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RESEARCH ARTICLE

GROWTH, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OFTHIOSEMICARBAZONE OF M-NITROBENZALDEHYDE.

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Abstract

Thiosemicarbazone of m-Nitrobenzaldehyde is an interesting organic crystal. It has been grown by slow evaporation solution growth technique (SESGT) using wood alcohol as solvent. The harvested crystals were purified by repeated recrystallization. The working groups of harvested crystals were examined by the Fourier Transform (FT-IR) spectral analysis. The UV-Visible Spectra are confirming the optical transparency. This is more helpful to use these crystals in electro optical applications. The harvested crystal Thiosemicarbazone of m-Nitrobenzaldehyde was characterized by proton nuclear magnetic resonance and of ^{13}C NMR spectra which show the molecular structure of the crystals. The TGA and DSC confirm the decay of the sample at 210oC. It further confirms the grown crystals Thiosemicarbazone of m-Nitrobenzaldehyde is thermally stable up to 210^{o}C. The second harmonic generation efficiency of the powdered Thiosemicarbazone of m-Nitrobenzaldehyde and was tested using Nd: YAG laser and it is found to be 5.6 times higher than that of urea.

Introduction:-

Thiosemicarbazone of m-Nitrobenzaldehyde is an organic crystal plays a significant function in application in optical communication and optical computing devices. In recent year, an intense research work has been carried out to identify a special variety of thermally stable optical material. Organic compounds are often determined by very weak Vander walls and hydrogen bonds and possess a high degree of delocalization. Hence, they are optically more nonlinear than inorganic crystals. The growth methods depend on organic crystal size, hardness, physical body, and large nonlinear optical susceptibilities compared to the inorganic crystals.The slow evaporation solution growth Technique (SESGT) is an important technique because large size, stability, optical crystals are being created by this technique [1-6]. The harvested crystals were characterized by FT-IR, UV, 1H and 13C NMR, TGA-DSC, XRD, Micro hardness analysis, and SHG efficiency studied [7-12].

Experimental

An organic crystal of thiosemicarbazone of m-Nitrobenzaldehyde was prepared by adopting general procedure [13-17]. To a hot solution of Thiosemicarbazone in methanol, a solution of m-Nitrobenzaldehydein methanol was added drop wise during thirty minutes. The mixture was stirred and refluxed for 4 hours. It was filtered and the filtrate was concentrated to half the loudness. Later on a slow evaporation of the concentrate at room temperature,

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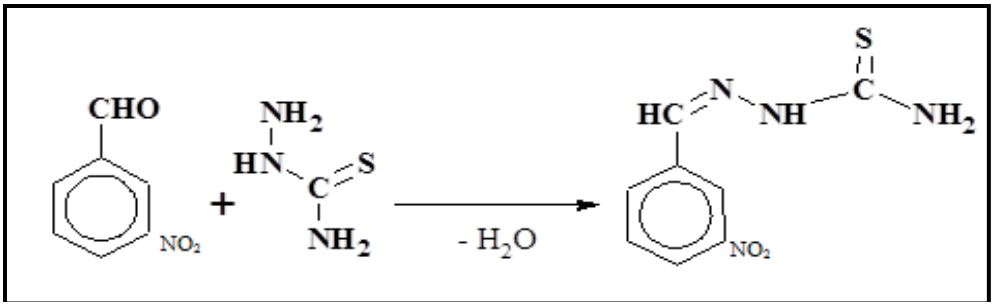
the Crystals were collected by filtration, rinsed with cold ethanol and dried in a void. These crystals are suitable for characterization studies.



m-Nitrobenzaldehyde + Thiosemicarbazide = Thiosemicarbazone of m-Nitrobenzaldehyde

