Synthesis, Growth, Structural and Optical properties of Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol single crystals

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Abstract

Epochal advances have been accounted recently in the field of non-linear optics in the area of material engineering and optoelectronic device technology. Theoretical considerations of molecular hyperpolarizability ( ) of the donor-acceptor substituted aromatic molecules show that the transfer of a proton from the electron-donor group of an acid to the electron acceptor group of a base could increase   for both resulting ionic species relative to the corresponding neutral molecules. To take the advantage of this, the cocrystallization of organic acid with organic base was studied. Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol salt was synthesized by dissolving dimethyl amino pyridine in 4-nitrophenol with the molar ratio 1:2 using acetone as solvent. Single crystals of DMAPNP were grown by slow evaporation. The structural properties were studied by X-ray diffraction analysis and Fourier Transform Infrared (FTIR) Spectroscopy and its optical studies were analyzed by UV-V is spectral analysis. Mechanical studies were taken by Vickers test.

Keywords: Slow evaporation growth, X-ray diffraction, FTIR, UV analysis

Introduction

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Epochal

advances have been accounted recently in the field of non-linear optics in the area of material Engineering and the associated optoelectronic device technologies (Zyss 1944). The design of organic polar crystals for quadratic nonlinear optical applications is supported by the observation that organic molecules containing p electron systems asymmetries by electron donor and acceptor groups are highly polarizable entities in which problems of transparency and crystal growth may arise from their molecular packing the 4-dimethylamino pyridinium di-hydrogen phosphate crystals have grown. The title compound is an ionic crystal in which the 4-nitrophenolate anion and the 4-dimethylamino pyridiniumcation result from proton transfer and neutral 4-nitrophenol stands as a third partner. In the title compound, the protonation and the resulting positive charge on the ring nitrogen of the pyridine derivative make the heteroatom a strong electron acceptor.

Theoretical considerations of the molecular hyperpolarizability ( ) of the donor-acceptor substituted aromatic molecules show that the transfer of a proton from the electron-donor group of an acid to the electron acceptor group of a base could increase   for both resulting ionic species relative to the corresponding neutral molecules (Ledoux *et al* 1997). To take the advantage of this, the crystallization of organic acid with organic base was studied.

This paper discuss the Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol salt was synthesized by dissolving dimethyl amino pyridine in 4-nitrophenol with the molar ratio 1:2 using acetone as solvent. Single crystals of DMAPNP were grown by slow evaporation technique**.** The spectral analysis has been carried out to identify the functional group of the crystals. The report of our work is presented and discussed here.

Experimental Procedure

Selection of suitable solvent is very definitive for the growth of good quality single crystals. The equilibrium solubility and its temperature dependence are essential for solution growth. In DMAPNP acetone as a solvent and stirrer for two hours the acetone should be evaporated and Yellow microcrystalline formed. Then the salt is dissolved in acetone stirrer for 1 hour. Finally filter the solution. Single crystals of DMAPNP have been grown from saturated solution (pH 3.26) of the synthesized salt of DMAPNP by the slow evaporation solution growth technique at 30°C using a constant temperature bath. Pale yellow crystals have been obtained over a time span of 10-15 days. The harvested crystals are shown in fig (2.1).

Fig (2.1) Single crystals of DMAPNP

(DMAP) is a weak Bronsted base that gains a proton in acidic solution and forms the salt of the respective acid. The reaction is a proton transfer reaction where a proton is transferred from the electron donor group of 4-nitro phenol to the electron acceptor group of DMAP. The resultant product is dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP), in which the 4-nitrophenolateanion and 4-dimethylamino pyridiniumcation result from proton transfer and neutral 4-nitrophenol stands as a third partner. From the molecular structure of DMAPNP, weinfer that the main component of the crystal to provide enhanced NLO efficiency is due to p-nitrophenol. The delocalization of the electronic cloud of the OH group is the cause for such enhanced NLO efficiency (Manivannan & Dhanuskodi 2004, Sherwood 1998). The molecular structure of DMAPNP is shown in fig (2.2).


