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Crystal Growth of Organic Material 2-Methyl-5-Nitroaniline by Slow Evaporation Technique

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Abstract
Single crystal of 2-methyl-5-nitroaniline (2M5NA), an organic material have been grown slow evaporation method at room temperature form the DMSO solvent. Good quality single crystals were grown within weeks. The unit cell parameters, space group, density and volume of 2M5NA were determined using single crystal X-ray diffraction technique and the crystal system is found a monoclinic system. From the UV-Vis-near IR transmittance spectrum, the good transparency is revealed from 200 nm to 1100 nm. The presence of functional groups and modes of vibrations were identified by FT-IF spectroscopy. Proton-NMR spectral studies revealed its structural identification. The thermal stability of the crystal was established by thermo gravimetric/differential thermal (TG/DT) analysis. The relative second harmonic generation (SHG) efficiency was measured by Kurtz-Perry powder technique is found to be better than that of KDP.

Keywords
Organic Single Crystal, Solution Growth, Single Crystal X-Ray Diffraction, Thermal properties, Non-linear optical material.

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INTRODUCTION:
Organic crystals have relatively weak intermolecular bindings and it is difficultly to grow high quality large size crystals compared with inorganic crystals [1-4]. The strong foundation of the modern technology without crystals, there would be no electronic industry, no photonic industry, no fibber optic communications, which depend on materials/crystals such as semiconductors, superconductors, non-linear optics, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Many researchers have reported on the Non linear optics using derivatives of aniline.

2-methyl-5-nitro aniline (2M5NA) is the derivative of aniline [5-9], and its containing nitro group and methyl group. This is commonly used as an intermediate in the synthesis of dyes, antioxidants, pharmaceuticals, gasoline, gum inhibitors, poultry medicines, and as a corrosion inhibitor. Strong hydrogen bonds occur due to the polarizable hydrogen atom covalently bonded to an electron-withdrawing donor nitrogen atom and interact with a partially negatively charged and comparatively less polarizable acceptor oxygen atom, which will also increase the molecular hyper polarizability. These types of compounds can easily be

grown into bulk crystals using cheap organic solvents at ambient conditions. The goal of this work, to investigate the single-crystal growth and characterization of 2M5NA compound, the grown crystals were characterized by FT-IR, ^{1}H-NMR, UV- Vis-NIR, TGA-DTA and single crystal X-ray diffraction studies.

SOLUBILITY AND CRYSTAL GROWTH:

2-methyl-5-nitro aniline (2M5NA) was commercially available. This is insoluble in water but soluble in methanol, ethanol, acetone, acetonitrile and other organic solvents such as DMSO and $CHCl_3$. The solubility in DMSO of this compound is very high and made the solution more viscous. The single-crystals of 2-methyl-5-nitro aniline (2M5NA), were subjected to slow evaporation at ambient temperature to allow crystal growth. 2M5NA (DMSO as solvent) Photographs of the as-grown single crystals of 2M5NA are shown in Fig.1.

Single crystals were grown in a beaker by slow evaporation solution growth technique at ambient temperature using DMSO as a solvent. The saturated solution of the compound in pure DMSO was prepared and if any undissolved impurities is removed by filtration. The beaker was covered with aluminum foil paper and allowed for slow evaporation. The tiny crystals were nucleated within weeks; they were allowed to grow to the larger dimension and then harvested. The crystal with the dimension 0.20 x 0.15 x 0.10 mm^3 was orange in colour respectively.

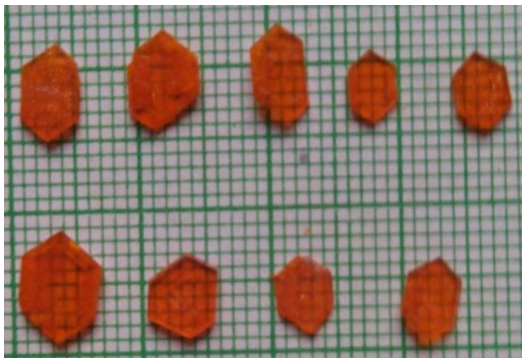

Figure 1 Single crystal of 2M5NA

RESULTS AND DISCUSSION:

Single crystal XRD analysis

A single crystal of 2M5NA crystal was obtained using DMSO as solvent. The crystal structures were solved by the direct method and refined by full matrix least-square technique using the SHELXL program. ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing 2M5NA are shown in Fig. 2.

