

## Structural analysis and optoelectronic applications of 2-aminopyrimidine with pimelic acid crystal

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This study investigates the reaction between 2-aminopyrimidine and pimelic acid, resulting in the formation of a novel crystal. The crystals were obtained through slow evaporation process. These crystals underwent PXRD testing to establish their crystalline properties. The values of the unit cell parameters are confirmed through SXRD analysis. The FTIR technique is applied to detect different functional groups present in the title crystals. The UV-Visible spectrum is recorded to find the band gap energy. From the photoluminescence spectrum the emission is observed at 353nm. The mechanical strength of the material against deformation is studied using Vickers micro hardness tester and the material is stated as soft material. The dielectric behaviour of the crystal is studied using LCRZ meter.

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### 1. Introduction

Organic crystal engineering is the area of research which studies the design and synthesis of solid-state structures with desired properties in recent past. Crystal structures are mediated with the aid of the intermolecular interactions. Organic hydrogen bonded crystals have been intensively studied in recent years due to their applications in telecommunications and other optical information processing. Among all the non-covalent interactions the hydrogen bonding performs an important role in the crystal engineering to design new materials with superior properties for optical and pharmaceutical purposes.

Studies into the advent of the multi component crystalline substances such as salts, co-crystals and solvates are presently undergoing a revival of interest in both academia and industry [1-7]. Cocrystals are the neutral chemical compounds that remain neutral while crystallizing together, whereas an organic salt is the result of the proton exchange between an acid and a base.

Heterocyclic compounds are the largest and most unique family of organic compounds [8]. Heterocyclic compounds have a wide variety of applications: they are predominant among the type of compounds which are used as pharmaceuticals [9], as agrochemicals and as veterinary products. They also find additional applications as sanitizers, developers, antioxidants, as corrosion inhibitors, as copolymers, dyestuff [10]. Heterocyclic compounds with excellent nonlinear optical (NLO) properties are highly important and have many uses in different fields such as nuclear science, optoelectronics etc [11].

Nitrogen containing heterocyclic ring such as pyrimidine has been stated due to its wide range of chemical and biological significance in medicinal chemistry [12-14]. Apart from that, pyrimidine confirmed its application in agricultural and industrial chemicals. Some of the pyrimidine derivatives are pesticides [15], herbicides and plant magnification regulators [16]. Aminopyrimidine derivatives are additionally present as the key components in many drugs. 2-aminopyrimidine represents one of the most biologically active classes of compounds, possessing a wide spectrum of biological and pharmacological activities such as antimicrobial [17], analgesic, antiviral, anti-inflammatory [18], antitubercular [19], antitumour [20] and antimalarial agent [21]. A large number of 2-aminopyrimidine-carboxylic acid crystals had been reported. 2-

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aminopyrimidine benzoic acid (2APB) [22], 2-aminopyrimidine succinic acid (2APS) [23], 2-aminopyrimidine oxalic acid[24],2-aminopyrimidine 3-nitrophthalic acid[25].

Most co-crystal design strategies are based on strong hydrogen bonds. It is therefore a possibility that the proton involved in the hydrogen-bonding will be transferred from the acid to the base. To determine whether or not a co-crystal or salt crystal is formed, the pKa-value is often considered [26]. In particular the dependence on  $\Delta pK_a$  value greater than 3 confirms the salt formation, whereas the  $\Delta pK_a$  value is less than 0 guarantees the formation of cocrystal and the value ranging between 0 and 3 ensures the salt or cocrystal formation. The  $\Delta pK_a$  value of 2-aminopyrimidine ( $pK_a=3.45$ ) and pimelic acid ( $pK_a=4.51$ ) is  $-1.06$  which guarantees cocrystal formation accordingly  $\Delta pK_a$  rule. With the available literature a work was carried out on the new crystal formation in the 2-amino pyrimidine with pimelic acid.

