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Second and third-order nonlinear optical and DFT calculations on 2-amino-5-chloro pyridinium-L-tartrate: A phasematchable organic single crystal

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ABSTRACT

Single crystals of 2-amino-5-chloro pyridinium L-tartrate have been successfully grown by controlled solvent evaporation technique. The crystal system and the lattice parameters of the grown crystals were reconfirmed by Single crystal X-ray diffraction (SXRD) measurements. UV-Vis-NIR spectrum was recorded for the grown crystal and optical band gap was calculated. Fourier transform infrared (FT-IR) spectroscopic studies were also performed for the identification of different modes present in the compound. The relative SHG efficiency of the material was investigated and the phase matching property of the crystal was also studied through the SHG dependence of average particle sizes. Further, the optical birefringence of the grown crystal was determined. The specific heat capacity of the title compound was measured using Differential Scanning Calorimetric studies. The photoconductivity study for the title compound was carried out. The DFT calculations were performed for the first time for this compound.

1. Introduction

In recent decades there have been significant interest shown in designing and developing new NLO materials because of their vital applications in the fields such as generation of higher harmonic frequencies, frequency mixing, self-focusing, electro-optic modulation [1], optical parametric oscillator [2], photo refractivity [3], Terahertz [4,5] etc. In general, NLO materials are expected to possess large nonlinear optical coefficients, suitable transparency and phasematchable properties [6–9]. Organic molecules, owing to their molecular flexibility exhibit improved NLO properties in an effective manner [10]. Such an organic molecule with significant NLO activity generally consists of π - electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end [11]. Under the action of applied electric field, conjugated π - electron moiety offers desired path way for the whole length of conjugation. Aekeroy et al. studied the relationship between hydrogen bonding, overall packing and crystal geometry in organic crystals and also involved in the development of NLO materials for their device oriented applications. The donor and acceptor groups provide a different approach of proton transfer connecting acidic and basic organic links in variety of cation-anion mixtures leading to the ground state charge asymmetry of the molecules in the product, which is required for second order and third order nonlinearity [12,13].

2-amino-5-chloro-pyridine (2A5CP) is a pyridine based compound possessing readily accepting nitrogen and donating electrons in the direction of assembling donor-acceptor (D-A) system, observed in general with various types of organic materials like carboxylic acids, benzoic acids and other acid derivatives. It is also understood that the existence of nitrogen in pyridine ring of 2A5CP favoured the formation of salts during reaction with various organic acids. However, in recent years the pyridine based organic compounds such as 4-dimethyl amino–N-methyl-4-stilbazolium tosylate [4,5], 2-amino pyridinium trichloro acetate [13], 4-dimethylaminopyridinium dihydrogen phosphate [14], 2-Aminopyridinium-4-Nitrophenolate Nitrophenol (2APNP) [15], 2,6-Diaminopyridinium-4-Nitrophenolate 4-Nitrophenol (DAPNP) [16], Dimethyl amino pyridinium-4-Nitrophenolate 4-Nitrophenol (DMAPNP) [17], 2-amino-4-methyl pyridinium-4-Nitro phenolate 4-Nitrophenol [18] have been reported to exhibit better NLO

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properties. Further, other organic compounds such as Imidazoilium-L-Tartrate [19], 2-amino-4-picolinium 4-aminobenzoate [20], 2-carboxy pyridinium dihydrogen phosphate [21], morpholinium p-hydroxy benzoate [22], Pyrrolidinium *p*-Hydroxybenzoate [23], 2-[2-(4-methoxy phenyl)-venyl]-1-methyl-pyridinium tetra fluoroborate (4MSTB) [24] have also been reported for their significant NLO related properties. However, only a selected group of the compounds listed above possessed high molecular polarizabilities due to their favourable alignment of π - delocalized electrons with enhanced second order and third order optical nonlinearities and also exhibited desirable physicochemical properties [24]. Recently, Draguta et al. have shown that a range of aminopyridine based salts could also be formed by reacting them with 4-Nitrophenol [25]. In this direction, a pyridine based cation, namely, 2-amino-5-chloro pyridinium was reacted with L-tartaric acid (anion) to form a new salt called 2-amino-5-chloro pyridinium-L-tartrate (2A5CPLTA) [26]. This material was found to crystallize with noncentrosymmetric space group $P2_1$, thus resulting in new material for second harmonic generation (SHG). This material was characterized for its structure by single crystal X-ray diffraction technique, functional group analysis performed with FTIR studies, thermal stability behaviour by TG/DTA analysis, Dielectric behaviour by dielectric measurements, microhardness measurements to identify the mechanical behaviour of the title compound [26]. However, optical properties such as phasematchability, refractive index, third order NLO coefficients and laser damage threshold values and quantum chemical calculations have not been reported for this material. Since these studies would provide in-depth understanding on nonlinear optical and physicchemical properties of 2A5CPLTA, detailed analyses have been performed and the results are presented in the present report.

