Synthesis, Growth and Characterization of 2, 6-Diaminopyridine: Phosphoric Acid (Dap: Pa) Co-Crystals for Third Harmonic Generations

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Abstract: *2, 6- Diaminopyridine: phosphoric acid (DAP: PA) co-crystals were grown by slow evaporation solution growth technique using ethanol as a solvent. Solubility studies were performed at different temperatures. The unit cell parameter values were confirmed by single crystal X-ray diffraction technique. Vibrational behavior of the grown crystal has been carried out by FTIR technique. Transparency of the grown crystals was tested using UV – Visible spectrophotometer. The mechanical behavior of the material has been studied using Vickers's micro hardness method. The non-linear optical behavior of the crystal is confirmed by Z-scan studies.*

Keywords: Crystal growth, X-ray diffraction, *FTIR*, *UV – Visible spectrophotometer*, Microhardness, *non-linear optical behavior*.

1. Introduction

The design of nonlinear optical (NLO) molecules has become a focus of current research in view of their potential applications in various photonic technologies. Materials with NLO activity find the use of as electro-optic switching elements for telecommunication and optical information processing. The NLO process requires materials that manipulate the amplitude, phase, polarization and frequency of optical beams. While variety of materials including inorganic, organ metallic, organic and polymeric have been studied for their NLO activity, organic materials which have been receiving the maximum attention in non linear optics. In addition to the advantage in synthesis, organic materials have ultra fast response time, photo-stability and large first order hyperpolarizability (β) values. In particular $\pi-$conjugated systems linking with donor (D) and an acceptor (A) show large NLO response and hence have been well studied by different experimental techniques.

Recently, organic crystals posse's non-linear optical properties, which have far, surpass those of inorganic materials has of cussed attention on the probable commercial potential of those materials. In the search of new organic non-linear optical crystal aromatic compounds with donar and acceptor substituent have been extensively studied. Organic materials with larger non-linear co-efficient have been discovered forbuilding acid-base hybrid crystals. The inorganic phosphoric acid easily forms molecular crystals with different organic bases which exhibiting NLO properties.

An essential condition to realize even order NLO processes in material is a noncentrosymmetric structure [1]. The NLO property of the crystal mainly depends on delocalized electron, charge transfer due π-conjucation and number of hydrogen presents in the material i.e., super molecular assembly.

1.1. Importance of 2, 6-diaminopyridine

2, 6-Diaminopyridine (DAP) came to the attention of the NCI Division of Cancer Biology (DCB) as the result of information collected for Summary Sheets on monoaminopyridines. 2, 6-Diamino-pyridine is a medium-production-volume chemical used as a pharmaceutical intermediate and a hair dye coupler in oxidation permanent formulations. The NLO property of 2, 6-Diaminopyridine based material is governed by the NLO characteristics of the constituent individual molecular chromophores. It is observed that chromophores containing D and A substituent's show larger NLO response.
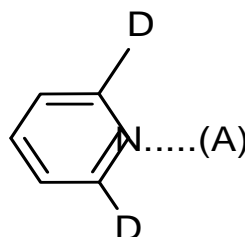
1.2. 2, 6-Diaminopyridine-Chemcial Details

CAS Registry No. : 141-86-6
Chemical Abstract Name : 2,6-Pyridinediamine (9CI)
Synonyms and Trade Name: 2,6-Diaminopyridine; 2,6 Pyridinediamine; 2,6-DAP, DAP.

Molecular Formula : $C_5H_7N_3$
Molecular Weight : Mol. wt: 109.130
Structural Class : Heterocyclic aromatic tertiary amine Derivative.

1.3. Chemical and Physical Properties
Description : Crystals (Lewis, 2002)
Boiling Point : 285 °C (Properties of Organic Compounds, 2001)

Melting Point : 121.5 °C (Properties of Organic Compounds, 2001)
Solubility : Soluble in water, acetone, ethanol, and methanol.

In this work, formation of newly hydrogen-bonded charge transfer co-crystals of 2,6-diaminopyridine:phosphoric acid with centrosymmetric lattice for third order harmonic generation (THG) applications has been reported.