The crystal formation has not been investigated yet. Hence this report discusses synthesis, crystal growth, structure and properties of crystalline 2-amino pyrimidine with pimelic acid (PYPI). Here single crystal X-ray diffraction, Powder x-ray diffraction, UV-visible studies, photoluminescence, microhardness, dielectric studies and Fourier Transform Infrared spectra are carried out in this project work.

## 2. Experimental section

### 2.1. Materials and methods

The precursor 2-aminopyrimidine (purity>98.0%) is received from TCI chemicals. The pimelic acid (98 %) was received from alfa aesar. The ethanol (99%) which is used as the solvent was received from SRL chemicals. All the chemicals were used without further purification for crystallization process.

### 2.2. Synthesis and crystallisation

The title crystal of 2 – aminopyrimidine (PY) with pimelic acid (PI) was grown by slow evaporation method. A 1:1 molar ratio of 2-aminopyrimidine (0.951g) and pimelic acid (1.6017g) were dissolved in 10 ml of distilled water and ethanol respectively. The pimelic acid was added drop wise in to the 2-aminopyrimidine solution. The mixed solution was stirred well using a magnetic stirrer at room temperature for 45 minutes. Then the solution was filtered through the A1 grade whatmann filter paper. The solution was kept under undisturbed place. The nucleation was started on the tenth day. Transparent good quality crystals were harvested on twenty third day. The photographic view of grown crystal PYPI is shown in the Figure 1.



*Fig. 1. The grown crystal PYPI.*

### 3. Experimental techniques

Single crystal X-ray diffraction data were collected on a Bruker Kappa APEXII diffractometer. Mo K $\alpha$  ( $\lambda = 0.71073$ ) radiation with a graphite monochromator was used. The unit cell parameters values are calculated. The title compound is subjected to powder X-ray diffraction studies using Bruker AXS D8 diffractometer to verify the crystalline nature. The FTIR spectrum of PYPI were recorded in KBr in the range between 400 and 4000  $\text{cm}^{-1}$  to identify the functional groups using Perkin Elmer 1 spectrophotometer at a resolution of  $1\text{cm}^{-1}$ . The optical absorption spectrum of PYPI was recorded on Perkin Elmer Lamda 35 spectrophotometer in ethanol solution. Photoluminescence emission spectra of PYPI were recorded using emission Perkin Elmer LS-45 spectrometer. Vicker's microhardness measurements were carried out using vicker's microhardness tester to determine the mechanical stability of the crystal. The dielectric constant and the dielectric loss studies were carried out at room temperature using LCRZ meter to establish the dielectric nature of the grown crystal.

### 4. Result and discussion

#### 4.1. Powder X-ray diffraction (PXRD)

Powder diffractogram displays significant information about the crystallinity of the beginning material as well as of grown crystalline material [27]. The squashed powder of PYPI crystal is subjected to powder X-ray diffraction analysis. The spectrum is recorded between  $10^\circ$  and  $50^\circ$ . The crystallinity and purity of the grown crystalline material are established via the distinguished, well-resolved Bragg's peak at the specific 2 theta angle.

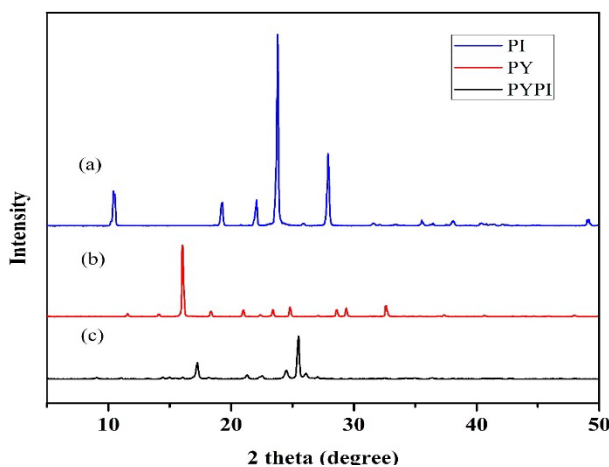


Fig. 2. Powder XRD pattern of PYPI crystal.

