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

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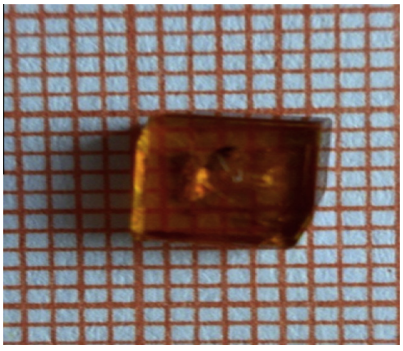
HIGHLIGHTS

- 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 up to 163 °C.
- The photoluminescence spectrum shows the green emission in the crystal.
- Micro hardness and etching studies have carried out for the grown crystal.

GRAPHICAL ABSTRACT



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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.

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, and N-(2-Napthyloxy methyl carbonyl) pyrrolidine in anticonvulsant

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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.

Table 1
Crystal data and structure refinement of 4NPY.

Empirical formula	$C_{10}H_{12}N_2O_2$
Formula weight	192.22
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Unit cell dimensions	a = 10.3270 (5) Å, α = 90°
	b = 9.9458 (6) Å, β = 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 × 0.30 × 0.25 mm^3
Theta range for data collection	2.94–24.87°
Index ranges	$-11 \leqslant h \leqslant 12$, $-8 \leqslant k \leqslant 11$, $-22 \leqslant l \leqslant 19$
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 ($I > 2\sigma$)	$R1$ = 0.0348, w$R2$ = 0.0932
R indices (all data)	$R1$ = 0.0582, w$R2$ = 0.1091
Largest diff. peak and hole	0.140 and −0.146 e Å^{-3}

Experimental

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 h. 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 4 mm × 3 mm × 3 mm have harvested. The as grown 4NPY crystals have shown in Fig. S1.

Table 2
Bond lengths (Å) and angles (°) 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 (°)	
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)

Results and discussion

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 Mo Kα radiation of wavelength λ = 0.71073 Å 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)° (Cremer and 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 4.00 Å. 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 Cu Kα (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.