2. Solubility Studies

To grow large size single crystal with good quality, the growth conditions such as solvent, temperature and pH have to be optimized. The solubility of the material is used to calculate the availability of the solute for the growth and to obtain the required size the crystals [3].

The solubility studies were carried out for different solvent at different temperature from 30 ^{o}C to 50 ^{o}C by gravimetric method. The corresponding solubility curve is presented in Fig.1 for ethanol. It shows that the solubility increases significantly with increasing temperature, which favors the growth of DAP: PA by slow evaporation technique at room temperature using ethanol as solvent.
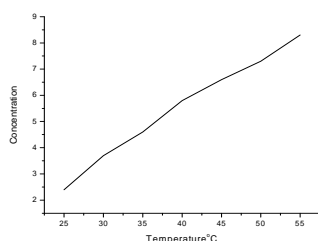

Figure 1: *Solubility curve for DAP: PA*

3. Experimental Method

DAP-PA was synthesized by using AR (Analytical Reagent) grade 2,6-Diaminopyridine and Phosphoric acid in the molar ratio of 1: 1. The reaction scheme of 2, 6- Diaminopyridine and phosphoric acid are given in Fig.2. The calculated amount of 2, 6- Diaminopyridine was added and dissolved in ethanol. Then the Phosphoric acid was slowly added into the DAP solution and mixture of the DAP and Phosphoric acid precipitated has been observed. Then the precipitate was filtered out and then dissolved in water to prepare supersaturated solution.

The solution was stirred using magnetic stirrer. The solution was filtered twice to remove the suspended impurities. The saturated solution DAP: PA was taken in a 250 ml beaker with a perforated lid to control the evaporation rate at room temperature for crystallization.

The solution was evaporated to dryness. After two weeks, well developed and good quality crystals were harvested from the mother solution. The polished crystal is shown in Fig. 3.
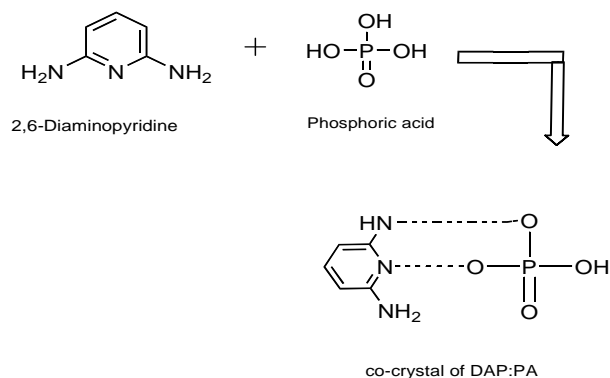

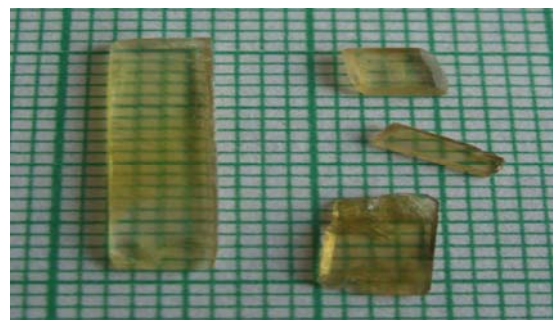**Figure 2:** Molecular structure formula for DAP: PA

Figure 3*: The polished crystal of DAP: PA

3.1. X-ray diffraction

The single crystal XRD data was collected using Enraf Nonius CAD4-F diffractometer having graphite monochromatic Mo Kα radiation. The lattice parameter value of DAP:PA crystals are a=7.47 Å, b=8.092 Å, c=8.16 Å, α=70.84°, β=75.12°, γ=84.94° and V=450.10 A^3 and crystal belong the Triclinic structure with space group p-1 [4]. The relevant crystallographic data and refinement details are presented in Table .1.