The powder X-ray diffraction pattern of the title crystal is depicted in the Figure 2. The apparent contrast between the peaks in the diffractogram of the starting materials and grown crystalline materials indicated the formation of the new crystal.

#### 4.2. Single crystal X-ray diffraction

Single crystal XRD evaluation has been carried out on the grown PYPI crystal to perceive the unit cell parameters and the crystal structure. The estimations of the unit cell parameters of PYPI crystal are carried out using the Bruker Kappa APEXII diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073$  Å). Single crystal X-ray diffraction reveals that the title crystal PYPI belongs to the monoclinic crystal system. The lattice parameter values are shown in the Table 1. Comparing the

cell parameters of PYPI with that of the parent compounds we can confirm the formation of new crystals.

Table 1. Unit cell parameter values of (a) 2-Aminopyrimidine (PY), (b) Pimelic Acid (PI) and (c) PYPI.

Cell Parameters	2-Aminopyrimidine (PY)	Pimelic Acid (PI)	Present work PYPI
a	14.862Å	17.7190Å	13.35Å
b	10.884Å	4.73030Å	15.88Å
c	5.633Å	9.67030Å	13.87Å
V	911.183A <sup>3</sup>	776.573A <sup>3</sup>	2585A <sup>3</sup>
$\alpha$	90.00°	90.00°	90.00°
$\beta$	90.00°	106.6430°	118.41°
$\gamma$	90.00°	90.00°	90.00°

### 4.3. Vibrational analysis

The FTIR spectrum of the grown crystal is recorded in the middle IR between 400 – 4000 cm<sup>-1</sup>. FTIR spectroscopy is widely used for the detection of functional groups of the synthesized compound. FTIR spectrum of the grown crystal is shown in the Figure 3.

The vibrational changes in the functional groups which are involved in hydrogen bonding such as carboxylate and N-H can be identified in the FTIR spectra. The N-H stretching vibration appeared at 3399 cm<sup>-1</sup> in the FTIR spectrum. The hetero aromatic structure show the presence of C-H stretching vibrations in the region of 3100-3000 cm<sup>-1</sup> which is the characteristic region for the ready identification of C-H stretching vibrations [28]. The FTIR peak at 3173 cm<sup>-1</sup> is attributed to C-H stretching vibrations of heteroaromatic substance in the compound. The aromatic ring stretching vibrations generally occurred in the region 1625-1420 cm<sup>-1</sup>. In the present work, the ring vibrations of PYPI appeared at 1590 cm<sup>-1</sup> in the FTIR spectra.

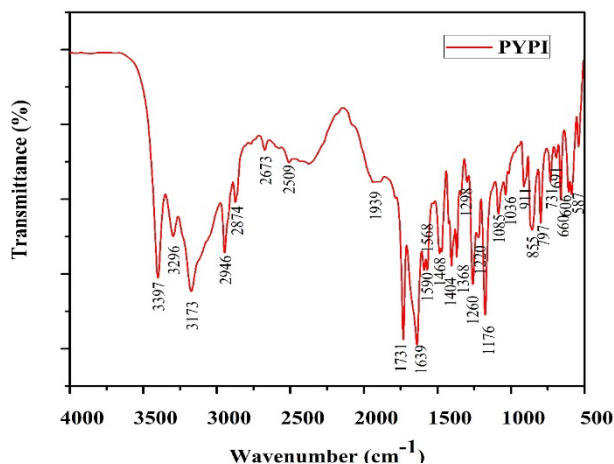


Fig. 3. FTIR spectrum of PYPI crystal.

The C-N stretching vibrations appeared at 1350-1250  $\text{cm}^{-1}$ . The C-N stretching vibrations are denoted by the peaks 1260  $\text{cm}^{-1}$ , 1298  $\text{cm}^{-1}$ , 1341  $\text{cm}^{-1}$  in the FTIR spectrum for the title crystal. The O-H stretching vibration is appeared at 3296  $\text{cm}^{-1}$  in the FTIR spectrum. The C=O stretching vibration is observed at 1731  $\text{cm}^{-1}$  and the C-O stretching vibration appeared at 1298  $\text{cm}^{-1}$ .