Result and Discussion:-

3.1. FT-IR Spectral analysis

Working groups present in the sample were analyzed using AVTAR370 DTGS FT-IR spectrometer in the wave number range from 400-4000cm-1 using a KBr pellet technique. Fourier transform infrared (FT-IR) spectrum is an important book, which gives sufficient information about the construction of a compound. In this technique almost all working groups in a molecule absorb characteristic within a definite range of frequency. The concentration of infrared radiation makes the various alliances in a molecule to stretch and bend with respect to one another. The Fourier Infra-red spectrum of the grown crystal is indicated in the figure. 2. The observed and their corresponding group identification is made in Table 1. The band obtained at 1600cm-1 is due to the establishment of the amine group between m-Nitrobenzaldehyde and thiosemicarbazide. Referable to the C=N and N-N is stretching, vibration the peaks observed at below 1540 cm-1. The peak observed in 1159.23cm^{-1} shows C=S is stretching vibration. The peak observed at 1530 cm^{-1}. Shows the presence of -NO_2 group the peak corresponds to aromatic C-H was observed in 1298cm^{-1}. At that point is, no peak observed at 2720 cm-1confirms the aldehyde functional group in m-Nitrobenzaldehyde of thiosemicarbazone. The spectral data obtained for the thiosemicarbazone of m-Nitrobenzaldehyde are well in accordance with theoretical and literature values.

Figure1:-FT-IR Spectrum of thiosemicarbazone of m-Nitrobenzaldehyde

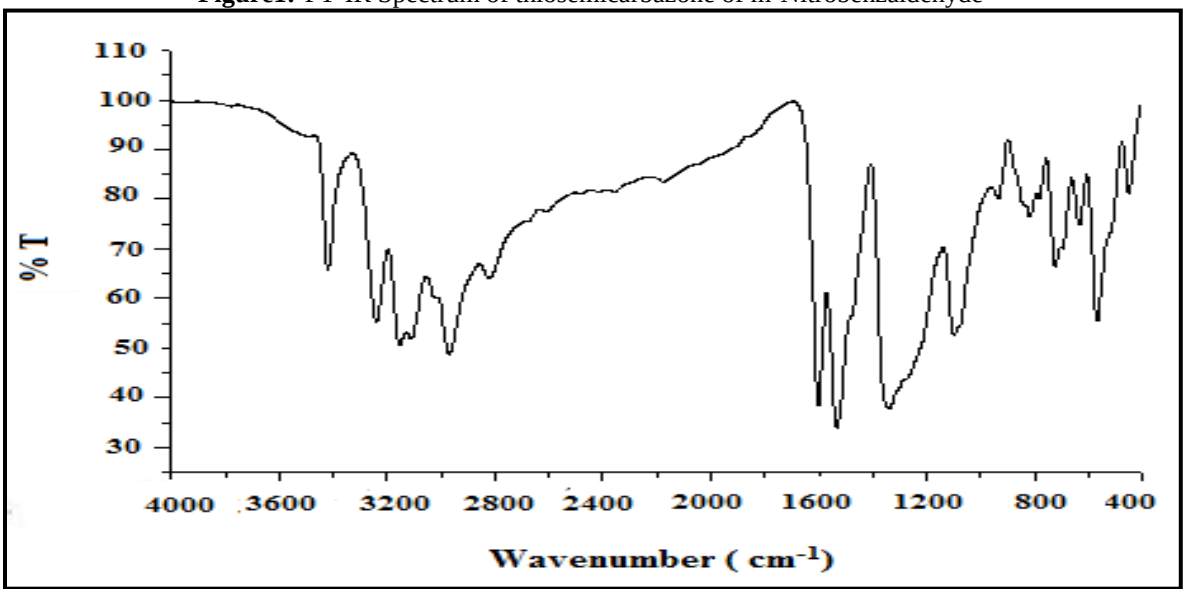


Table1:-FT-IR Spectral data of thiosemicarbazone of m-Nitrobenzaldehyde

S. No	Frequency cm^{-1}	Group designation

1	3419	N-H amine group
2	3252	N-H Stretching
3	1298	Aromatic C-H
4	1540	N-N Stretching
5	1530	C-NO_2 group
6	1600	C=N imine group
7	1159	C=S Stretching
8	1107	NH_2 rocking

3.2 UV- Visible Spectral studies

Ultraviolet-Visible Spectroscopy is also known as electronic spectroscopy. UV- (200-400nm) and Visible (400-800nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after if passes through a sample or after reflection from a sample surface. This is characteristic of a particular compound, Qualitative and Quantitative estimation of the compound are possible by this non destructive technique. The purity of chemically synthesized m-NBTSC compound was carried by measuring the UV-Visible spectra between 200-900 nanometer. UV-Visible spectroscopy analysis has been performed using a Perkin-Elmer Lambda-35 spectrophotometer operated at a settlement of 1 NM as a function of response time. The recorded UV-Visible spectrum proves the highly transparent nature of the material between 500-900nm.

