



PREPARATION, SPECTRAL CHARACTERISATION BAND GAP ENERGY OF 2-NITROBENZYLIDENE OF TOLUIDINE

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ABSTRACT

An organic crystals of 2-Nitrobenzylidene of toluidine has been successfully grown from aqueous solution by slow evaporation method at room temperature from the solvent methanol. The functional groups have been confirmed using Fourier transform infrared (FTIR) analysis. The placement of protons was identified from ¹³C and ¹H Nuclear Magnetic Resonance Spectroscopy (NMR) spectral analysis. UV-visible spectral analysis, Band gap energy for dielectric property of the crystals also determined.

KEYWORDS: Crystal growth, Organic crystals, slow evaporation technique, Spectral characterization and Band gap energy.

INTRODUCTION

Crystals

Crystal growth is a vital and fundamental part of material science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other millions and millions of applications.

It is evident that study of crystals is bound to throw light on the intrinsic nature of the solid state and hence the introduction of a new branch in physical chemistry known as chemical crystallography or crystal chemistry.

A crystal is defined as homogeneous (time., of uniform chemical composition) portion of solid substance, having a very regular structure i.e., bonded by plane faces, making definite angles with each other, resulting in a typical and distinctive symmetry and geometric form.

Behind every new solid-state device there stands a single crystal and the explosion in solid-state device development, which followed the invention of the transistor in 1948. This means that many new crystals had to be grown and fabricated in order to assess their device properties. The ever-increasing application of semiconductor-based electronics creates an enormous demand for high quality semi conducting, ferro electric, piezoelectric, oxide single crystals.

Crystallization

Crystallization is a process of crystal growth where in solid particles are formed within a homogeneous phase. This process describes the separation and purification of solid products from solution.

The word "Crystal" originates from the Greek word which means coldness or ice. The father of crystal fabrication technology is a Verneuil with his flame fusion growth method he described in 1902.

REVIEW OF LITERATURE

Organic molecular materials have emerged as a new class of promising non linear materials because of their superior qualities over inorganic materials^[1] some of the advantages of the crystalline organic materials are large damage thresholds in laser beam and large birefringence. Organic materials are in increasing demand, as they are better candidates for NLO and electro-optic device applications than those of inorganic materials. Although organic materials have been known for their applications in semi-conductors,^[2] Superconductors^[3] & NLO devices,^[4,5] Very little attention has been focused on the dielectric and polar properties of pure and binary organic materials future photonics technology is dependent on the design, synthesis & characterization of materials exhibiting, in particular, second-order NLO properties.^[6]

Growth and electrical properties of high purity organic molecular crystals like anthracene, naphthalene, perylene, benzophenone were extensively studied.^[7] The findings demonstrate that it is reasonably realistic to assume that molecular materials may play a role in future electronics not only in the form of polymeric case and insulating plastics but also in electrically active device structures.

The very early part of materials research on organic crystals starts with aromatic hydrocarbons, which have been, through not extensively, need for scintillation counting. The growth of organic crystals starts with synthesis and purification of the starting materials. Detailed account on the preparation of aromatic hydrocarbon stating materials in particulars benzophenone, anthracene has been detailed by many others.^[8,9,10]

MATERIAL AND METHODS

Material

2-Nitro benzaldehyde, toluidines were procured and used without further purification. All organic solvents were purchased from Merck and dried before use, IR spectra in the range $400\text{--}4000\text{cm}^{-1}$ were obtained on a Perkin Elmer spectrum version 10.4.2 FTIR spectrophotometer using KBr pelleting technique.

Methods

Preparation and characterization of 2-nitrobenzylidene toluidine

In order to modify the NLO property of Toluidine— a condensation product of Toluidine with 2-Nitrobenzaldehyde was prepared by adopting standard procedure. The reagents used were analar grade (E-Merck company). About 15.1 grams of analar 2-Nitrobenzaldehyde was suspended in about 10ml of methanol. To this 0.5ml of concentrated sulphuric acid was added continuously. The warm solution was filtered and a solution of 12.12 grams of Toluidine was added 10ml of methanol. The solid derivative was separated and washed with aqueous methanol and dried. The melting point of the derivative was determined and compared with its theoretical melting point (127°C) and found to be in good agreement, which shows the purity of the sample. This derivative was subjected to various characterization studies viz UV, FTIR, ^1H NMR, ^{13}C NMR and BAND GAP ENERGY. Spectral studies show the presence of functional groups.

