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PII: S1386-1425(14)01750-8
DOI: http://dx.doi.org/10.1016/j.saa.2014.11.086
Reference: SAA 13022

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 8 January 2014
Revised Date: 4 August 2014
Accepted Date: 20 November 2014

Please cite this article as: M. Nirosha, S. Kalainathan, P.G. Aravindan, Growth and characterization of a new organic single crystal: 1-(4-Nitrophenyl) pyrrolidine (4NPY), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: http://dx.doi.org/10.1016/j.saa.2014.11.086

# Growth and characterization of a new organic single crystal: 1-(4-Nitrophenyl) pyrrolidine (4NPY)

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**Abstract**

A new 1-(4-Nitrophenyl) pyrrolidine single crystal has grown by slow evaporation solution growth technique. The grown crystal have characterized by single crystal x-ray analysis, and it shows that 1-(4-Nitrophenyl) pyrrolidine crystallizes in the orthorhombic space group Pbca, with cell parameters a = 10.3270 (5) Å, b = 9.9458 (6) Å, c = 18.6934 (12) Å, and Z = 8. Powder XRD pattern confirmed that grown crystal posses highly crystalline nature. The functional groups have identified by using FTIR spectral analysis. The absorbance and the luminescence spectra of the title compound have analyzed using UV–Visible and PL spectra. The thermo analytical properties of the crystal have studied using TG/DTA spectrum. The mechanical property of the grown crystal has determined using Vickers micro hardness measurement. The grown features of the crystal have analyzed using etching technique.

**Keywords:** Crystal structure, Growth from solution, characterizations

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## 1. Introduction

In recent years, the interest of organic materials having aromatic rings has increased considerably. Organic materials offer flexibility to molecular design, large nonlinear response over a broad frequency range and high damage resistance to optical radiation. Hence these materials make it desirable to replace electronic switching circuits in computing and telecommunication systems [1-4]. The presences of heterocyclic in all kinds of organic compounds are of interest in electronics, optics, biology, and materials science. Heterocycles have used as additives and modifiers in industrial applications including reprography, information storage, plastics, solvents, antioxidants and vulcanization accelerators. Optically active pyrrolidine rings remain an area of intense research due to their natural occurrence found in natural alkaloid products and as bio-molecules [5]. The various N - substituted pyrrolidine compounds such as N - (substituted phenyl) pyrrolidine – 2 - carboxamide, N - substituted 2, 5-dimethyl pyrrole, N - (2 - Napthyloxy methyl carbonyl) pyrrolidine in anticonvulsant activities has also well known [6-8]. The title compound 1 - (4 - Nitrophenyl) pyrrolidine (4NPY) is an intermediate compound in the synthesis of 1 - (4 - aminophenyl) pyrrolidine sulfate, and it has synthesized from 1 – chloro – 4 - nitrobenzene. The chlorinated nitro aromatic compounds are good precursors to introduce nitrogen substituent, hence acts as a starting materials for the preparation of various N-heterocycles and a number of industrial chemicals [9-10]. Nitrobenzene compounds possess high contribution of anharmonic electron-phonon interaction and can be used as a material for the fast-response, degenerate four-wave mixing. Optical-grade organic single crystals of substituted pyrrolidine derivatives with high optical nonlinearities and low melting temperatures are promising materials for optoelectronics, and nonlinear optical (NLO) applications [11]. The discoveries of new materials exhibiting nonlinear optical properties in

combination with other desirable physical properties (optical transparency, thermal, optical and mechanical stability) continue to be an important research goal in nonlinear optics [12-13]. The present work deals with the synthesis, growth, crystal structure and characterizations of novel organic single crystal, of 1-(4-Nitrophenyl) pyrrolidine.

