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ORIGINAL ARTICLE **OPEN ACCESS**

Dielectric, Transmittance properties of the organic material 2-methyl-5-nitroaniline

V. Bhakyajothi[1*], Celestina[1], V.S.Sangeetha[1] and Saurabh Srivastava[2]
1.Department Of Chemistry, Dhanalakshmi Srinivasan College of Arts and Science for Women(A), Perambalur, India.
2.Reader, Babu Banarasi Das University, Lucknow, U.P., INDIA)
Email: chemjothy@gmail.com

ABSTRACT
2-methyl-5-nitroaniline (2M5NA), an organic substance, was produced as a single crystal using a slow evaporation process at ambient temperature. The hyper saturation of the liquids is confirmed by the solubility curve. Within a few weeks, good single crystals were formed. With the help of a single crystal X-ray diffraction technique, the unit cell characteristics, space group, density, and volume of 2M5NA were identified. The crystal structure was discovered to be a monoclinic system. The range of good transparency, from 200 nm to 1100 nm, can be seen in the UV-Vis-near-IR transmittance spectrum. FT-IR spectroscopy was used to detect the presence of functional groups and vibrational modes. At all temperatures, the relationship between frequency and the dielectric constant and loss of as-grown crystals is inverse.
Keywords: *Organic Single Crystal; Solution Growth; Single Crystal X-Ray Diffraction; Thermal properties; Non-linear optical material.*

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INTRODUCTION

In comparison to inorganic crystals, organic crystals have relatively weak intermolecular bonds and are more difficult to form into big, high-quality crystals[1-4]. the solid framework on which modern technology is built. Electronic, photonic, and fibre optic industries all depend on crystals for their components, including semiconductors, superconductors, non-linear optics, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, piezoelectric materials, electro-optic materials, acousto-optic materials, photosensitive materials, refractory materials of various grades, and crystalline films for microelectronics and There have been numerous studies on nonlinear optics employing derivatives of aniline. The derivative of aniline[5-9] is 2-methyl-5-nitro aniline (2M5NA), which contains both nitro and methyl groups. In the manufacture of colours, antioxidants, pharmaceuticals, fuels, gum inhibitors, poultry medications, and rust inhibitors, this is frequently utilised as an intermediate. Strong hydrogen bonds form when a polarizable hydrogen atom interacts with a partially negatively charged, less polarizable oxygen atom and forms a covalent link with an electron-withdrawing donor nitrogen atom, which also increases the polarizability of the molecule. These kinds of compounds can be readily crystallised in bulk utilising inexpensive organic solvents under ambient conditions.
The goal of this work, to investigate the single-crystal growth and characterization pure 2-methyl-5-nitro aniline (2M5NA),the grown crystals were characterized by FTIR, NMR, UV- visible-NIR, Bandgap energy

MATERIAL AND METHODS

Crystal structures of all the grown crystals were arrived at by single crystal XRD analysis carried out using a Bruker×8 k diffractometer with Mo Ka (λ=0.177 Å) radiation. Diffraction data was collected at room temperature to identify the structure, space group and volume of the unit cell and to estimate the lattice parameters. The ^1H NMR spectra were recorded on a BRUKER 400 MHz NMR spectrometer using DMSO as solvent. The room temperature Fourier transform infrared spectra of 2M5NA were recorded in the range 400-4000 cm $^{-1}$ at a resolution of ±5 cm^{-1} using a BRUKER spectrophotometer equipped with a $LiTaO_3$ detector, a KBr beam splitter, a He-Ne laser source and a boxcar atomization used for 250 averaged interferograms collected for both the sample and the background.

RESULTS AND DISCUSSION

Solubility and Crystal growth

To promote crystal formation, the 2-methyl-5-nitro aniline (2M5NA) single crystals were slowly evaporated at room temperature. 2M5NA (DMSO as solvent) (DMSO as solvent) Fig.1 displays images of the 2M5NA single crystals while they were being formed. Commercially, 2-methyl-5-nitro aniline (Aldrich) was offered. This is insoluble in water but soluble in organic solvents like DMSO and CHCl3, as well as methanol, ethanol, acetone, and acetonitrile. This chemical had a very high solubility in DMSO, which increased the viscosity of the solution.[4,5,6]

At room temperature and using DMSO as a solvent, single crystals were produced in a beaker using the slow evaporation solution growth approach. The chemical was produced as a saturated solution in pure DMSO, and any undissolved contaminants were filtered out. The tiny crystal was nucleated within one week. The crystal with the dimension 0.20 x 0.15 x 0.10 mm^3 was orange in color respectively. The laboratory grown crystals of 2M5NA is shown in Figure 1.