2-Nitrobenzylidene of toluidine

To obtain good quality crystal saturated solutions of Toluidine and 2-Nitrobenzylidene of toluidine were prepared in CHCl_3 . These two saturated solutions were mixed thoroughly and allowed for slow evaporation at room temperature. Good transparent orange colored mixed crystals of 2-Nitrobenzaldehyde of Toluidine and Toluidine was obtained in one to two days. These crystals were harvested and subjected to various characterization studies.

Photo Graph



Recrystallized 2-nitrobenzylidene of toluidine

Crystal was allowed to grow for about three to four weeks at room temperature without disturbing the containing solution and was harvested.

RESULT AND DISCUSSION

These crystals were harvested and subjected to characterization studies viz. FT-IR spectral studies shows the functional groups present in the mixed crystal, UV studies shows the types of electronic transition present in the crystal. ^1H nucleus is by far the most commonly studied by NMR spectroscopy because of its high natural abundance and the fact that it is invariably present in the majority of organic compounds and ^{13}C is also an important nucleus because carbon forms the backbone of all organic compounds and valuable structural information can be derived by ^{13}C NMR spectroscopy.

Spectral characterization

Characterization is a tool for the measurement of physical and chemical properties of materials. Characterization provides a basis for understanding and improving the characteristics of material for specific applications. Characterization of a material essentially depends on the characterization and experimental techniques involved with tools of sophisticated technology.

**IR Study

The IR Spectra showed characteristic bands at 1629cm^{-1} for compound 1, 1566cm^{-1} for compound

FT-IR spectral analysis

Infrared Spectrum is an important record, which provides more information about the structure of the compound. In this technique almost all functional group in a molecule absorb characteristically within a definite range of frequency,

The FTIR Spectral analysis of 2-Nitrobenzylidene of toluidine was carried out of PERKINELMER SPECTRUM Version 10.4.2 FTIR Spectrophotometer using the KBr Pelleting technique. The FTIR spectrum Scanned between 400 and 4000cm^{-1} which is shown in figure 5.5. The observed characteristic correlated with the standard and theoretical peak values, The N-H Stretching found at 1568cm^{-1} . The C-H group Stretching is assigned to 3017cm^{-1} . The C=N stretching is observed at 1568cm^{-1} . The NO_2 asymmetric stretching is at

1516 cm^{-1} , The NO_2 symmetric stretching is found at 1361 cm^{-1} , The C-NH stretching Coupling between NH in plane bending and C-N stretching vibration is found at 1309 cm^{-1} . The variable strong peak in the frequency range 973-1192 cm^{-1} C-H in plane bending its phenyl ring. Absent of C=O because 1600 to 1725 no peaks.

Wave Number cm^{-1}	Assignment
3017	C-H Stretching Vibration its aromatic
2850	CH_3 Stretching
1566	C=N stretching
787	N-H Wagging and twisting

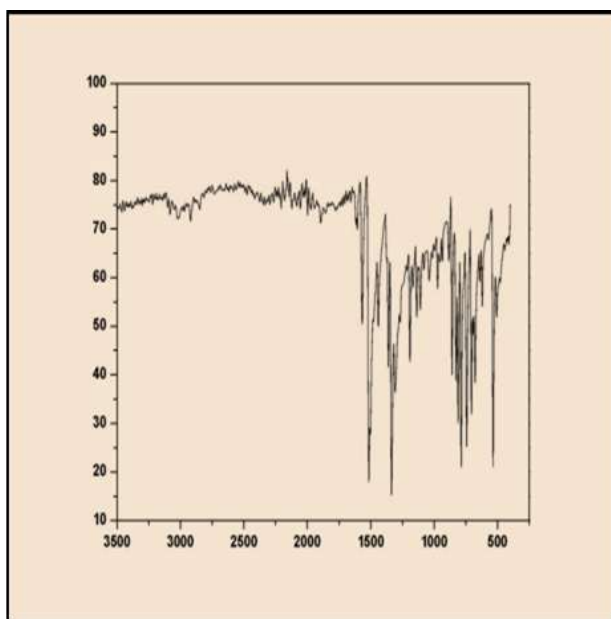


Figure FT-IR Spectrum of 2-Nitrobenzylidene of toluidine.

UV spectrum analysis

The UV spectrum provides information regarding the functional groups and transparency of the grown 2-Nitrobenzylidene of toluidine. The UV-Visible spectral analysis of 2-Nitrobenzylidene of toluidine was performed in JASCO UV VIS NIR, Model V-670 beam spectrophotometer.

**UV Study

The UV Spectra showed characteristic bands observed λ_{max} values are 256 nm.