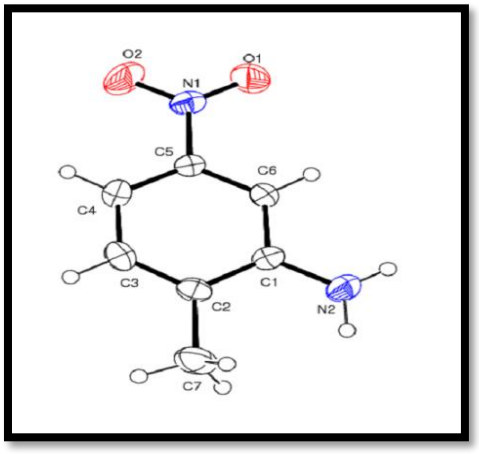

Figure 2. ORTEP structure of 2M5NA

The molecules with atom numbering are shown with the unit cell projected down the b-axis. 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 Å3. The observed crystallographic data of the single crystals of 2M5NA are given in Table 1.

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	α = 90°.
b = 5.66880(10) Å	β = 92.767(2) °.
c = 13.5802(2) Å	γ = 90°.
Volume	736.057(19) Å3
Z	4
Density (calculated)	1.373Mg/m3
Absorption coefficient	0.103 mm-1
F(000)	320
Crystal size	0.200 x 0.150 x 0.100 mm3
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 F2
Data / restraints / parameters	1421 / 3 / 109
Goodness-of-fit on F2	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	n/a
Largest diff. peak and hole	0.208 and -0.174 e.Å-3

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. **FTIR spectral analysis:**

Fourier transform infrared analysis of 2-methyl-5-nitro aniline (2M5NA) 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. 3.

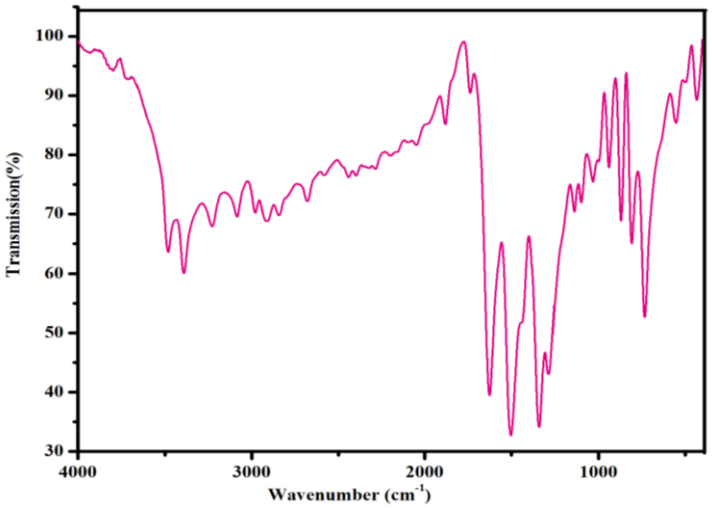

Figure 3 FT-IR spectrum of 2M5NA

The wave-numbers of the peaks and their assignment are given in Table 2. The band observed at 3391 cm^{-1} is due to the associated N-H stretching vibrations of 2-methyl 5-nitro aniline moiety. The absorption bands at 3083 correspond to the aromatic C-H stretching vibrations respectively. The C-H asymmetric and corresponding symmetric stretching vibrations of the methyl group are observed at 2914 and 2842 cm^{-1} respectively. The characteristic NO_2 asymmetric and symmetric stretching vibrations are observed at 1503 cm^{-1} and 1340cm^{-1} respectively. The aromatic C-C stretching vibrations are exhibited at 1286 cm^{-1}. The aromatic C=C stretching vibrations are exhibited at 1626 cm^{-1}. The C-H in-plane bending vibration and the C-H out of plane bending vibrations are observed at 869 cm^{-1} and 733 cm^{-1} respectively. The vibrational bands observed below 500 cm^{-1} are due to the skeletal vibrations [10,11].

