed to report the growth, structural, optical, electrical, mechanical, laser damage, powder SHG and phase matching studies of 2A5MPNB. Furthermore, quantum chemical calculations such as frontier molecular orbitals and hyperpolarizability have been calculated for the 2A5MPNB crystal.

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https://doi.org/10.1016/j.optlastec.2018.01.053
0030-3992/

2. Experimental

2.1. Material synthesis

Pure specimens of 2-amino 5-methylpyridine and 4-nitrobenzoic acid were purchased and used without further purification. Equimolar solutions of the two reactants were prepared separately in methanol and henceforth mixed together. The resulting solution was stirred well for about half an hour. The charge transfer molecular complex. 2-amino 5-methyl pyridinium 4-nitrobenzoate was obtained. The product was filtered off and repeatedly recrystallized from methanol to improve the quality of the product (see Scheme 1).

2.2. Solubility

To grow good optical quality single crystals of considerable size, the selection of solvent is very important. For choosing the most suitable solvent for crystal growth, valuable information can be obtained through solubility test. To carry out the crystal growth by solution method the solubility estimation has been done by dissolving 2A5MPNB in different solvents. The solvents which dissolve 2A5MPNB were examined using pure methanol and methanol-acetone (1:1) mixture. The solubility was measured by adding an excess amount of 2A5MPNB in the solvent at constant temperature (30 °C) and it was continuously stirred to attain homogenous concentration over the entire volume of the solution. On reaching the saturation point, the content of the solution was analyzed gravimetrically. This process was repeated for different temperatures (30–50 °C) with the internal of 5 °C for methanol and methanol-acetone (1.1) mixture respectively. Fig. 1 shows the solubility diagram. It was found that 2A5MPNB exhibits high positive solubility temperature gradient in the methanol than in methanol-acetone itself. Hence methanol has been chosen as the solvent for crystal growth.

2.3. Crystal growth

In accordance with the estimated solubility, a saturated solution of 2A5MPNB in methanol was prepared, stirred well for about an hour to dissolve the complex completely. The solution was then filtered through a quantitative Whatman 41 grade filter paper to remove the suspended impurities. The filtrate was kept aside unperturbed in an atmosphere most suitable for the growth of single crystals. To control the evaporation rate the top of the beaker was encircled with a perforated thin polythene sheet. Finally, the solution was left undisturbed for crystal growth Well grown-needle shaped single crystals of the title material were harvested in a typical growth period of ten days (Fig. 2a). The BDFH morphology was obtained from Mercury software using the CIF file of the 2A5MPNB crystal structure as input (Fig. 2b).

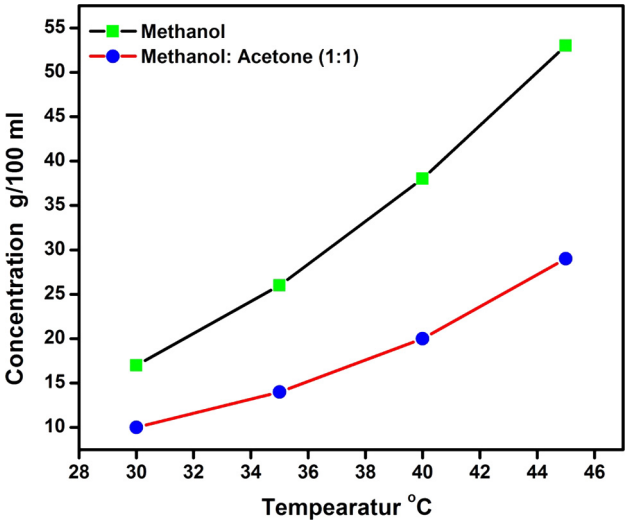


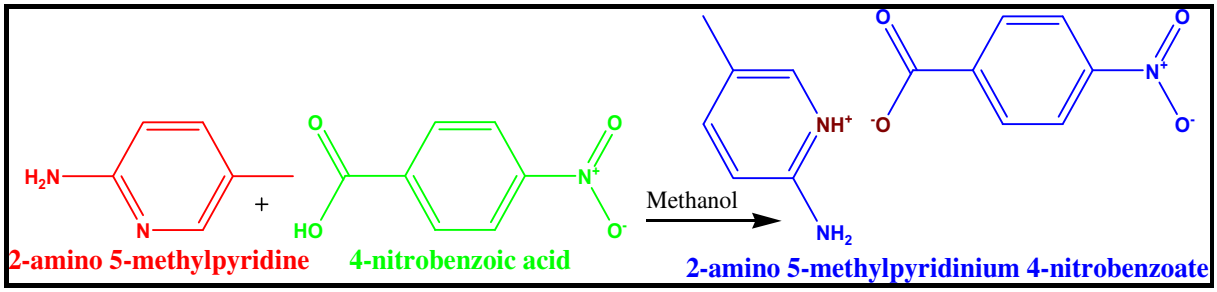
Fig. 1. Solubility and Meta stable curves for 2A5MPNB crystal.

2.4. Characterization

The unit cell parameters and the intensity data at 298 K for the title compound were obtained on an Oxford Diffraction Xcalibur Gemini single crystal X-ray diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). The powder X-ray spectrum of 2A5MPNB was carried out using XPERT-PRO X-ray diffractometer by employing Cu Kα radiation. In order to confirm the functional groups, powder samples of the grown 2A5MPNB was subjected to FTIR studies using Perkin- Elmer FTIR spectrometer for the wavelength range 4000–400 cm^{-1} by KBr pellet technique. The optical transmittance spectrum for the grown crystal was recorded using a Perkin-Elmer Lambda 35 Spectrophotometer in the wavelength range from 200 to 1100 nm. Dielectric studies were measured using the Hioki 3532-50 LCR meter. Photoconductivity measurements for the grown 2A5MPNB crystals were taken using Keithley electrometer (Model 6517B-. Mechanical studies were carried out at room temperature using Vickers Microhardness tester. To study the thermal stability of the grown crystal the TG-DTA analysis was carried out using an STA 1500 thermal analyzer from room temperature to 600 °C in an inert atmosphere of nitrogen at a heating rate of 20 °C/min. A Q-switched Nd:YAG laser with the fundamental wavelength of 1064 nm was used to study the powder SHG efficiency.

2.5. Computational details

Quantum chemical calculations of the title compound were carried out with Gaussian 03 software [13] program and the GaussView [14] molecular visualization program. The Donor and



Scheme 1. Reaction scheme of 2A5MPNB in methanol.