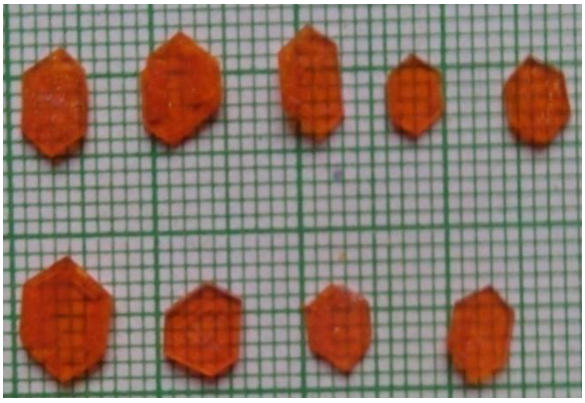

Fig.1 Single crystal of 2M5NA

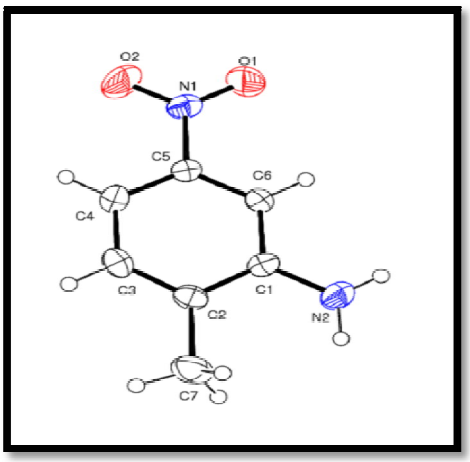

Fig.2.Molecular structure of 2M5NA

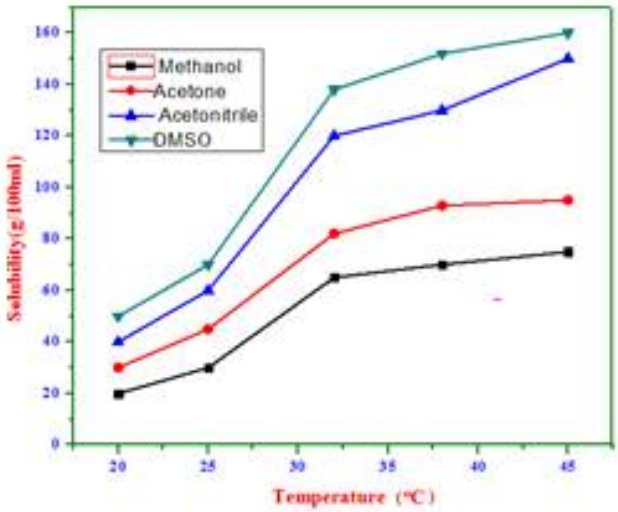

Fig.3. Various Solubility nature of 2M5NA

Single crystal XRD analysis:

Using DMSO as the solvent, single crystals of the 2M5NA crystal were produced. The SHELXL programme was used to solve the crystal structures using the direct method and improve them using the complete matrix least-square methodology. Figure 2M5NA depicts the ORTEP (Oak Ridge Thermal Ellipsoid Plot) sketch. 2. The unit cell is projected down the b-axis to depict the molecules with atom numbering. The 2M5NA crystal belongs to monoclinic system and the estimated lattice parameters are a = 9.57240(10) Å, b = 5.66880(10) Å, c = 13.5802(2) Å, α= 90°, β= 92.767(2)°, γ = 90°. and V =736 $Å^3$. The observed crystallographic data of the single crystals of 2M5NA are given in Table 1. The N-C bond distance in 2M5NA are [C(1)-N(2)] 1.369(2) Å, [C(1)-C(6)] 1.396(2) Å, C(3)-H(3) 0.9300 Å , [N(1)-O(2)] 1.213(2) Å, [N(2)-H(2B)]0.871(15) Å, [N(2)-C(1)-C(2)] 118.99(15) Å, [C(6)-C(1)-C(2)] 121.11(16) Å, [C(6)-C(5)-

C(4)] 123.03° (15), [O(2)-N(1)-O(1)] 122.05° (16), [C(1)-N(2)-H(2B)] 120.7 ° (15), [C(2)-C(7)-H(7A)] 109.5° respectively. The shorter C-C bond distance in 2M5NA indicate high rotation barrier. The monoclinic system with space group $P2_1/n$ and the 'c' parameter is larger compared to'a' and 'b' parameters possibly due to anisotropic thermal expansion, since methyl group substitution in phenyl ring leads to lower rotation barrier.[5,6,7]

Table 1. Crystal data and structure refinement for 2M5NA.