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

Assignments	Wavenumbers cm^{-1}	
	experimental	observed
N-H (str) 1 amine	3391	3300-3500
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	720-667	733

UV-visible-NIR spectral studies:

The optical transmission was 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. The lower cutoff wavelength of the 2M5NA crystal was around 526.65. Hence, this crystal can be used for the suitable optical applications due to its wide transparency range in the part of visible region above 526.65 nm and in the entire near infrared region.

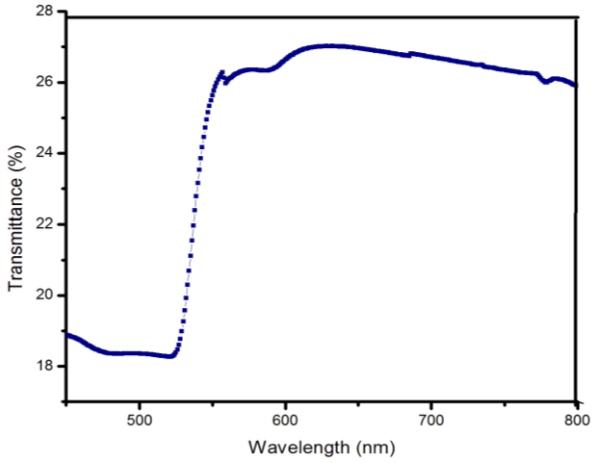

Figure 4. UV-Vis-NIR Spectra of 2M5NA

Proton NMR spectral analysis:

Nuclear magnetic resonance (NMR) spectral analysis is an important analytical technique used to determine the structures of organic compounds. Fig.5. shows that the proton NMR spectra of the molecule 2M5NA, exhibits a singlet 2.14 ppm (S, 3H, CH3) due to the presence of methyl group. The primary amine hydrogen (N-H) signal appeared at 3.37 ppm as a sharp singlet. Two doublet peaks were observed at 7.54 ppm (d, 2H, ArH) and 7.15 ppm (d, 2H, ArH) due to the presence of aromatic protons of phenyl ring. Doublet of doublets were observed at 7.28 & 7.30ppm (dd, 2H, ortho & meta) in aromatic compounds however, significant spilliting does not coming from ortho proton coupled to each other but also come from meta proton (even para) due to the conjugated π bonds.

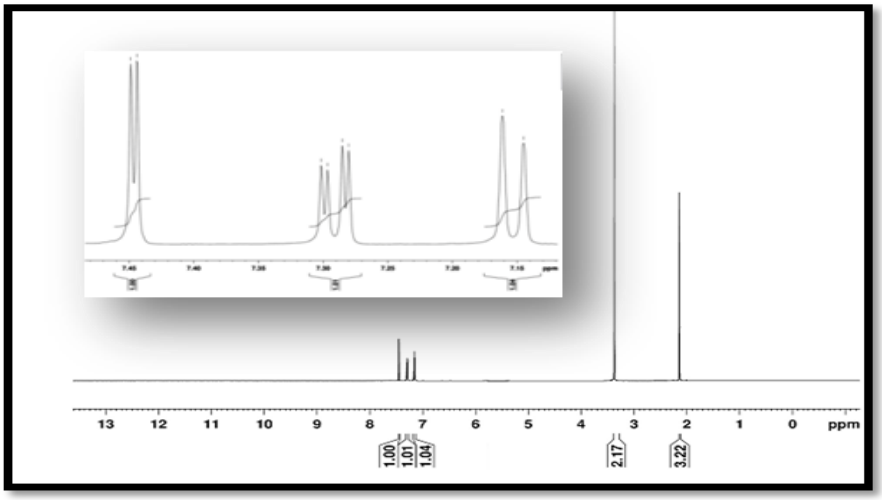

Figure 5 Proton NMR spectra of 2M5NA

Thermal analysis:

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves 2M5NA are presented in Fig.6. The thermal analysis of grown crystal was carried out between 35˚C and 250˚C at a heating rate 10˚C min^{-1} in nitrogen ambient using Perkin Elmer Diamond TG/DTA instrument. The thermal analyses are used to find out the weight loss (TGA) and melting point (DTA) of the grown 2M5NA single crystal. In differential thermal analysis, the material undergoes an irreversible sharp endothermic transition at 108 ^{0}C, which corresponds to its melting point. Below the melting point there is no endothermic or exothermic peak, which illustrates the absence of isothermic transition in grown single crystal. The material dissociates after melting. The TGA curve indicates that the sample is stable and there is no phase transition upto 108^{0}C. The single crystal is strong indication of the purity of the crystal as well as its perfection.

