



A Convenient Route to Synthesize and Grow 2-Amino 5-Nitro Pyridinium Nitrate Crystals for Laser Generation

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Abstract : An organic nonlinear optical (NLO) crystalline salt 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) was successfully synthesized from Pyridine. From Pyridine, we have synthesized 3-Nitro Pyridine (3NP). 3-Nitro Pyridine (3NP) with reaction of Ammonia on KMnO_4 gave 2-Amino 5-Nitro Pyridine (2A5NP). The as obtained synthesized salt of 2-Amino 5-Nitro Pyridine (2A5NP) was mixed with concentrated Nitric acid with appropriate stoichiometric ratio to obtain 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN). The synthesized 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) was taken for solubility studies. Based on the solubility study, attempts will be made to grow single and bulk crystals of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) by slow evaporation method and by using assembled temperature reduction apparatus technique. The powdered sample of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) confirmed the second harmonic generation (SHG) using Nd:YAG laser.

(Received July 2013, Accepted September 2013)

1. Introduction

There is a considerable interest in the synthesis of organic second order non linear optic materials (SONLO) because of their potential use and applications in telecommunication, optical computing, optical data storage and optical information processing. They have high nonlinearities and rapid response to electro-optic effect when compared with inorganic materials [1-3]. A lot of organic compounds with polarized and conjugated system has the potential to exceed inorganic compounds [4]. Hence there is a need to use molecules with high molecular hyper polarisability (β) and acentric crystal structures to obtain crystals with high second order nonlinear susceptibility. A cation with high (β) and a counter anion can be introduced to improve the arrangement of molecules [5-6]. Many researchers have tried to grow the derivatives of 2-Amino 5-Nitro Pyridine (2A5NP) adducts and they have already reported. In the present report we have further extended our effort in the synthesis of 2-Amino 5-Nitro Pyridine (2A5NP) crystalline adducts from 3-Nitro Pyridine (3NP). The pyridine ring system occurs in the structures of many natural products, pharmaceutical and agro chemicals compounds, and other commercial substances. A wide range of synthetic methods has, therefore been developed, both for construction of the pyridine ring and its substitution [7]. Unfortunately, one of the most important classes of aromatic substitution reaction, electrophilic aromatic substitution, takes place with great difficulty and only under forcing condition, Owing to the electron deficient character of the pyridine ring. Recently nitration of pyridine at 350°C gave a 12% yield of 3-nitropyridine, and even this low yield could not subsequently be reproduced by den Hertog et al., who obtained a 6% yield under the same conditions [8]. Recently Jan M. Bakke has investigated the nitro aromatic compounds by Dinitrogen Pentoxide (N_2O_5) and found that with liquid SO_2 as solvent, was an especially powerful nitrating system [9]. Based on this

report we have decided to try this strategy on the pyridine itself in order to get 2 Amino 5-Nitro Pyridine(2A5NP) crystalline salt.

2. Synthesis of 3-Nitro Pyridine (2A5NP)

To obtain 3- Nitro Pyridine (3NP), we treated pyridine with N_2O_5 . The resulting mixture was dissolved in nitro methane. The reaction mixture was poured into water saturated with SO_2 and then to obtain 45% of yield of 3-Nitro Pyridine (3NP).

3. Synthesis of 2-Amino 5-Nitro Pyridine (2A5NP)

The starting material was synthesized by taking 3- Nitro Pyridine (3NP), which was synthesized already with ammonia as solvent in 1:1 stiochiometry ratio [8]. The required amount of starting material for the synthesis of 2-Amino 5-Nitro Pyridine (2A5NP) salt was achieved. The purity of synthesized salt was further improved by successive recrystallization process.

4. Synthesis of 2-Amino 5- Nitro Pyridine Nitrate (2A5NPN)

Masse et al have published a series of organic inorganic crystals of 2-Amino 5-Nitro Pyridine (2A5NP) and inorganic acids such as Arsenic acid for NLO materials. 2-Amino 5-Nitro Pyridine (2A5NP) allows growth of numerous salt such as 2A5NP dihydrogen phosphate, 2A5NP acetophosphate, 2A5NP dihydrogen arsenate, 2A5NP chloride, 2A5NP bromide, 2A5NP L-mono tartarate [10-13]. Here in, we report organic inorganic crystals of 2-Amino 5-Nitro Pyridine (2A5NPN) combined with Nitric Acid.

5. Material synthesis

The commercially available 2A5NP (Merck purity >98%) is a weak Bronsted base and can acquire a proton in strongly acidic aqueous medium ($\text{pH} < 2$). This induces the dissolution of

this molecule in an aqueous acidic medium by forming the 2A5NP cation and leads to the synthesis of hydrogen-bonded salts with conjugated bases of strong or medium acids. The organic inorganic 2-Amino 5-Nitro Pyridine (2A5NPN) salt was dissolved in Nitric acid at 50°C in Millipore water of resistivity 18.2M Ω cm[14].

6. Solubility Study of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN)

The synthesized salt was used to measure the solubility of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) in distilled water. A 250 ml of beaker filled with 100 ml of distilled water was placed inside a constant temperature bath whose temperature was set at 30°C. An acrylic sheet with circular hole at the middle through which a spindle from an electric motor placed over the sheet was introduced in the solution. A Teflon paddle was attached at the end of the rod for stirring the solution. 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) salt was added in a small amount. The addition of the salt and stirring were continued till the formation of precipitate, which confirmed the saturated state of the solution. The solubility study of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) was carried out by measuring an amount of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) salt that dissolved in water at 30°C, 35°C, 40°C, 45°C, and 50°C. The solubility of 2-Amino 5-Nitro Pyridinium Nitrate (2A5NPN) at room temperature was found to be seven grams in 100 ml of water.

7. Growth of 2A5NPN

The supersaturated solution of 2-Amino 5-Nitro Pyridine (2A5NPN) was prepared in accordance with the solubility data. Single crystals of 2-Amino 5-Nitro Pyridine (2A5NPN) were grown from aqueous solution using slow solvent technique. The solvent of the supersaturated solution was allowed to evaporate through the perforated lid of the container. Numerous tiny crystals were formed at the bottom of the container due to spontaneous [4].

nucleation. Among them, transparent and defect free samples were chosen as seed for growing bulk crystals. By seeding the supersaturated solution and evaporating the solvent, good optical quality crystals with dimensions $2 \times 2 \times 3 \text{ mm}^3$ were harvested after a period of 60 days. Since the solubility is moderate and the evaporation rate is slow, the dimension of harvested are found to be appreciably larger.

8. Conclusion

Starting from Pyridine we have synthesized 3-Nitropyridine (3NP). From 3-Nitro Pyridine (3NP) we have successfully yielded about 45% of 2-Amino 5-Nitro Pyridine (2A5NP). The facile method was adopted to grow 2-Amino 5-Nitro Pyridine Nitrate (2A5NPN). Their solubility and crystal growth procedure were discussed.

Acknowledgements

The authors (M. Ambrose Rajkumar, S. Stanly John Xavier, D. Prem Anand) would like to thank the Board of Research in Nuclear Sciences - Department of Atomic Energy (BRNS-DAE) (File no: 2012/34/63/BRNS/2865 dt: 01 March 2013) for funding this major research project.

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