## 2. Experimental

### 2.1. Synthesis and Growth

4NPY have prepared by following the procedure in ref [9]. The calculated amounts of pyrrolidine, $Na_2CO_3$, 2-propanol have combined with 4 -chloronitrobenzene with water. The mixture has refluxed for 1 hour. The resultant mixture has filtered washed with cold water and dried in vacuo at 50°C. The final product has purified by recrystallization process using ethanol as solvent. In order to grow the single crystals of 4NPY, a saturated solution have prepared at room temperature (30°C) using ethanol as solvent and placed in a constant temperature bath. When solution evaporates, the saturation gradually attains supersaturated level leading to nucleation and the growth of the crystals. Within two weeks of time, the crystals of appreciable size 4mm x 3mm x 3mm have harvested. The as grown 4NPY crystals have shown in Fig.S1.

## 3. Results and discussion

### 3.1. Single crystal and Powder XRD

The single crystal X-ray diffraction (XRD) analysis of 4NPY crystal have carried out using ENRAF NONIUS X-ray diffractometer with $MoK_\alpha$ radiation of wavelength $\lambda$=0.71073Å at room temperature and the unit cell parameters, and morphology of the grown crystal has identified. The morphology of the grown crystal has shown in Fig S2. The structure of the grown crystal has solved by the direct method and computerized by the full matrix least square technique using the SHELXL program. The compound crystallized in orthorhombic system and Pbca space group

(Table 1). The related reported structures have compared with the present crystal structures [14-15]. The bond distances and angles have agreed with standard reported structures [16]. The selected bond distances and angles have listed in Tables 2. The torsion angles represent the orientation of nitro group with benzene plane by -3.4°. The conformation of pyrrolidine ring system has an envelope on C8 atom which has evidenced from the lowest mirror symmetry of 0.7.3(10) ° (D. Cremer & J.A. Pople) **[17].** The twisted nitro group results short contact between O2 and H2 by distance 2.44 Å. The mean plane calculation shows C8 atom having highest deviation in respect of other atoms in pyrrolidine ring. The observed site occupation factors of pyrrolidine ring system shows disorder by 0.705(10):0.295(10) and with their sum constrained unity. The hydrogen atoms have fixed by geometrically on their parent atoms, with C-H distance in the range 0.93-0.97 Å. Fig. S3 shows the molecular structure with the numbering scheme of 4NPY molecule. Apart from the van der Waals interactions, crystal packing has stabilized by C-H...π and π…π interactions. One of the hydrogen atom (H10D) at X, Y, Z interact with the centroid of a benzene ring at 3/2-X, 1/2+Y, Z with distance of 2.88 Å, angle D-H...A= 124°; D...A= 3.52 Å and zigzag chain ride in the b axis [Fig.1]. The aromatic π…π interaction exists with another benzene ring at 2-X, 2-Y, and 2-Z by 4.00Å. The purity and crystalline nature of 4NPY compound has confirmed by recording powder X-ray diffraction pattern using a RICHER SEIFERT X-ray diffractometer employing $CuK_{\alpha}$ (1.54058 Å) in the range of 10-70° in the steps of 0.02°. The well defined Bragg's peaks at particular 2 theta angles in the powder XRD spectrum has shown in Fig.2. It reflects good crystalline nature of the grown crystal. The peaks have indexed using APPLEMAN program from the 2 theta values. The lattice parameters calculated from powder xrd analysis are in good agreement with the data obtained from single crystal XRD analysis.

### 3.2 FTIR spectrum

The FTIR spectrum of the grown crystal has recorded in the middle IR between 400-4000 $cm^{-1}$. It has carried out using FT-IR 4100 type-A spectrophotometer employing KBr pellet technique at room temperature. FTIR spectroscopy has widely used for the detection of functional groups of the synthesized compound **[18].** The recorded spectrum of 4NPY has shown in Fig.3. The peak observed at 1109.07 $cm^{-1}$ is due to the presence of C-N asymmetric stretching of the heterocyclic ring present in the compound. The peak observed at 3388.93 $cm^{-1}$ has assigned to the presence of four asymmetric $CH_2$ of the heterocyclic ring. The peak at 1523.76 $cm^{-1}$ confirms the presence $NO_2$ vibration. The presence of symmetric C-N bond has confirmed by the peak observed at 1193.94 $cm^{-1}$. The peaks observed at 2858.51 $cm^{-1}$, and 2976.16 $cm^{-1}$ are due to the presence of four C-H bonds present in the compound.