2. Experimental details

2.1. Synthesis of and growth of 2A5CPLTA

Analytical grades of 2-amino 5-chloro pyridine ($C_5H_5ClN_2$) and tartaric acid ($C_8H_8O_3$) were purchased from Sigma Aldrich and used without further purification. The title compound was prepared by adding one mole of 2-amino 5-chloro pyridine and one mole of tartaric acid in methanol solvent. The reaction mechanism of 2-amino 5-chloro pyridinium tartrate is shown in Scheme 1. The two separately prepared solutions were mixed together and stirred well for about 3 h to get a homogeneous solution and was filtered through Whatmann 41 filter paper. The beaker containing the filtrate was then covered using thin polythene sheet to prevent the quick evaporation. Care was taken to minimize the temperature gradient and mechanical shake. The filtrate was kept in a bath whose temperature could be controlled by a Programmable temperature controller for the growth (Model: 3216; accuracy ± 0.01 °C**).** The HPLC grade methanol was used as a solvent for the growth of single crystals of 2A5CPLTA. The slow evaporation solution growth method was used to grow the single crystals at room temperature. The grown crystals present inside beaker were taken out carefully with the help of cleaned forceps. The typical dimension of crystal was about 6 × 5 × 2 mm^3, were dried and then used in X-ray diffraction studies. The grown crystal of 2A5CPLTA is shown in Fig. 1.

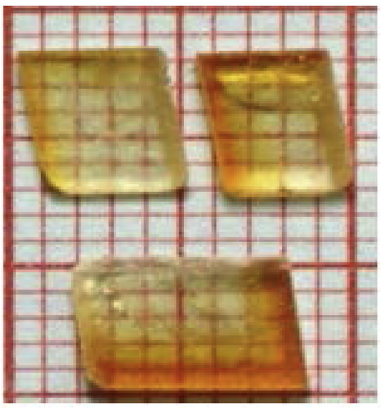
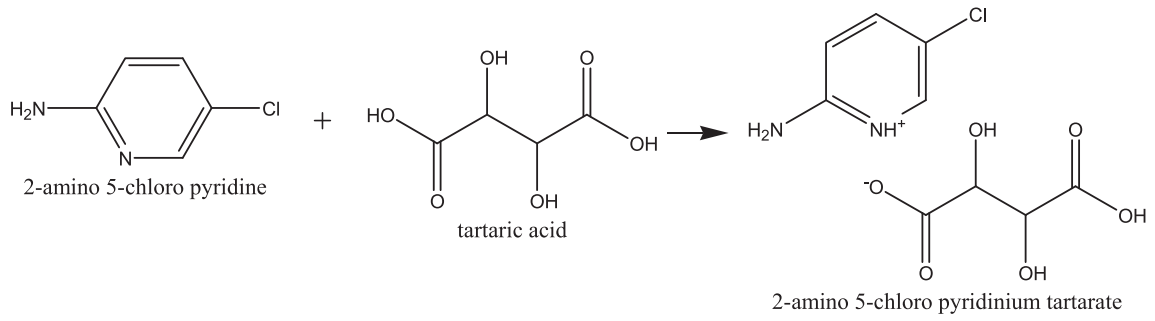


Fig. 1. 2A5CPLTA single crystals from methanol solvent.

2.2. Solubility studies

The variation in solubility with Metastable Zone width measured at various temperatures is shown in Fig. 2. The solubility and Metastable Zone width plot are useful to decide optimal growth and improvement in crystallization procedure. The solubility of any material in a given solvent indicates nucleation, availability of solute substance for the growth process and determines the cooling rate [27]. Supersaturation would be a driving force for growing better quality crystals and it has an effect on quality of the crystals. The solubility of a substance should be moderate to grow better quality single crystals. It is also expected that the solute must remain in the solution till elevated level of supersaturation has been achieved in the solution to encourage spontaneous nucleation. The solubility of 2A5CPLTA was measured in methanol solvent as a function of temperature between 25 and 45 °C in steps of 5 °C. The saturated solution was prepared in a well-controlled thermal environment. The excess amount of solute was stirred well for nearly 5 h before each and every sample was taken out from the beaker. Solubility was then measured gravimetrically. In order to get homogeneous mixture, the solution was filtered first and then it was preheated to 5 °C above its saturated temperature. Then the solution was kept free at same temperature for 2 h before



Scheme 1. Reaction mechanism of 2-Amino 5-chloro pyridinium-L-tartrate.