#### 4.4. UV-Visible spectral analysis

The optical absorption spectrum of PYPI is recorded in the range of 300-800 nm on an UV-Vis spectrophotometer with ethanol as the solvent. From the absorption spectrum which explains the band structure and the type of transition involved in the molecular structure. The optical absorption spectrum of PYPI in ethanol solution is depicted in the Figure 4. The maximum absorbance for the PYPI in ethanol solution was observed at 297 nm which is associated to  $n-\pi^*$  transition and this transition was due to the presence of auxochromic group (NH<sub>2</sub>) in PYPI sample.

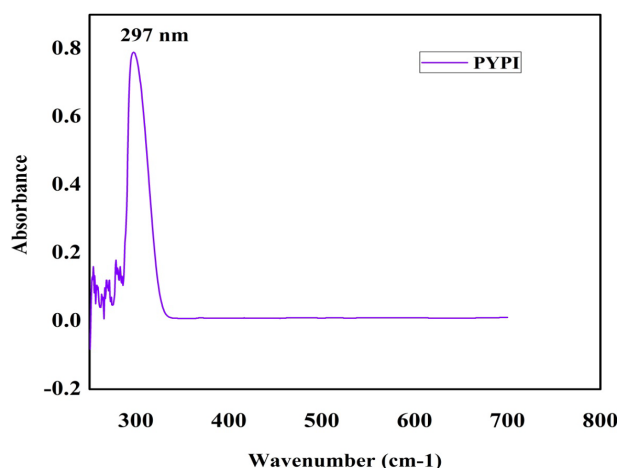


Fig. 4. UV- Visible spectrum of PYPI crystal.

The band gap for the grown crystal of this work is calculated using the following relation

$$E = 1.234 \times 10^3 / \lambda_{\text{max}} \text{ eV}$$

The band gap value of the title crystal is calculated as 4.15 eV. This value of band gap is quite close to the optimum band gap required for the absorber in a single solar cell [29].

#### 4.5. Photoluminescence spectral studies

Photoluminescence (PL) spectral analysis is one of the advantageous techniques from which the electronic structure of the material can be studied. Photoluminescence is the phenomenon in which electronic states of solids are excited by light of particular energy and the excited energy is released as light. Particularly it is extensively used to find out the impurities and predicts unique way of utilizations in lighting advances. PL emission spectrum was recorded between 300 and 800 nm. The emission peak was observed at 353 nm reveals the violet emission of the observed sample. The PL emission spectrum is depicted in the Figure 5. This characteristic PL emission may find potential applications in optical devices [30].

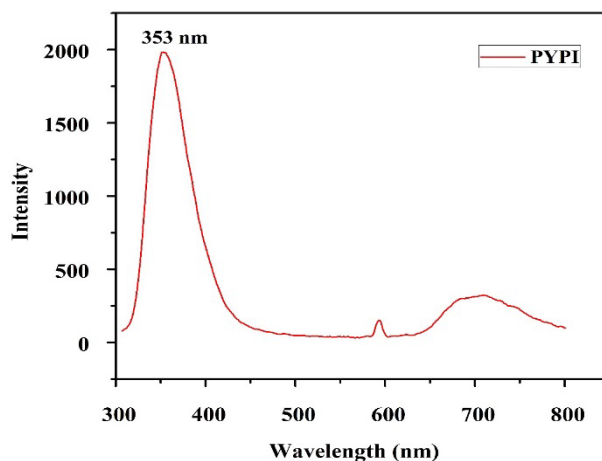


Fig. 5. Photoluminescence spectrum of PYPI.