### 3.3 UV-visible studies

The UV-Vis-NIR spectrum gives information about the structure of the molecule. The absorption of UV and visible light involves promotion of the electron in the σ and π orbital from the ground state to higher states **[19].** The UV-vis spectrum has carried out using ELICO SL 218 double beam UV–vis spectrophotometer in the range 190-1100 nm. The spectrum has recorded for 2mm thickness crystal and as shown in Fig.4. From the spectrum, it has seen that the crystal has a lower cut-off wavelength of 529nm. The crystal shows its transparency from 530-1100nm. The crystal shows its transparency from 530-1100nm. Optical band gap value has calculated from the Tauc's plot between the absorption coefficient $(\alpha h\upsilon)^{1/2}$ and photon energy ($h\upsilon$). The band gap obtained from the graph for 4NPY has shown in Fig.S4. The optical band gap value of 4NPY is

2.21 eV. The lower band gap of the title material suggests that it may be utilized in visible light-responsive devices and ambipolar organic thin film transistors [20-21].

### 3.4 Photoluminescence studies

The Photoluminescence spectrum provides information of different energy states available between the valence band and conduction band responsible for radiative recombination [22]. The PL spectrum have recorded using Jobin Yvon-Spex spectrofluorometer (Fluorolog version 3: Model FL3-11) at room temperature for a spectral resolution of 0.2nm; 450W high pressure xenon lamp acts as an excitation source. The PL intensity is most probably dependent on the crystalline nature and structural perfection of the grown crystal. Fig. 5 represents the PL spectrum of 4NPY single crystal. The sample has excited at 529 nm. The emission spectrum has recorded between 540-720 nm. The broad emission band appeared in the region 552-567 nm owing to the emission of green radiation. The luminescence in the green spectral regime, which is of the high importance for display and solid-state lighting applications [23].

### 3.5 Thermal analysis

Thermo gravimetric methods have mainly limited to decomposition and oxidation reactions and to physical processes such as vaporization, sublimation and desorption. Thermo grams provide information about decomposition patterns and weight loss of the materials [24]. Thermo gravimetric analysis and differential thermal analysis (TG/DTA) for 4NPY have recorded using a SDT Q600 V8 instrument. The analyses have carried out in an atmosphere of nitrogen at a heating rate of 10°C/min for the temperature range 30°C -1000°C. The Thermogravimetric spectrum of 4NPY has shown in Fig.6. The title compound exhibited good resistance to thermal

decomposition up to 163°C. The compound undergoes decomposition in a single stage which starts at 163°C and completes at 227°C.

### 3.6 Micro hardness studies

Micro hardness studies have carried out with Mututoyo MH-112 micro hardness tester using Vickers diamond pyramidal indenter attached to a metallurgical microscope. The hardness of the material plays a significant role in device fabrication. Micro hardness studies have applied to understand with plasticity of the substance [25]. Experiment has carried out with Mututoyo MH-112 micro hardness tester using Vickers diamond pyramidal indenter attached to a metallurgical microscope. Crystal with flat and smooth faces free from any defects has chosen for the static indentation tests. The indentations have made at room temperature with a constant indentation time of 10s. Vickers microhardness test has carried out on (001) face of the grown crystal. The surface has gently polished with water. Then the polished crystal has correctly mounted on the base of the microscope and indented gently by applying loads 10-100g with a dwell time of 10s. At least five indentations have made on sample for each load. The indented surface has examined under the microscope. The lengths of the two diagonals of the indentations have measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading. The average diagonal lengths measured at each time. The Vickers microhardness number of the crystal $H_v$ has calculated using the formula.

$$H_v = 1.8544 \frac{P}{d^2} \qquad (1)$$

Where P is the load applied, and d is the mean diagonal length of the indentation. The plot between load (P) and ($H_v$) of 4NPY single crystal is shown in Fig.S5. It is evident from the plot that the microhardness value decreases with the increasing load.