The UV-VIS-NIR Spectrum of 2-Nitrobenzylidene of toluidine is shown in figure 5.6. The observed peaks in the UV absorbance spectrum of 2-Nitrobenzylidene of toluidine are assigned to the corresponding functional groups with reference to the standard values, The 2-Nitrobenzylidene of toluidine is coloured compound. The absorption is observed between 400 and 800 nm,

λ_{max} value nm	Transition
256	$\pi-\pi^*$
351	$n-\pi^*$

The observed λ_{max} values are 256 nm are due to $\pi-\pi^*$ transitions. $n-\pi^*$ transition observed at 351 nm.

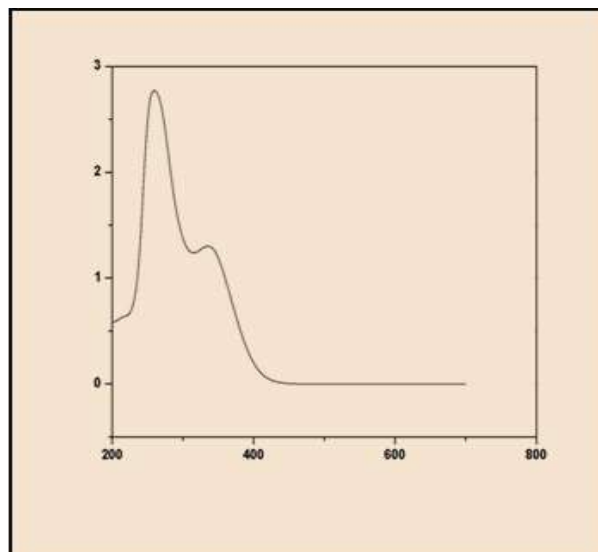


Figure-UV-visible spectrum of 2-nitrobenzylidene of toluidine

NMR Spectral Analysis

^1H NMR spectral analysis

The Nuclear Magnetic Resonance Spectral analysis is useful in the determination of the molecular structure based on the chemical environment of the magnetic nuclei such as ^1H , ^{13}C , ^{31}P etc., even at low concentrations. The ^1H NMR spectral analysis was carried out on the 2-Nitrobenzylidene of toluidine crystals in BRUKER 300 NMR spectrometer at 300 MHz using DMSO as solvent. The ^1H NMR spectra of 2-Nitrobenzylidene of toluidine is shown in figure 5.7.1. The ^1H NMR spectrum confirmed the presence of an aromatic system. There is a multiplet at $\delta=7.637$ ppm indicates the presence of aromatic protons. The NH_2 proton of hydrazide is observed at 8.085 ppm as singlet. The $-\text{NH}$ proton is observed at 2.390 ppm. The ^1H -NMR Spectrum of 2-Nitrobenzylidene of toluidine shows a signal observed at $\delta=8.085$ ppm corresponds to the NH_2 protons of hydrazide group. A singlet at $\delta=2.390$ ppm confirms the NH proton. The multiplet observed between 7.754 and 8.959 ppm confirms the presence of aromatic protons. The presence of a peak at $\delta=7.759$ ppm indicates the $\text{HC}=\text{N}$ protons. The peaks at $\delta=2.390$ ppm confirm the CH protons. The signal at $\delta=1.582$ ppm indicates the residual protons present in CDCl_3 solvent.

Spectrum	Signal at δ ppm	Group identification
^1H	7.637	Aromatic system
	8.085	The NH_2 proportion of hydrazide group
	7.759	$\text{HC}=\text{N}$ protons
	2.390	$-\text{CH}$ proton