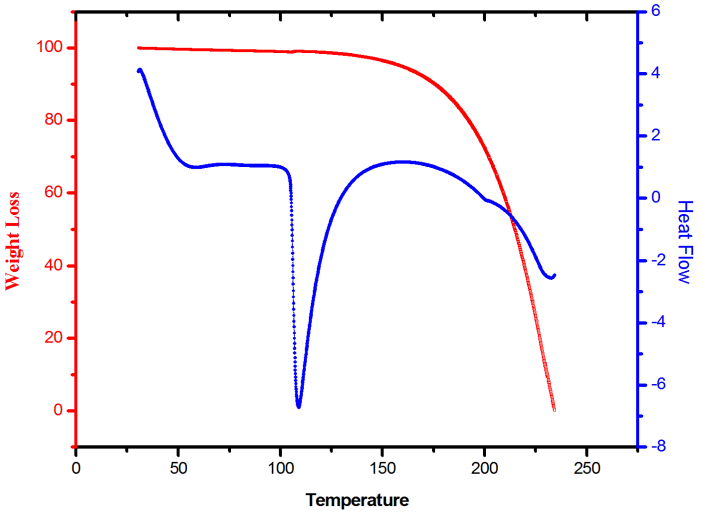

Figure 6 TGA-DTA curves of 2M5NA

CONCLUSION:

Organic materials, 2-methyl-5-nitro aniline was giving good quality single crystals of these compounds could be grown from DMSO solvent by slow evaporation technique at ambient temperature. 2M5NA crystallize in the monoclinic system ($P2_1/n$). The presence of various functional group confirmed by FT-IR spectroscopic analysis. The optical transmission spectrum of grown crystal was characteristic of 2M5NA crystal occurs at 526.65 nm. Proton NMR study was confirmed by molecular structure of the crystal. The sharp endothermic peak indicates high quality of crystal formed as well as transparent. This crystal is thermally stable up to 381 K.

REFERENCES:

[1] J.Y. Courtois, Nonlinear Optics, Collection of the French Society of Optics (SFO), 2002.

[2] P. Prabukanthan , R. Lakshmi, G. Harichandran, C. Sudarsana Kumar, Syntheis, structural, optical and thermal properties of N-methyl-N-aryl benzamide organic single crystals grown by a slow evaporation technique, J. Mol. Str. 1156: 62-73, (2018).

[3] P. Gunter, Nonlinear Optical Effects and Materials, first ed., Springer-Verlag, Berlin Heidelberg, Germany, 2000.

[4] J. Zyss, Molecular nonlinear optics: Materials, Physics, and devices, first ed., Academic Press, New York, 1993.

[5] C.P. Smyth, Dielectric Behavior and Structure (McGraw-Hill, New York, (1965), 132-140

[6] R. Lakshmi and P. Prabukanthan, Growth and characterization of 2-amino-3- nitropyridine organic single crystals grown by slow evaporation technique, World J. Pharm. Res. 7(3):1129-1137 (2018).

[7] R. Lakshmi and P. Prabukanthan, Studies on the Growth and Characterization of N-methyl-4-nitroaniline Organic Single Crystal Grown by Slow Evaporation Technique, Inter. J. Sci. Res. 6(5): 864-869 (2017).

[8] R. Lakshmi and P. Prabukanthan, Crystal growth, dielectric and thermal studies on 4-methyl-4-nitroaniline:isophthalic acid molecular adduct crystals, Euro. J. Eng. Res. Sci. 2(3): 7-11, (2017).

[9] Radhakrishnan Lakshmi, Peethambaram Prabukanthan, Gurusamy Harichandran, and C. Sudarsana Kumar, Synthesis, Crystal Growth, and Optical Characterization of a Novel Nonlinear Optical Organic Material: N,N-Diarylbenzamide. Cryst. Res. Technol. 54: 1700146(2019).

[10] Donald.L.Pavia, Gary M.Lampman, George S. Kriz, Third Edition, “Introduction to Spectroscopy” 2008.

[11] R. Silverstein, G.C. Bassler, T.C. Morrill, John Wiley & Sons, 1981.