Crystallographic data	2M5NA
Empirical formula	C7 H8 N2 O2
Formula weight	152.15
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions a = 9.57240(10) Å b = 5.66880(10) Å c = 13.5802(2) Å	 α = 90°. β = 92.767(2)°. γ = 90°.
Volume	736.057(19) $Å^3$
Z	4
Density (calculated)	1.373 Mg/m^3
Absorption coefficient	0.103 mm^{-1}
F(000)	320
Crystal size	0.200 x 0.150 x 0.100 mm^3
Theta range for data collection	4.263 to 25.999°.
Index ranges	-11<=h<=11, -6<=k<=6, -16<=l<=16
Reflections collected	11120
Independent reflections	1421 [R(int) = 0.0307]
Completeness to theta = 25.242°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7423 and 0.6821
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1421 / 3 / 109
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1053
R indices (all data)	R1 = 0.0630, wR2 = 0.1234
Extinction coefficient Largest diff. peak and hole	n/a 0.208 and -0.174 $e.Å^{-3}$

FTIR spectral analysis:

Fourier transform infrared analysis of 2-methyl-5-nitro aniline compound carried out using KBr pellet technique in the wave length between 4000 and 400 cm^{-1} and the recorded IR spectra are shown in Fig. The wave-numbers of the peaks and their assignment are given in Table 2.[10,11,12].

Table 2. Frequencies of the fundamental vibrations of 2M5NA.

Assignments	**Wavenumbers cm^{-1}**	
	experimental	**observed**
N-H (str) 1° amine	3300-3500	3391
C-H (str)	3100	3083
C=C in a aromatic ring	1650	1626
NO_2 (str) symmetric –(aromatic)	1355	1340
NO2 (str) asymmeric	1550	1503
C-C str	1200	1286
C-N str	1350	1340
C-H out of plane (oop)	720-667	733

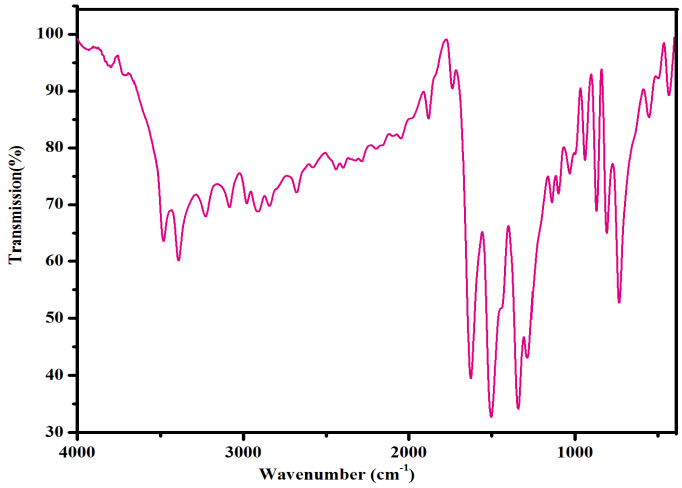

Fig.4. FT-IR spectra of 2M5NA

UV-visible-NIR spectral studies:

The optical transmission were recorded from UV-Vis- IR in the wavelength range of 200-1100 nm^{-1}. The recorded the optical transmission spectrum of grown crystal of 2M5NA is shown in Fig 4.