**3.7 Etching studies**

The microstructure has revealed by a surface treatment using an appropriate chemical reagent in a procedure termed etching [26]. To investigate the perfection of crystalline sample, etching studies has done using deionized water as an etchant at room temperature for etching times of 30s, 45s, and 60s. Etch patterns have analyzed using a Carl Zeiss metallurgical micro-scope (Axios kop 40 MAT) in the reflection mode. Etching technique helps to develop some features such as growth striations, etch spirals; rectangular etch pits etc., on the crystal surface. The etching studies have carried out on the fresh cleavage surface (001) plane of the single crystal. During etching reaction at the perfect lattice, the energy barrier $E_a$ (activation energy) is substantially higher than at the defect. Hence etch rates at defect sites are higher than etch rates of the perfect lattice giving rise to the formation of etch pits at defect sites. The specimen surface must first be ground and polished to a smooth and mirror like finish. This can be accomplished by using successively finer abrasive papers and powders. Surface layer has removed by means of etching a fresh surface appeared gave clear etch pits. Fig.S6 (a) shows the surface of the crystal before etching. It is clear from the image that the grown crystal has a smooth surface. Fig.S6 (b & c) shows the formation of triangular pits on the surface of the crystal for etch time of 30 and 45 sec. When the etching time increased for 60s, the pattern remains the same, but the size of the etch pits has slightly increased which as shown in Fig.S6 (d). This may due to the presence of dislocation caused by thermal stresses which has imposed on the growth surface [27].

## 4. Conclusions

A new organic 1-(4-Nitrophenyl) pyrrolidine single crystal have synthesized by slow evaporation technique. Crystal of size 4mm x 3mm x 3mm have obtained at room temperature. The single crystal X-ray diffraction confirms that the grown crystal belongs to the orthorhombic crystal system with the space group Pbca. From the FTIR spectrum, the presence of functional groups of the material has confirmed. The lower cut off wavelength through UV-Vis spectrum is 529 nm. The PL spectrum shows green emission in the crystal. The micro hardness studies revealed that the crystal develops cracks for load above 100g. The thermal analyses reveal that the crystal has good stability up to 163°C. Hardness study indicates that the hardness decreases with increasing load. The chemical etching study shows the triangular etch patterns. The shape of the etch pit increases on increasing the etching time.

**Acknowledgements**

The author acknowledges Dr. U. Madhusudhanan, IGCAR for PL studies and SAIF, IIT madras for proving the S-XRD facility. The authors are also thankful to VIT University for providing excellent research facilities.