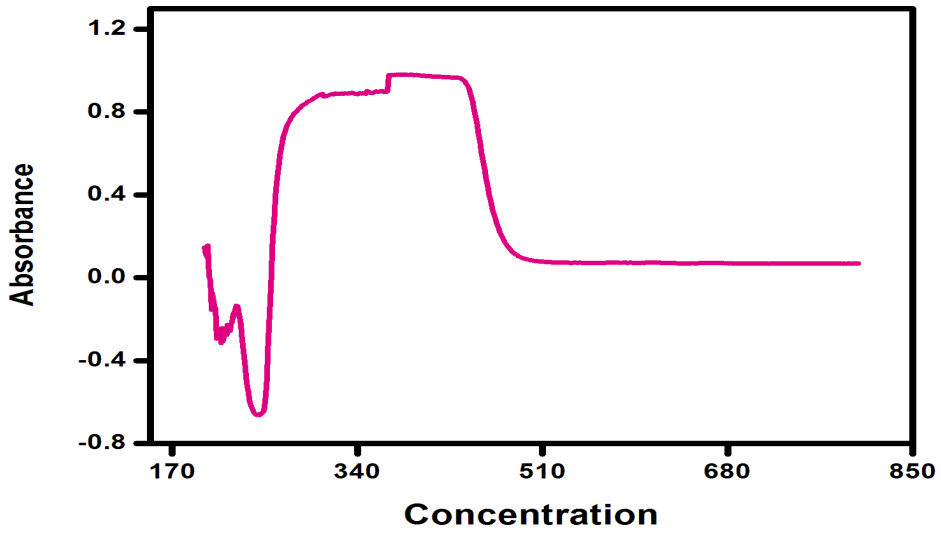


Figure 2:-UV-Visible Spectrum of Thiosemicarbazone of m-Nitrobenzaldehyde

3.3. Raman Spectral analysis

Raman is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopic analysis is commonly employed in chemistry to provide a structural fingerprint by which particles can be distinguished. The Raman spectrum of the thiosemicarbazone of m-Nitrobenzaldehyde crystal was recorded from 200 to 800 cm1 at room temperature