Table 1: Structural details of DAP: PA
Identification code : DAP: PA
Empirical formula : $C_5H_{10}N_3O_4P$
Formula weight : 207.13
Crystal system : Triclinic,
Space group : p-1

Cell Parameters	DAP:PA
a (A^0)	7.4675
b (A^0)	8.0924
C (A^0)	8.1590
α (deg)	70.840
β (deg)	75.115
γ (deg)	84.93
Volume (A^0)^3	450.1

3.2. Vibrational Studies

In order to analyses qualitatively the presence of DAP:PA in the crystal, Fourier transform infrared spectrum has been taken for the powder sample. The spectrum was recorded in the wavelength range from 400 cm^{-1} to 4000 cm^{-1}. The mid FTIR spectra of DAP:PA was recorded at room temperature using BRUKER Fourier transform infrared spectrometer, The observed FTIR spectrum is given in Fig.4. The strong absorption in the range 1242 – 1764 cm^{-1} is evidentially due

to the nitro compound of the molecules. The N-H, O-H, C-H and absorptions are measured into a continuum, which occurs at the frequency range $1622 – 850$ cm^{-1}. The absorption around 1672 cm^{-1} is assigned to C-O stretching [5]. In the case of DAP:PA crystal, a very strong absorption peak at 3365 cm^{-1} is due to the O-H stretching vibration and a strong absorption peak at 1495 cm^{-1} due to the N-O stretching vibration. The very strong absorption peak at 873 cm^{-1} due to the Aromatic P-O Stretching vibration [6]. The spectral data and their assignment for DAP: PA is given in Table.2.
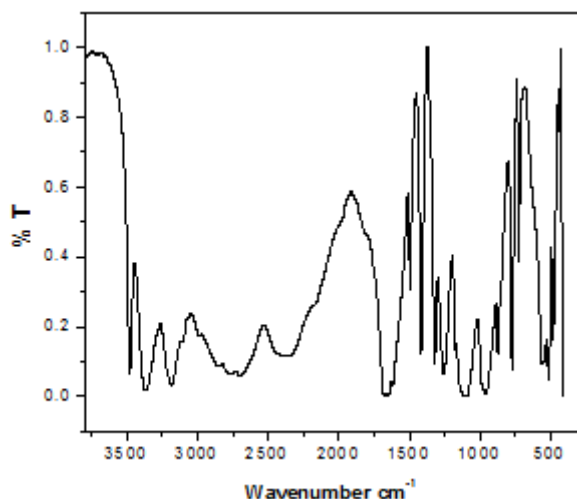

Figure 4: FTIR spectrum for DAP: PA single crystal

Table 2: Vibrational modes of FTIR spectrum

Observed wave number (cm^{-1})	Assignment
3478	(O- H) Intermolecular Stretching
3365	(O- H) Stretching
3184	(O- H) Stretching
2699	H - C = O Stretch
1672	C = O Stretch
1495	N-O Asymmetry Stretching
1415	C – C stretch (in ring)
1318	C – N stretch
1257	Organic phosphates(P=O Stretch)
1092	C – N stretch
958	= C – H bend
873	Aromatic (P - O Stretch)
772	N-H wag
722	N-H wag
512	N=O stretching

3.3. Optical Studies

The optical property of the material gives information regarding the composition nature and the quality of the crystal. The present experimental study may be assisted in understanding electronic structure of the optical band gap of DAP: PA crystal.

The transparency of DAP: PA crystal was measured using PerkinElmer Lambda 35 UV-Visible spectrophotometer in the range of 190-1100 nm and the transmittance spectrum of the crystal is shown in Fig. 5. It is evident that the percentage of transmittance for DAP: PA crystal is high in visible region.

In Fig.6, there is no absorption peak occurred at 355 nm which helps to bring the material for NLO application [7]. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme.
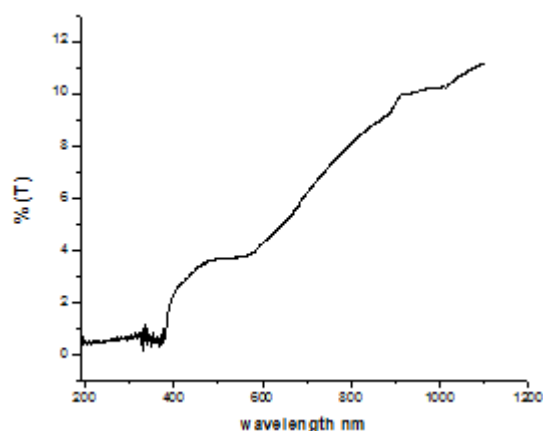