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**Figure captions**

Fig.1 packing diagram of 4NPY

Fig.2 powder xrd spectrum of 4NPY

Fig.3 FTIR spectrum of 4NPY

Fig.4 absorbance spectrum of 4NPY

Fig.5 Luminescence spectrum of 4NPY

Fig.6 TG/DTA spectrum of 4NPY

**Fig.1 packing diagram of 4NPY**

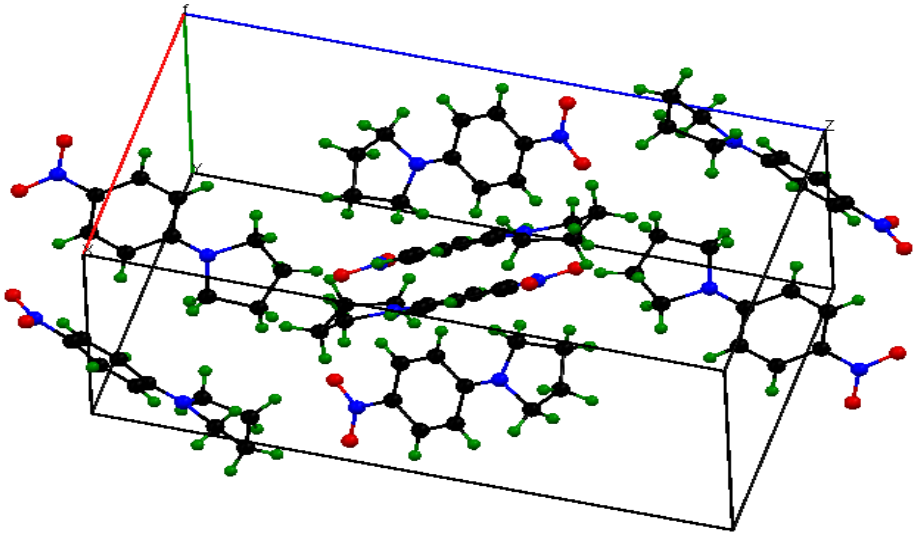


**Fig.2 Powder xrd spectrum of 4NPY**

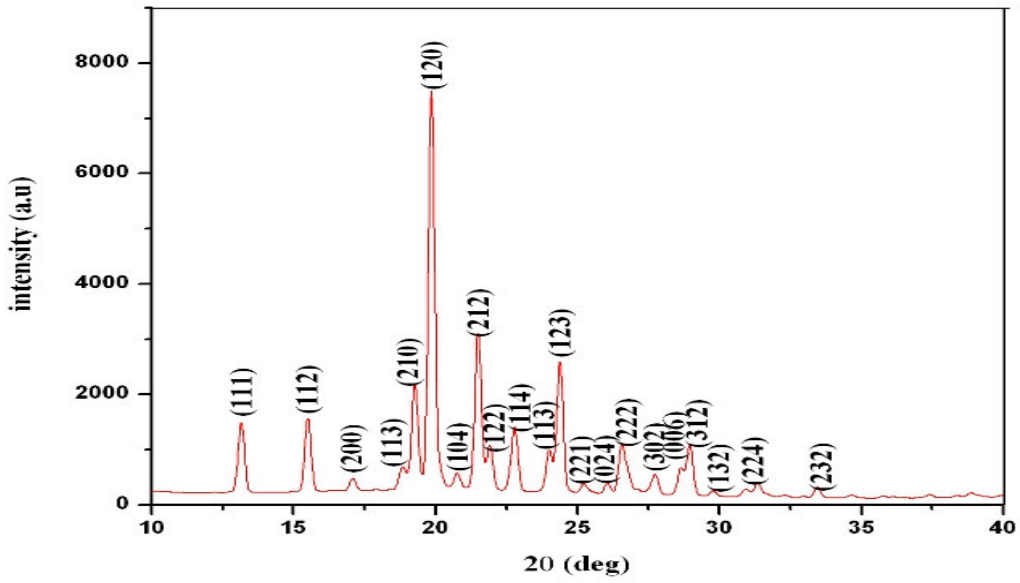



**Fig.3 FTIR spectrum of 4NPY**

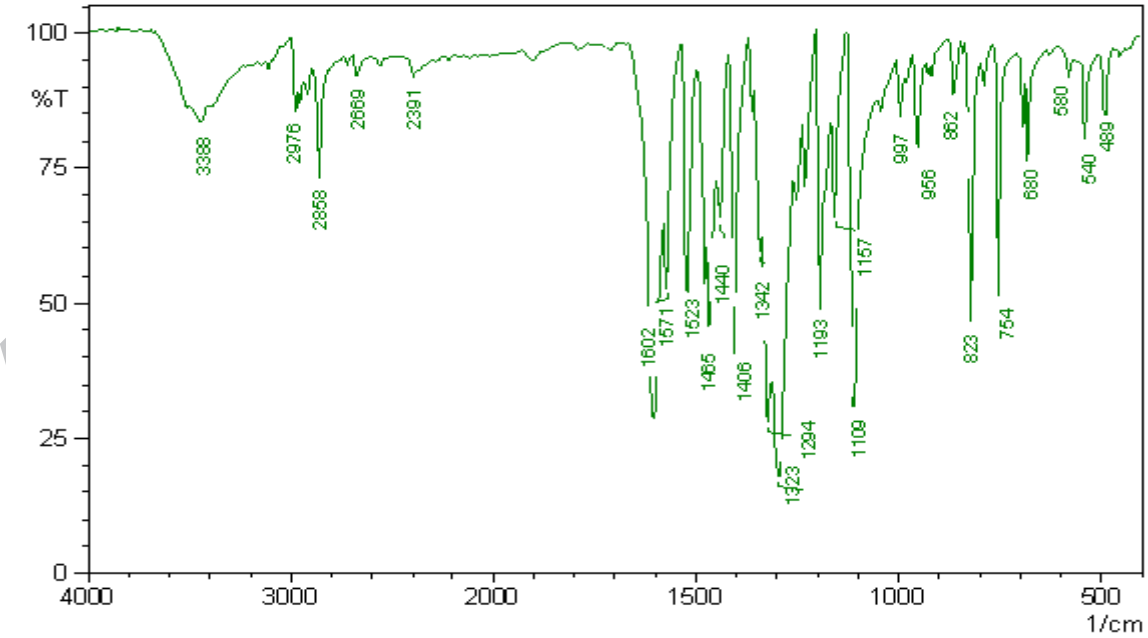


**Fig. 4 Absorbance spectrum of 4NPY**

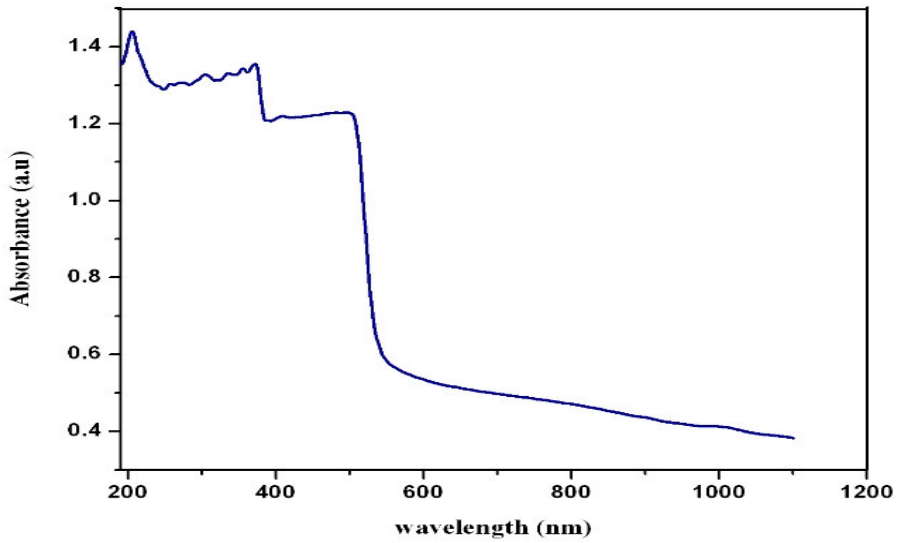



**Fig. 5 Luminescence spectrum of 4NPY**

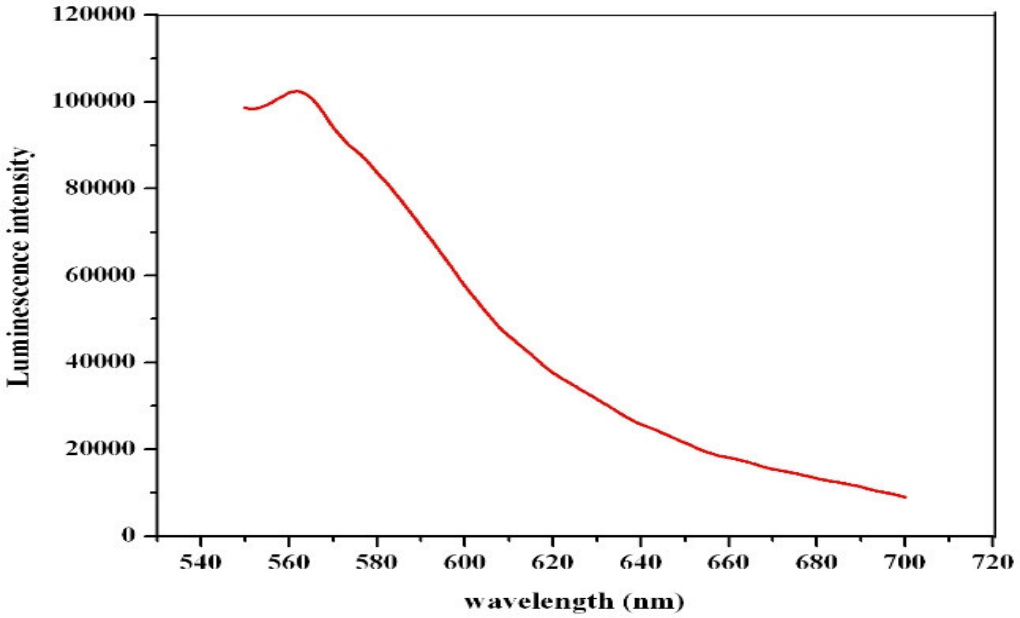


**Fig.6 TG/DTA spectrum of 4NPY**

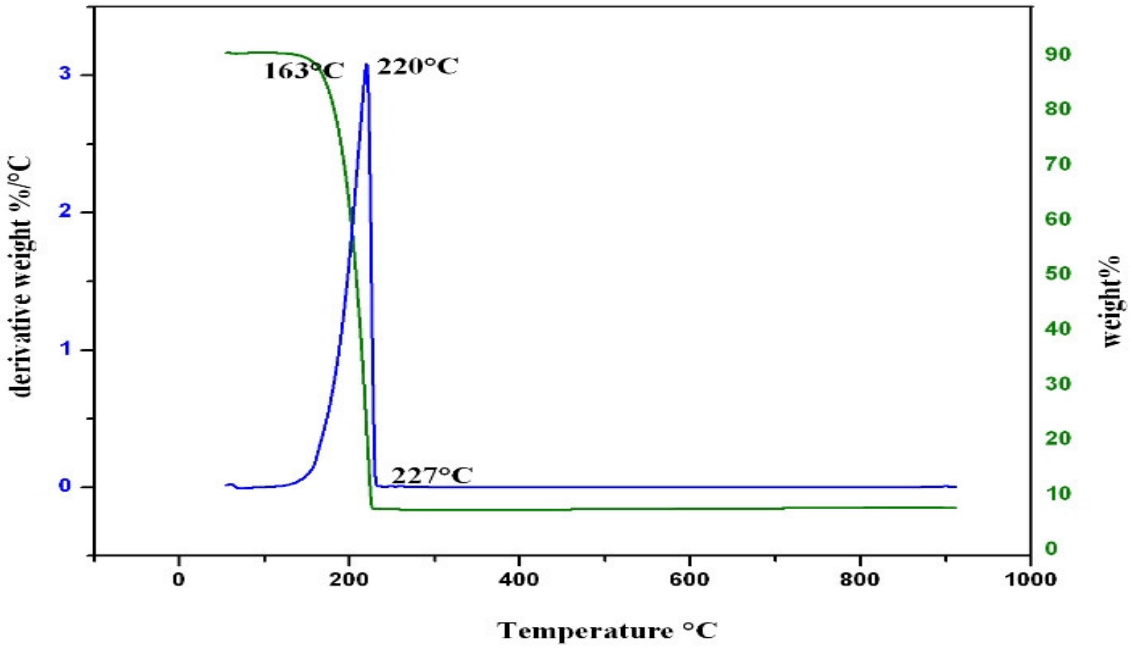