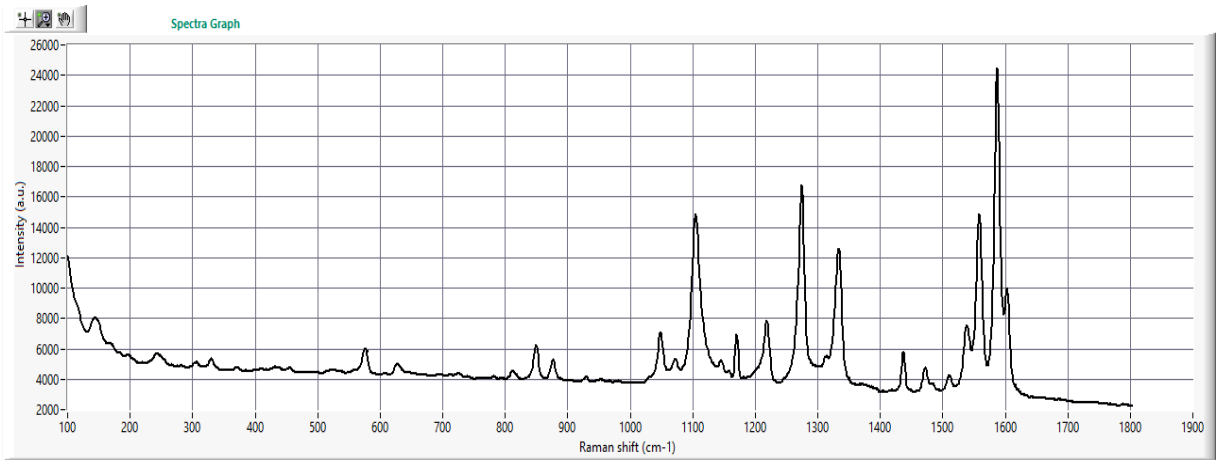


Figure3:-Raman of Thiosemicarbazone of m-Nitrobenzaldehyde

3.3 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, 13C, 31P etc., even at low concentrations. The 1H NMR spectral analysis was run out of them-Nitrobenzaldehyde of thiosemicarbazone in BRUKER 300 NMR spectrometer using DMSO as solvent. The 1H NMR spectra of thiosemicarbazone of m-Nitrobenzaldehyde is shown in image 4. A signal observed at δ=8.24ppm is corresponds to the NH_2 protons of hydroxide group. A singlet at δ=8.055 ppm confirm the NH proton. The multiplied observed between δ=7.370 and 7.801ppm confirms the presence of aromatic protons. The presence of peak at δ=4.216 ppm indicates the HC=N protons. The signal at δ=3.451ppm shows the HOD signals of the solvent. The peaks at δ=1.276 confirms the CH protons. The signal at δ=2.501indicates the residual protons present in DMSO d6 solvent [150]. The spectral data obtained for the m-Nitrobenzaldehydes of thiosemicarbazone are well in accordance with theoretical and literature values.

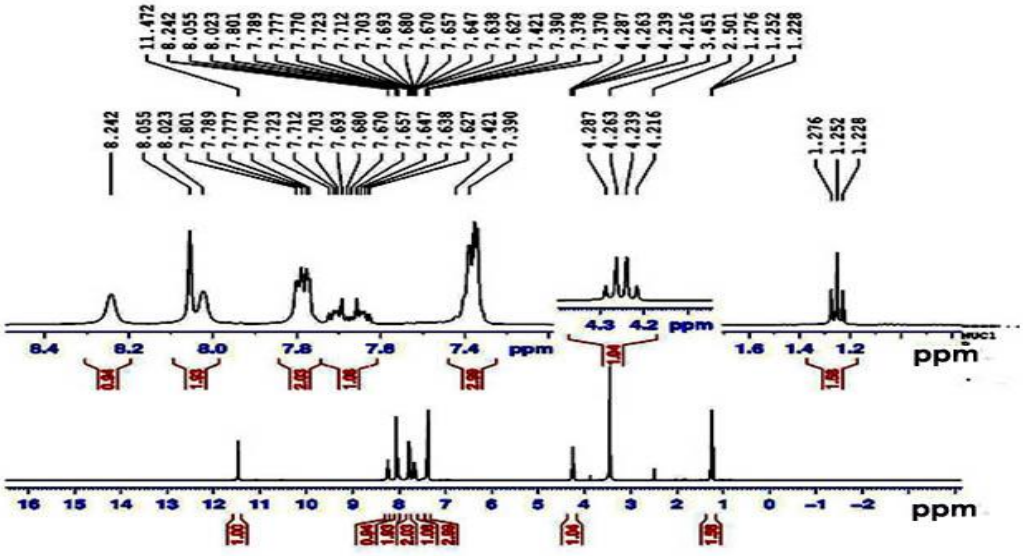


Figure 4:-^{1}H-NMR Spectrum of Thiosemicarbazone of m-Nitrobenzaldehyde

^{13}C-NMR Spectral analysis

The^{13}C NMR spectra of m-Nitrobenzaldehyde of thiosemicarbazone was recorded using BRUKER 300 NMR spectrometer using DMSO as solvent. The13C NMR Spectrum of m-Nitrobenzaldehyde of thiosemicarbazone is shown in image 5. The amine group is mapped by the signal at δ=167.01ppm The multiple peak at δ=127.36-

134.74ppm represents the bearing of the benzine ring. The bearing of a peak at δ=13.94ppm confirms the substituted aromatic compound. The presence of residual protons present in DMSO d6 observed at δ=40 ppm. The absence of peak at 25 and 17ppm confirms the absence of methylene aliphatic group. The correlation of the signals observed in 1H and 13 C NMR spectra with the functional group is recorded in Table 3. This correlation is well in accordance with the theoretical and standard values.