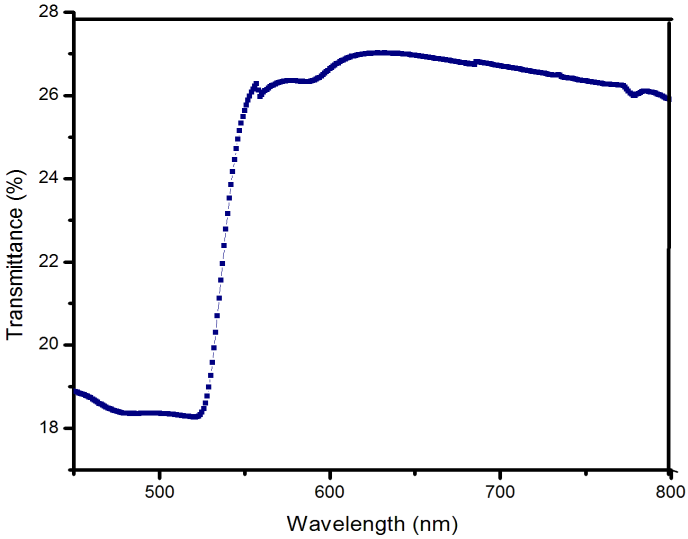

Fig5. UV-Vis-NIR Spectra of 2M5NA

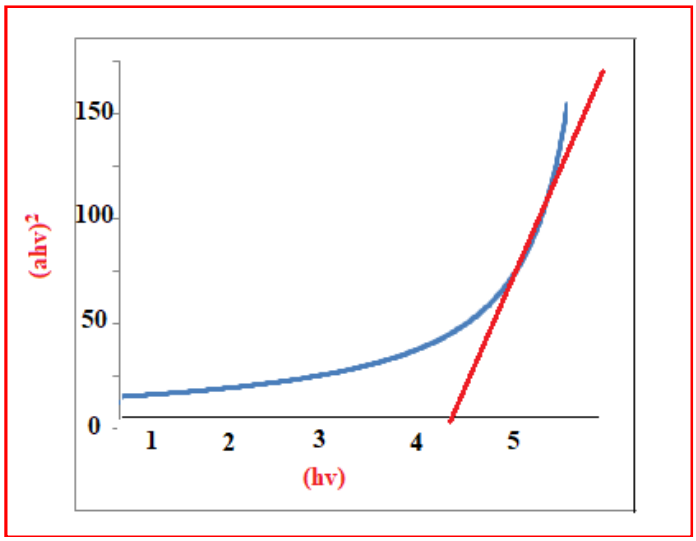

Fig.6 Photon energy versus $(\alpha hv)^2$ of 2M5NA

The 2M5NA crystal's lower cutoff wavelength was around 526.65. As a result, this crystal's extensive transparency range in the visible region above 526.65 nm and in the entire near infrared region makes it appropriate for optical applications. Figure.5 demonstrates that the band gaps are 4.58 eV, respectively. [13,14,15] Due to the material's high transmittance in the visible region, optoelectronic applications may be possible. The spectral information mentioned above made it abundantly evident that 2M5NA crystal was an extremely transparent crystal. Electron withdrawing group methoxy increases the double bond character by redistributing the π electrons in a more highly shared arrangement. This will increase the bond force constant and it may be resulting in a varying transparency of compound 2M5NA

Dielectric Studies

The electrical properties of a material medium as a function of temperature and frequency can be determined using the dielectric studies on significant characterisation. It was demonstrated how the as-grown 2M5NA single crystals' dielectric constant varied with frequency and temperature. The graphic shows that for all temperatures, the dielectric constant and dielectric loss decrease with increasing frequency. The contribution of four polarisations, including space charge, orientation, electronic, and ionic polarisation, may be responsible for the high dielectric constant of 2M5NA single crystals at low frequencies, while the gradual loss of significance of these polarisations may be the cause of its low value at higher frequencies.

In the graphs of 2M5NA single crystals, the dielectric constant value was shown to rise as the temperature rose. Space charge polarisation is the cause of the high value of the dielectric constant at low frequency. The manufacturing of materials for photonic, electro-optic, and NLO applications must take into account the low dielectric constant at higher frequencies. [17] High frequencies are reported to have low values for dielectric loss. For 2M5NA single crystals, the behaviour of low value dielectric loss with high frequency shows that the crystal has improved optical quality with lower defect density.[18,19]

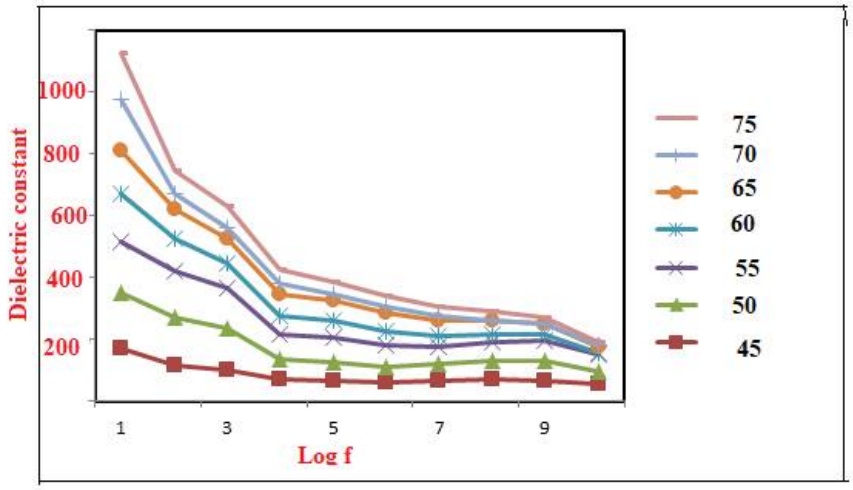

Fig7.Plot of dielectric constant versus frequency for 2M5NA

CONCLUSION

Single crystals of these molecules, 2-methyl-5-nitro aniline, could be produced from DMSO solvent using a slow evaporation process at room temperature. In the monoclinic system (P21/n), 2M5NA crystallises. FT-IR spectroscopy investigation verified the existence of several functional groups. The 526.65 nm wavelength of the grown crystal's optical transmission spectrum, which is a 2M5NA crystal characteristic. And band gap energy is 4.58Ev. The dielectric studies confirm to the, temperature rises cause an increase in the formed crystals' dielectric constant.

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