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

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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 were in solid particles are formed within 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 particulars, second-order NLO properties.[6]

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.
Growth and electrical properties of high purity organic molecular crystals like anthracene, naphthalene, perylene, benzophenone were extenssively 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 400-4000 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 10 ml of methanol. To this 0.5 ml of concentrated sulphuric acid was added continuously. The warm solution was filtered and a solution of 12.12 grams of Toluidine was added 10 ml of methanol. The solid derivative was separated and washed with aqueous methonal 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, H¹NMR, C¹³NMR 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 CHCl₃. These two saturated solutions were mixed thoroughly and allowed for slow evaporation at room temperature. Good transparent orangecolored 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.

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 ¹³C is also an important nucleus because carbon forms the backbone of all organic compounds and valuable structural information can be derived by ¹³C 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 Spectrashow characteristic bands at 1629 cm⁻¹ for compound 1, 1566 cm⁻¹ for compound 2

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 4000 cm⁻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 1568 cm⁻¹. The C-H group Stretching is assigned to 3017 cm⁻¹. The C≡N stretching is observed at 1568 cm⁻¹ The NO₂ asymmetric stretching is at
The observed $\lambda_{\text{max}}$ values are 256 nm are due to $\pi-\pi^*$ transitions. $n-\pi^*$ transition observed at 351 nm.

The UV absorption spectrum of 2-Nitrobenzylidene of toluidine shows two characteristic bands observed $\lambda_{\text{max}}$ values are 256 nm and peak at 351 nm.

<table>
<thead>
<tr>
<th>Wave Number $\text{cm}^{-1}$</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>3017</td>
<td>C-H Stretching Vibration its aromatic</td>
</tr>
<tr>
<td>2850</td>
<td>CH$_3$ Stretching</td>
</tr>
<tr>
<td>1566</td>
<td>C=N stretching</td>
</tr>
<tr>
<td>787</td>
<td>N-H Wagging and twisting</td>
</tr>
</tbody>
</table>

Figure UV-visible spectrum of 2-nitrobenzylidene of toluidine

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 $^1$H, $^{13}$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 300NMR spectrometer at 300 MHz using DMSO as solvent. The 1H NMR Spectra of 2-Nitrobenzylidene of toluidine shows signal observed at $\delta=7.637$ ppm indicates the presence of aromatic proton. The NH2 proton of hydrazide is observed at 8.085 ppm as singlet. The – NH proton is observed at 2.390 ppm. The 1H NMR Spectrum of 2-Nitrobenzylidene of toluidine shows the signal at $\delta=8.085$ ppm correspond to the NH2 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 peak at $\delta=7.759$ ppm indicates the HC=N protons. The peaks at $\delta=2.390$ ppm confirms the CH protons. The signal at $\delta=1.582$ ppm indicates the residual protons present in CDC13 solvent.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Signal at $\delta$ ppm</th>
<th>Group identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>7.637</td>
<td>Aromatic system</td>
</tr>
<tr>
<td></td>
<td>8.085</td>
<td>The NH2 proportion of hydra side group</td>
</tr>
<tr>
<td></td>
<td>7.759</td>
<td>HC=N protons</td>
</tr>
<tr>
<td></td>
<td>2.390</td>
<td>-CH proton</td>
</tr>
</tbody>
</table>

**UV Study**

The UV Spectrashowed characteristic bands observed $\lambda_{\text{max}}$ values are 256 nm.

The UV-VIS-NIR Spectrums of 2-Nitrobenzylidene of toluidine are 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 iscoloured compound. The absorption is observed between 400 and 800 nm.

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ value nm</th>
<th>Transition</th>
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<tbody>
<tr>
<td>256</td>
<td>$\pi-\pi^*$</td>
</tr>
<tr>
<td>351</td>
<td>$n-\pi^*$</td>
</tr>
</tbody>
</table>

Figure FT-IR Spectrum of 2-Nitrobenzylidene of toluidinie.
Figure 1H NMR Spectrum of 2-Nitrobenzylidene of toluidine.

\[^{13}\text{C} \textrm{nmr} \] Spectral Analysis

In the \(^{13}\text{C} \) NMR spectral studies also used to determine the molecular structure of the compound. The \(^{13}\text{C} \) 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. The multiplet observed at \( \delta = 77.52, 77.09, 76.67 \)ppm shows the presence of C-NO\(^2\) singlet observed at \( \delta = 21.10 \) ppm shows the presence of methyl group.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Signal at ( \delta )ppm</th>
<th>Group Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{13}\text{C} )</td>
<td>154.82, 129.29, 124.23</td>
<td>Aromatic carbon</td>
</tr>
<tr>
<td></td>
<td>77.52, 77.09, 76.67</td>
<td>C-NO(^2)</td>
</tr>
<tr>
<td></td>
<td>131.02</td>
<td>HC=N protons</td>
</tr>
</tbody>
</table>

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 benzylidene 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.

REFERENCES