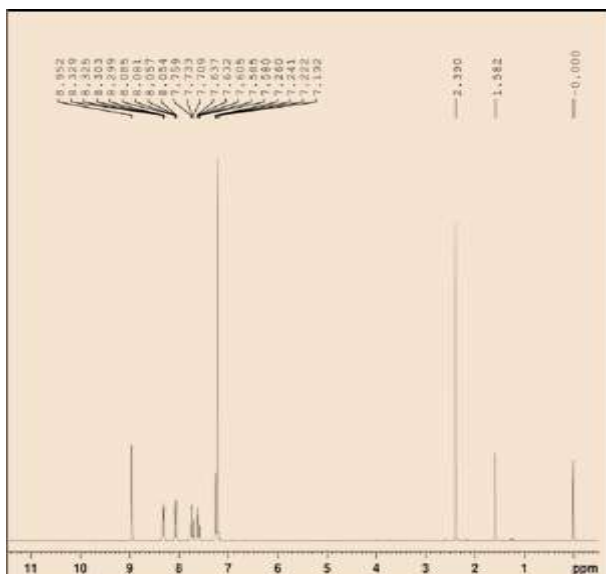
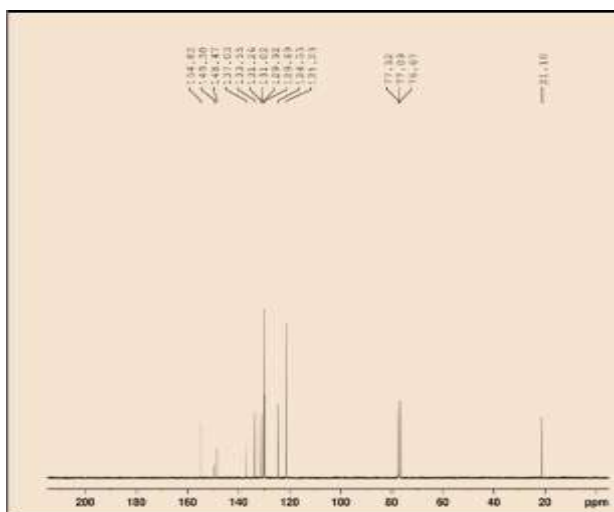


Figure 1 ^1H NMR Spectrum of 2-Nitrobenzylidene of toluidine.

^{13}C nmr Spectral Analysis

In the ^{13}C NMR spectral studies also used to determine the molecular structure of the compound. The ^{13}C NMR spectra of 2-Nitrobenzylidene of toluidine is shown in figure 3.7.2. The singlet observed at $\delta=129.29$ ppm shows the presence of aromatic carbon. The peak observed at $\delta=129.29$ ppm confirms the sp^2 hybridized carbon atom. The singlet at $\delta=77.52$ sp^2 hybridized carbon atom. The methoxy carbon proves the peak observed at $\delta=129.92$ ppm and $\delta=129.69$ ppm. The multiplet observed at $\delta=77.52, 77.09, 76.67$ ppm shows the presence of $\text{C}-\text{NO}_2$ singlet observed at $\delta=21.10$ ppm shows the presence of methyl group.



spectrum	Signal at δ ppm	Group identification
^{13}C	154.82, 149.38, 129.29, 124.23	Aromatic carbon
	77.52, 77.09, 76.67	$\text{C}-\text{NO}_2$
	131.02	$\text{HC}=\text{N}$ protons

Band gap energy determination

For the preparation of specimen the sample was left on a glass slide with tweezers. Then it was covered with another glass slide and taps was used on the both side of slide so that the sample remained fixed. For optical measurements, crystal of 2-Nitrobenzylidene of toluidine mixed the toluidine in CHCl_3 have been set in an UV – 1201 Spectrophotometer (Shimadzu) with the wavelength range 325nm – 1100nm.

The band gap 2-Nitrobenzylidene of toluidine was found to be 2.65 eV.

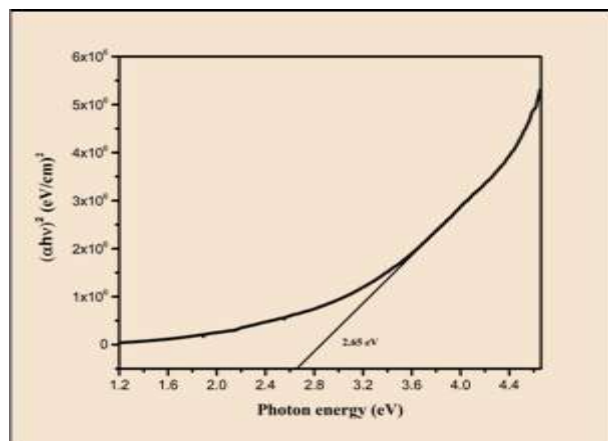


Figure 5.8: Band gap energy measurement of 2-Nitrobenzylidene of toluidine.

CONCLUSION

There are various reports available in the literature for the growth and characterization of 2-Nitro benzaldehyde of mixed with Toluidine using methanol as solvent and the study of band gap energy measurement and spectral analysis of 2- Nitro benzylidane of toluidine has been reported.

Suggestions for future work

The grown organic crystals can be used to fabricate opto-electronic and NLO applications. A detailed study on the determination of crystal structure can be made for the crystals reported in this investigation. It will explain the cause for variation of thermal stability, UV cut-off wavelength and SHG efficiency of the crystals. The effect of impurities with different percentage on the growth of these crystals can be carried out to study the change in their properties. Further possible derivatives of the crystals may be synthesized and investigated for the improvement on dielectric properties and more.

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