Di methyl amino pyridine   +   4-nitro phenol   →   Dimethyl amino pyridinium 4-nitrophenolate 4- nitrophenol
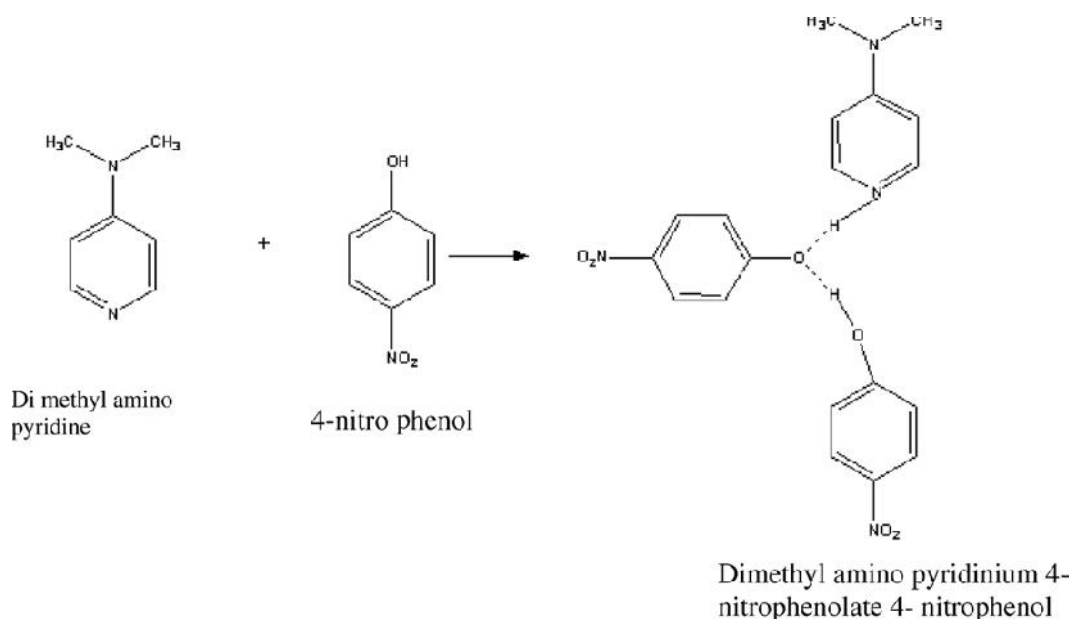
Fig (2.2) Molecular structure of DMAPNP

Characterization

X-ray diffraction

The structural properties of single crystals of DMAPNP have been studied by X-ray powder diffraction technique. The X-ray diffraction studies were carried out using RICHSEIFERT diffractometer with Cu K (k = 1.5406 A˚) radiation and the spectrum is shown in figure (3. 1). From the powdered X-ray data which is represent in Table (3.1), the various planes of reflections were indexed using XRDA program and the lattice parameters were evaluated. The evaluated lattice parameters are a = 6.332(3) A˚, b = 11.975(7) A˚, c = 24.914(6) A˚ and was well matched with the reported values. The volume of the unit cell is 1889.277 A$^{\circ 3}$ and is having four formula units in the unit cell.
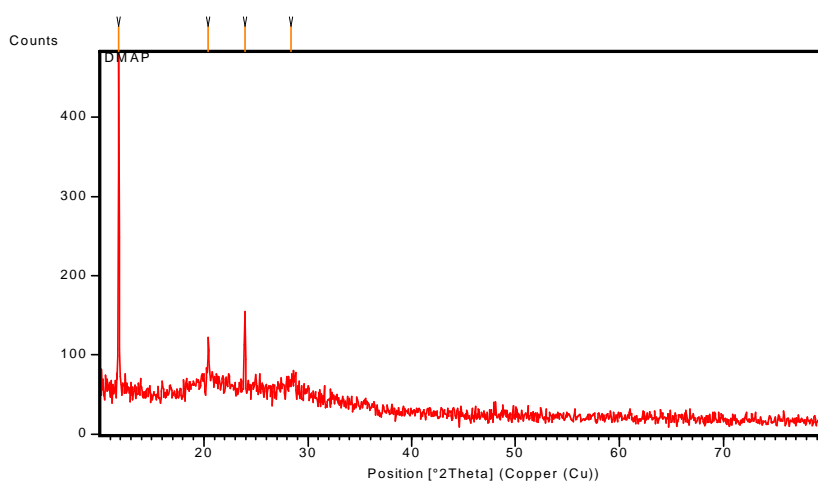
Fig(3.1) X – ray diffraction spectrum