Figure 5:-^{13}C -NMR Spectrum of m-Nitrobenzaldehyde of thiosemicarbazone

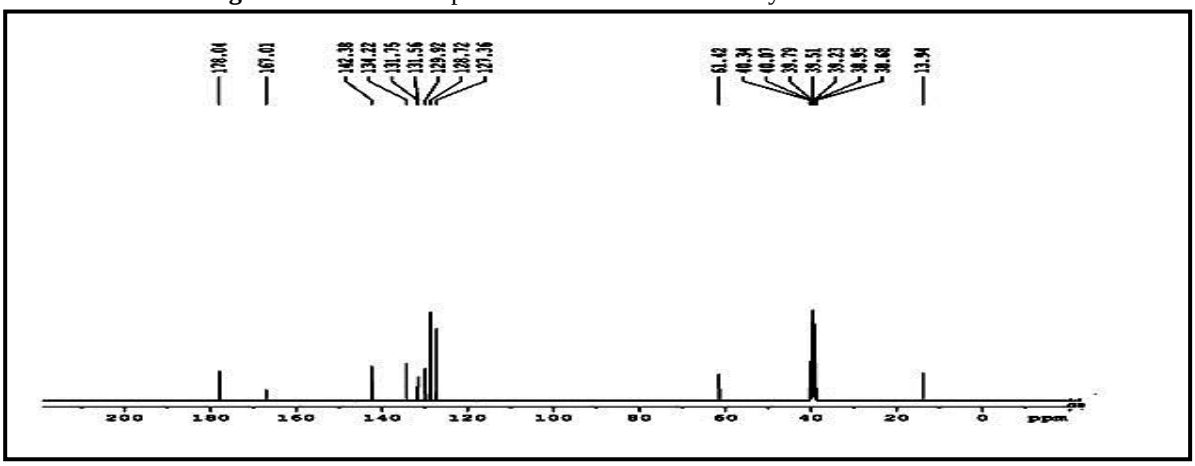


Table 3:-NMR Spectral data of m-Nitrobenzaldehyde of thiosemicarbazone

Spectrum	Signal at δ ppm	Group identification
^{1}H	8.242	NH_2 proton of hydrazide
	8.055	NH-proton
	7.370-7.801	Aromatic protons
	4.216	HC=N protons
	1.276	CH protons
^{13}C	167.01	Imine group
	142.38	C=S group
	127.36-134.74	Benzene ring
	13.94	Substituted aromatic compound

3.6 Nonlinear optical studies

At Kurt's and Perry second harmonic generation (SHG) test [32] was performed to determine the NLO efficiency of Thiosemicarbazone of m-Nitrobenzaldehyde crystal. The grown crystal was powdered with a uniform particle size and bundled in a micro capillary of uniform bore and was illuminated using spectra physics quanta ray DHS2.Nd:YAG laser is applied to test second harmonic generation (SHG) of growing crystals, The SHG efficiency obtained for Thiosemicarbazone of m-Nitrobenzaldehyde is about 5.6 times that of Urea.

Conclusion:-

Thiosemicarbazone of m-Nitrobenzaldehyde was prepared by using a methanol solution by assuming a standard routine. The crystal was grown by slow evaporation solution growth technique (SESGT). The presence of Nitro group and the nature of the protons were identified by FT-IR and ^{13}C; ^{1}H NMR Spectral analysis**.** The UV-Visible spectrum reveals that the grown crystal is transparent in the wavelength area. Thermal stability of the crystal was confirmed by TGA/DSC studies. The NLO test confirms the SHG efficiency of Thiosemicarbazone of m-Nitrobenzaldehyde

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