**Table 1**

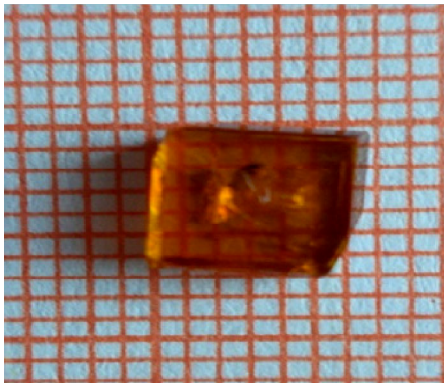
Crystal data and structure refinement of 4NPY

| | |
|---|---|
| Empirical formula | $C_{10}H_{12}N_2O_2$ |
| Formula weight | 192.22 |
| Wavelength | 0.71073Å |
| Crystal system | Orthorhombic |
| Unit cell dimensions | a = 10.3270 (5) Å, α = 90° |
| | b = 9.9458 (6) Å, = 90° |
| | c = 18.6934 (12) Å, γ = 90° |
| Volume | 1920.00(19) $Å^3$ |
| Z, Density (calculated) | 8, 1.330 $Mg/m^3$ |
| Absorption coefficient | 0.094$mm^{-1}$ |
| F(000) | 816 |
| Crystal size | 0.30 x 0.30 x 0.25 $mm^3$ |
| Theta range for data collection | 2.94 to 24.87°. |
| Index ranges | -11≤h≤12, -8≤k≤11, -22≤l≤19 |
| Reflections collected | 8501 |