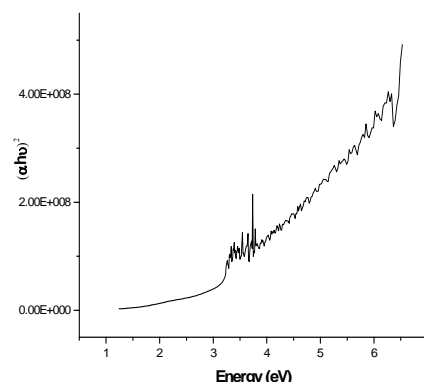**Figure 5:** Transmittance Spectrum of DAP: PA crystal

Figure 6: Band gap energy

The energy gap of the material is determined by the absorption spectra [8, 9]. The absorption co-efficient α is determined by following equation.

$$\alpha = (2.3026 \times \log (1/T))/d \text{ ------------ (1)}$$

Where T is the transmittance, d is the thickness of the crystal. The energy gap of the material was calculated by the following equation,

$$\alpha h\upsilon = A [h\upsilon - E_g]^{1/2} \text{ ------------ (2)}$$

Where A is a constant, E_g the optical band gap, h is the Plank's constant and υ is the frequency of the incident photons and n is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of electronic transitions responsible for absorption [10].

Thus the band gap is obtained by plotting $(\alpha h\upsilon)^{1/n}$ versus $h\upsilon$ in the high absorption range followed by extrapolating the linear region of the plots to $(\alpha\upsilon h)^{1/n} = 0$ [11]. The graphs were plotted for different values of n and the maximum point was connected only for n=2, which shows the direct type transmittance involved in this material. From the Fig. 6 the band gap for DAP: PA crystals calculated. The value of band gap energy is 3.90 eV.

3.4. Mechanical studies

The important properties of any device materials are its mechanical strength, which will represent by its hardness [12]. Hardness of the grown crystal was measured using Leitz-Wetzler hardness tester fitted with a Vicker diamond pyramidal indenter and attached to a Leitz incident light microscope. The load variations in measurement were applied over a fixed interval of time 15 sec.

The hardness is generally measured as the ratio of applied load to the indentation on the surface area of the material [13]. The micro hardness value was calculated by the following equation,

$$H_v = 1.8544 \times P/d^2 \ (kg/mm^2) \ \text{------------ (3)}$$
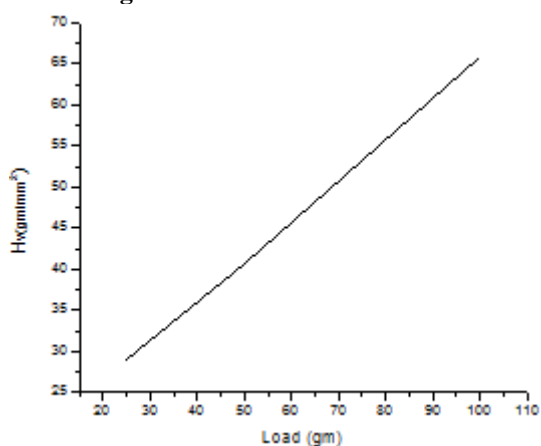
Where H_v the Vicker hardness number, p is the applied load (kg) and d is the diagonal length (mm) of the indentation. Fig.7 shows the variation of H_v as a function of applied load ranging from 25 gm to 100 gm for the DAP: PA crystal.