#### 4.6. Microhardness studies

Hardness is one of the fundamental mechanical properties of solid material [31]. Microhardness testing is an extensively used technique for measuring the hardness or resistance of the materials. The hardness of a particular material is the measure of its resistance to plastic deformation. This everlasting deformation can be completed by indentation, bending, scratching or cutting. The important property of any device material is its mechanical strength, represented by its hardness. Microhardness analysis was carried out using Vicker's microhardness tester fitted with a diamond indenter. The title compound was placed on the Vicker's microhardness tester and subjected to series of different loads over a regular interval of time. Loads ranging from 10 to 100 g were used for vicker's microhardness studies with regular indentation time of 15 s for all samples. The hardness was calculated using the relation

$$H_v = 1.8544 d \times (p / d^2) \text{ Kg/mm}^2$$

where 'P' is the magnitude of a load applied to the given sample and 'd' is the diagonal length of the impression created by the indentation [32]. The plots of hardness number  $H_v$  versus load P and also  $\log P$  versus  $\log d$  are given in the Figures 6(a) & 6(b).

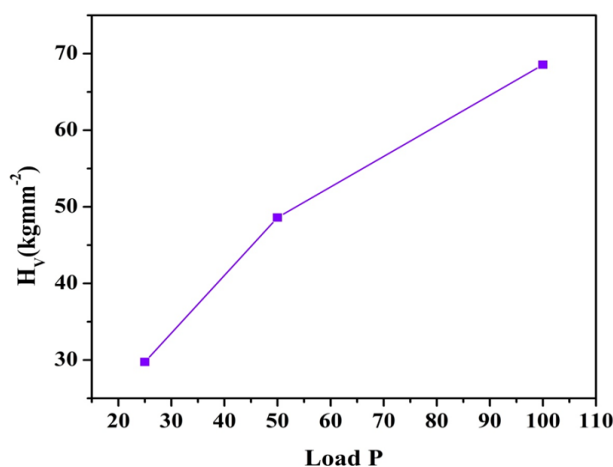


Fig. 6. (a) Plot of  $H_v$  Vs load P.

Here the hardness test is carried upto 100 gms and at higher load beyond 100gms a cracking occurs, so hardness test cannot be taken beyond 100 gms. The relation between the applied load and the diagonal length  $d$  of the indenter is established by meyer's law

$$P = ad^n$$

where  $n$  is the meyer's index. It can be determined from the slope of the straight line.

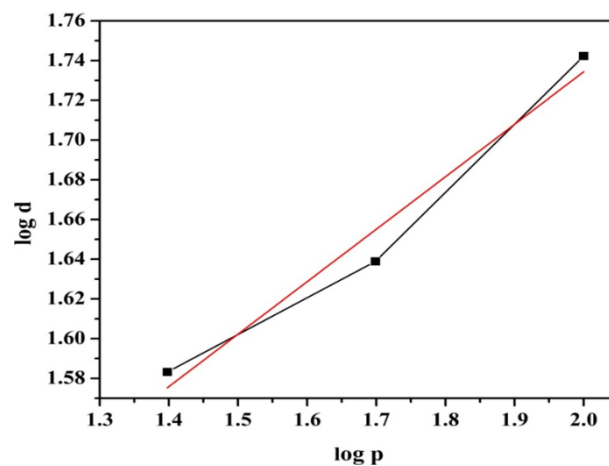


Fig. 6. (b) Plot of  $\log P$  Vs  $\log d$ .

From careful observations on different materials onitsch [33] and Hanneman [34] stated that the value of 'n' lie between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials. The value of  $n$  obtained for the title crystal is 2.4 and it is concluded as soft materials.

#### 4.7. Dielectric studies

The dielectric characteristics of the material are important to find out the lattice dynamics of the crystal. It is additionally beneficial to recognize the nature of the defects in grown crystal.

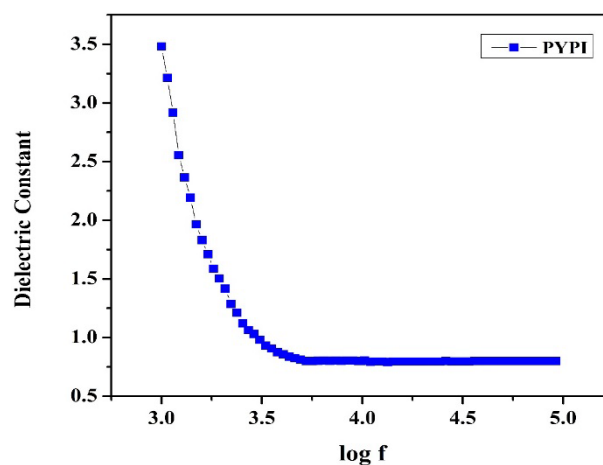


Fig. 7. (a) Dielectric constant Vs frequency.