| Independent reflections | 1663 [R(int) = 0.0236] |
| Completeness to theta = 24.87° | 99.8% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/ restraints/ parameters | 1663 / 157 / 174 |
| Goodness-of-fit on $F^2$ | 1.072 |
| Final R indices [I>2σ] | R1 = 0.0348, wR2 = 0.0932 |
| R indices (all data) | R1 = 0.0582, wR2 = 0.1091 |
| Largest diff. peak and hole | 0.140 and -0.146 e.$Å^{-3}$ |

**Table 2**
Bond lengths (Å) and angles (deg) for 4NPY

| Bonds | Bond lengths (Å) |
|---|---|
| C(1)-N(1) | 1.433(2) |
| C(4)-N(2) | 1.299(8) |
| N(1)-O(1) | 1.2280(2) |
| N(1)-O(2) | 1.2265(2) |
| N(2)-C(7) | 1.462(9) |
| N(2)-C(10) | 1.455(9) |
| N(2')-C(7') | 1.468(2) |
| N(2')-C(10') | 1.472(2) |
| *Bond angles (deg.)* | |
| C(4)-N(2)-N(7) | 124.5(7) |
| C(4)-N(2)-C(10) | 125.5(8) |
| C(4)-N(2')-C(7') | 123.8(2) |
| C(4)-N(2')-C(10') | 120.3(2) |
| O(1)-N(1)-C(1) | 118.91(2) |
| O(2)-N(1)-C(1) | 119.36(2) |
| C(6)-C(1)-N(1) | 120.06(2) |
| C(2)-C(1)-N(1) | 120.14(2) |

**Graphical abstract**



**Highlights**

- 1-(4-Nitrophenyl) pyrrolidine**,** a new organic single crystal has grown by slow evaporation technique.
- The absorbance spectrum shows the lower cut off wavelength at 529 nm.
- The Thermogravimetric analysis shows that the crystal has stable upto 163°C.
- The Photoluminescence spectrum shows the green emission in the crystal.
- Micro hardness and etching studies have carried out for the grown crystal.