Table 3: Hardness of DAP: PA

| Load (g)	H_v (Kg /mm2)
25	29
50	40.6
100	65.7
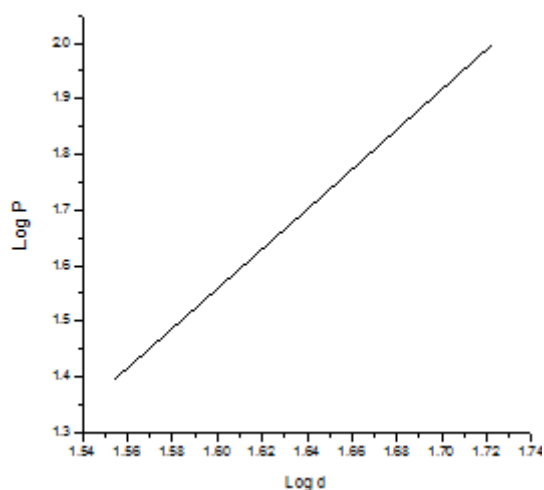
Figure 7: Hardness for DAP: PA

Figure 8: For Mayer index

It is clear from the Fig.7. That H_v increase with the load. The plot of log p verses log d shown in Fig.8. The slop of the straight lines gives 'n'.

Where n is the Mayer index. From the value of n one can determine the mechanical nature of the material. If n>2 the material having soft category and if n<2 the material having hard category to indentation. For DAP: PA the Mayer's index number is 2.36 and the DAP: PA material belongs to soft material category.

3.5. Nonlinear optical studies (Z-scan analysis)

The third-order nonlinear property of the DAP: PA single crystals of thickness of 2 mm were determined by the Z-scan technique. In close-aperture test, the sample is simply scanned across the focal point of a 632.8 nm laser beam past a short-focal-length lens. As the sample passes through the focal point of the beam, the power density changes. Variation in transmitted light intensity through the aperture is related directly to nonlinear optical (NLO) refractive index of the material [14]. The closed aperture and the open aperture curves of DAP: PA is shown in figure 9 & 10 respectively.
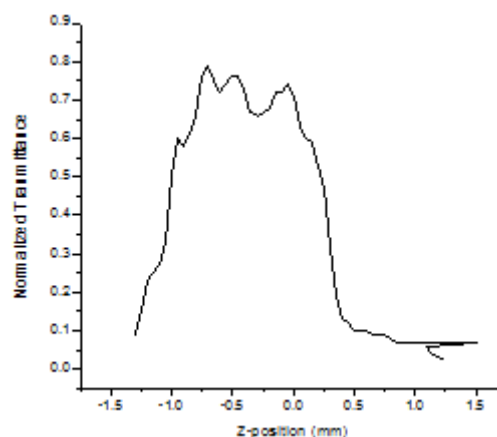
Figure 9: Closed aperture curve of DAP: PA.
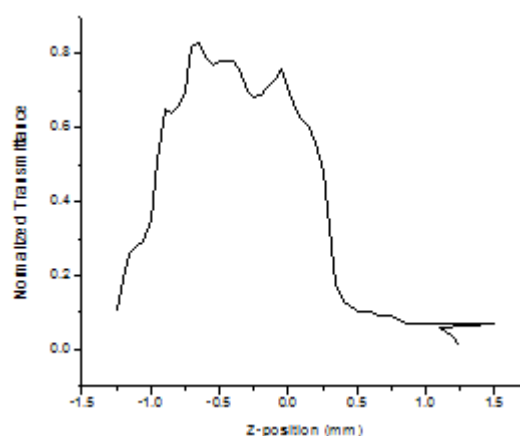
Figure 10: Open aperture curve of DAP: PA

Instead of getting perfect Gaussian peak beam we getting only the little bit scattered beam for our crystal. From that beams we are known that our crystal itself got the third order nonlinear property from the Z-scanning method.

4. Conclusion

The co-crystal of 2, 6-Diaminopyridine: Phosphoric acid (DAP: PA) has been grown by slow evaporation solution growth technique at room temperature using ethanol as

solvent. The single crystal XRD study reveals that the crystal belongs to Triclinic system and the unit cell parameter values are a=7.47 Å, b=8.092 Å, c=8.16 Å. The functional group presents in the molecules were analyzed by FTIR technique and the assignments are tabulated. Transmittance spectrum shows the DAP: PA crystal is transparent in the visible region. From Taug relation, the energy gap of the crystal is 2.95 eV. From the Vicker's microhardness test, the hardness value is increased with increasing load. The NLO property has been analyzed and the third harmonic generation efficiency of the DAP: PA co-crystal is revealed from the Z-scan method by the Gaussian peak beam fit.

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