The dielectric properties are directly related to the electro-optic property of the crystal[35]. The dielectric constant and the dielectric loss were studied using LCRZ meter. The dielectric constant and the dielectric loss of the grown PYPI crystal were recorded. The dielectric constant and the dielectric losses were derived using the relation

$$\epsilon' = Cd / \epsilon_0 A$$

and

$$\epsilon'' = \epsilon' \tan \delta$$

where 'C' is the capacitance in, 'd' is the thickness of the material, 'A' is the area of the sample, ' $\epsilon_0$ ' 'the permittivity of free space ( $\epsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ ) and '  $\tan \delta$ ' is the degeneracy factor.

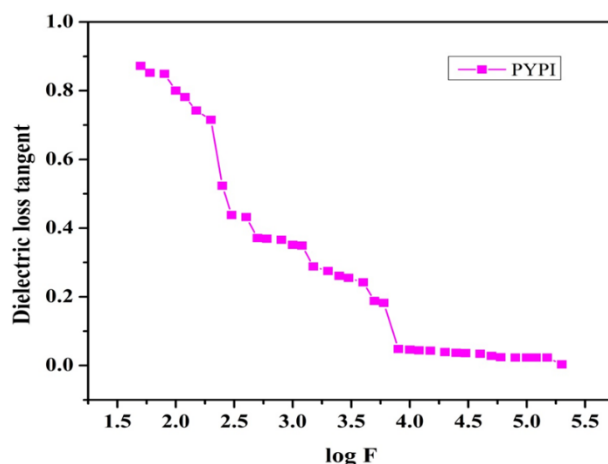


Fig. 7. (b). Dielectric loss Vs frequency.

The variation of dielectric constant ( $\epsilon_r$  and the dielectric loss ( $\epsilon''$ ) with frequency at room temperature are depicted in the Figures 7(a and b). From the graph it is obvious that the dielectric constant and the dielectric loss decreases as frequency increases and vice versa. The dielectric constant of the materials is due to the contribution of all for polarizations (electronic, ionic, dipolar and space charge polarization) which depends on the frequency. The higher values of dielectric constant at low frequencies are due to space charge polarization and also the crystal lattice defects. The low value of dielectric constant at higher frequency may be due to loss of the magnitude of the polarization [36, 37]. The lower dielectric loss at higher frequency in this present work suggests that the title sample possess enhanced optical quality with lesser defects. The lower value of dielectric constant at high frequency is important for extending the application in photonics and electro-optic – devices.

## 5. Conclusion

The crystals of 2- aminopyrimidine pimelic acid have been grown successfully by slow evaporation method at room temperature using ethanol as the solvent. Powder X-ray diffraction pattern verified for the crystalline nature of the PYPI crystal. The difference between the peaks of the parent compound and the resulting mixture reveals the formation of the new crystals. The calculated unit cell parameter values from SXRD study which reveal that the modified crystal structure of the grown PYPI crystal. The various functional groups present in the crystal PYPI are identified by FTIR spectral studies. The UV-Visible analysis establishes maximum absorption at 297nm which ensure the band gap for this grown crystal PYPI is 4.15eV.



From the photoluminescence studies, the violet emission was confirmed by the peak 353nm. The microhardness study suggests that the hardness number increases with increase in load. The result suggests that the title crystal belongs to soft materials According to the current investigation, the title sample has improved optical quality and fewer flaws because of the lower dielectric loss at higher frequencies. The lower value of dielectric constant at high frequency confirms that the grown crystal can be extended for the application in photonics and electro –optic – device fabrication.

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