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
11.809(2)	328(18)	0.092(8)	7.48797	100.00
20.43(2)	39(7)	0.22(7)	4.34440	12.02
23.922(6)	88(13)	0.11(3)	3.71682	26.92
28.37(7)	18(2)	1.7(2)	3.14372	5.34

Table (3.1) X – ray diffraction data

Fourier transform infrared and transmission

The mid Fourier transform infrared spectra of DMAPNP was recorded at room temperature in the region 400-4000 cm^{-1} using Perkin Elmer Fourier transform infrared Spectrophotometer, model SPECTRUM RX1, using KBr pellets containing a fine DMAPNP powder obtained from the grown single crystals, equipped with LiTaO$_3$ detector, KBr beam splitter, He–Ne Laser source and boxcar atomization used for 250 averaged interferogrammes collected for both the sample and the background. Strong and broad vibrational bands observed around 3088, 1602, 1486, 1331 and 1298 cm^{-1} confirmed the presence of functional groups N-H, C-N, O-H, NO$_2$ and C-H respectively. The spectrum of DMAPNP is shown below and values are tabulated.
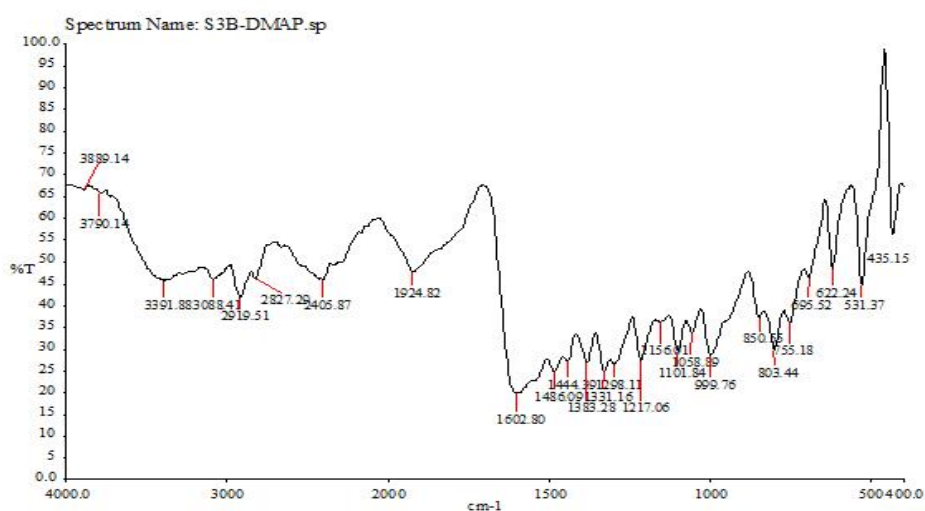

Fig (3. 2) FT-IR spectrum of DMAPNP

Assignments from FT-IR

Wave number(cm$^{-1)}$	Assignment
3088	(N-H)
1602	(C-N)
1486	$_{as}$(O-H)plane
1331	$_s$(NO$_{2)}$
1298	(C-H)plane
1101	(ring stretch)
999	(ring stretch)

Table (3.2)

UV–Vis studies

For optical device applications, the transparency in the near IR region is significant rather than the visible region because, 1.3 lm and 1.5 lm wavelengths are used in optical telecommunication systems. The absorption spectrum for the title crystal was recorded using a Varian Cary 5E UV–Vis–NIR spectrophotometer in the region 200–2000 nm (NishaSanthaKumari & Kalainathan 2009). The UV–Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron in the r and p orbital from ground state to higher energy state (Gunasekaran & Ponnusamy 2006, KrishanLal & Bhagavannarayana 1989).

The UV–Vis–NIR absorption spectrum of DMAPNP is shown in Fig (3.3). The absorption in this region is due to overtones of some fundamental vibrations of nitro group in 4-nitro phenol. The Optical UV-Vis absorption spectrum shows that the absorption band is found at 400 nm and there is less absorption band between 420 nm and 1400 nm. Hence the crystal is expected to be transparent to all UV-Vis radiation in between these two wavelengths.
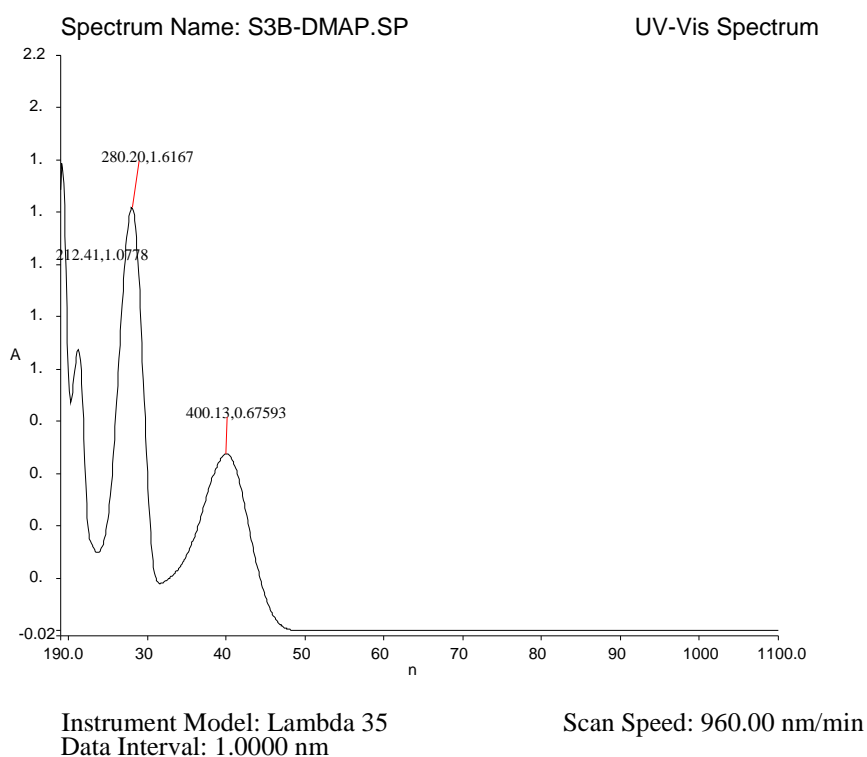
Fig (3.3) Absorption UV spectrum

Mechanical Studies of Dmapnp

Mechanical studies were taken by Vickers test. The mechanical studies data was given below in tabulated form

LOAD:25g

S.NO	L1	L2	HV
1	32.07	35.31	40.8
2	32.22	35.43	40.5

LOAD:50g

S.NO	L1	L2	HV
1	40.70	42.91	53.15
2	40.80	42.62	53.12

LOAD:100g

S.NO	L1	L2	HV
1	50.10	54.24	68.1
2	50.88	54.77	68.9

Variation of Load *vs* HV

LOAD P (gm)	HV(kg/nm$^{3)}$)
25	40.65
50	53.13
100	68.5

From the above datasthe graph is drawn between load vs HV and is shown in fig (3.4).When load increases HV increases.
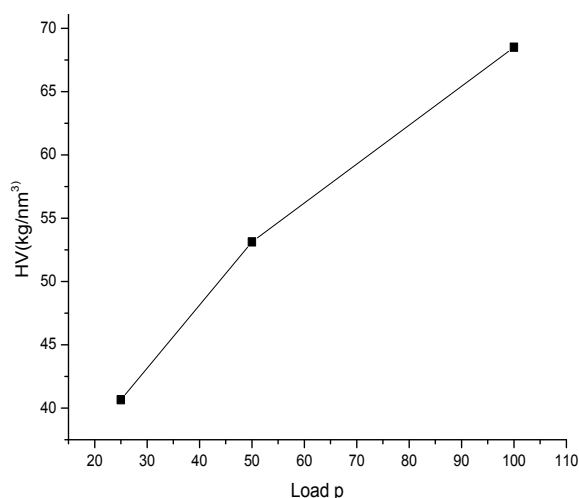
Fig (3.4) Variation of Load *vs* HV

Conclusion

DMAPNP crystals are grown by the slow evaporation solution growth technique at 30°C using a constant temperature bath.Pale yellow crystals have been obtained over a time span of 10-15 days. The structural properties were studied by X-ray diffraction analysis and Fourier Transform Infrared Spectroscopy and its optical studies were analyzed by UV - Vis spectral analysis. Mechanical studies were taken by Vickers test.

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