RESEARCH ARTICLE

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

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Manuscript Info

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 13C NMR spectra which show the molecular structure of the crystals. The TGA and DSC confirm the decay of the sample at 210°C. It further confirms the grown crystals Thiosemicarbazone of m-Nitrobenzaldehyde is thermally stable up to 210°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,
the Crystals were collected by filtration, rinsed with cold ethanol and dried in a void. These crystals are suitable for characterization studies.

\[
\text{CHO} + \text{NH}_2 \xrightarrow{\text{HN}} \text{C} \xrightarrow{\text{S}} \text{NH}_2 - \text{H}_2\text{O} \rightarrow \text{HC} \xrightarrow{\text{N}} \text{NH} \xrightarrow{\text{C}} \text{NH}_2
\]

\[\text{m-Nitrobenzaldehyde} + \text{Thiosemicarbazide} = \text{Thiosemicarbazone of m-Nitrobenzaldehyde}\]

**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\(^{-1}\)confirms 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

| S. No | Frequency cm\(^{-1}\) | Group designation |
|-------|-----------------------|-------------------|
|       |                       |                   |

Table1:-FT-IR Spectral data of thiosemicarbazone of m-Nitrobenzaldehyde
|    |     |                  |
|----|-----|-----------------|
| 1  | 3419 | N-H amine group |
| 2  | 3252 | N-H Stretching  |
| 3  | 1298 | Aromatic C-H    |
| 4  | 1540 | N-N Stretching  |
| 5  | 1530 | C-NO₂ group     |
| 6  | 1600 | C=N imine group |
| 7  | 1159 | C=S Stretching  |
| 8  | 1107 | NH₃ rocking     |

3.2 UV-Visible Spectral studies

Ultraviolet-Visible Spectroscopy is also known as electronic spectroscopy. UV-Visible (200-400nm) and Visible (400-800nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after it 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.

![UV-Visible Spectrum](image)

**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 cm⁻¹ at room temperature.
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 $\delta=8.24$ppm is corresponds to the NH$_2$ protons of hydroxide group. A singlet at $\delta=8.055$ ppm confirm the NH proton. The multiplied observed between $\delta=7.370$ and $7.801$ppm confirms the presence of aromatic protons. The presence of peak at $\delta=4.216$ ppm indicates the HC=N protons. The signal at $\delta=3.451$ppm shows the HOD signals of the solvent. The peaks at $\delta=1.276$ confirms the CH protons. The signal at $\delta=2.501$indicates the residual protons present in DMSO d$_6$ solvent [150]. The spectral data obtained for the m-Nitrobenzaldehydes of thiosemicarbazone are well in accordance with theoretical and literature values.

$\text{13}^C$-NMR Spectral analysis

The$^{13}$C NMR spectra of m-Nitrobenzaldehyde of thiosemicarbazone was recorded using BRUKER 300 NMR spectrometer using DMSO as solvent. The$^{13}$C NMR Spectrum of m-Nitrobenzaldehyde of thiosemicarbazone is shown in image 5. The amine group is mapped by the signal at $\delta=167.01$ppm The multiple peak at $\delta=127.36$-
134.74 ppm represents the bearing of the benzine ring. The bearing of a peak at $\delta=13.94$ ppm confirms the substituted aromatic compound. The presence of residual protons present in DMSO d6 observed at $\delta=40$ ppm. The absence of peak at 25 and 17 ppm confirms the absence of methylene aliphatic group. The correlation of the signals observed in 1H and 13C 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](image)

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

| Spectrum | Signal at $\delta$ 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 DHS2Nd: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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Reference:
1. Manivannan S, Danuskodi S. Growth and characterization of a new organic nonlinear crystal: Semicarbazone of N-dimethylaminebenzaldehyde Crystal growth 257 (2003) 305-308.
2. Vasudevan G, Anbusrinivasan P, Madhurambal G, Mojumdar SC. Thermal analysis effect of dopants Spectral characterization and growth aspect of KAP crystals. J Therm Anal Calorim 2009 (96) 99-102. Anbusrinivasan P, Pandian G.V, Determination of Nucleation Temperature, metastablezone with spectral analysis of sulphanilic acid grown from Ethanol-Water as growth medium; Ultra chemistry vol 8 (1), 83-90 (2012).
3. Ramachandra Raja C, Ramamoorthy K, Manimekalai R, Growth and spectroscopic characterization of ethylene diamine tetra acetic acid (EDTA) doped Zinc sulphatehepta hydrate-A semi organic NLO material, Spectrochimica Acta Part A 99:23-26.
4. Madhurambal G, Ramasamy P, Anbusrinivasan P, Vasudevan G, Kavitha S, Mojumdar SC, Growth and characterization studies of 2- bromo-4”-Chloro-acetophenone (BCAP) crystals. J Therm Anal calorim 2008; 94:59-62.
5. Anbusrinivasan P, Pandian G.V. Determination of Nucleation Temperature, metastablezone with spectral analysis of sulphanilic acid grown from Ethanol-Water as growth medium; Ultra chemistry vol 8(1), 83-90 (2012).
6. Ramalingam S, Anbusrinivasan P, Periandy S: FT-IR and FT-Raman Spectral Investigation, Computed IR-Intensity and Raman activity analysis and frequency estimation analysis on 4-chloro-2-bromoaceto phenone was – HF and DFT calculations; Spectrochimica Acta part A 2011 (78) 826-834.
7. Yuan-Zhang, Yonggangwang, Yunxiache, Jiminezheng Growth and properties of two new organic nonlinear optical crystals; Hydroxyethyl ammonium-l-tartrate monohydrate and Hydroxyethyl ammonium-o-tartrate monohydrate. J crystal growth 299 (2007) 120-124.
8. Rajasekaran M, Anbusrinivasan P, Mojumdar SC, Growth, Spectral and thermal characterization of 8-hydroxyquinoline, J. Therm calorim (2010) 100:827-830.
9. Sankaranarayanan K, Ramasamy P, Unidirectional crystalization of large diameter benzophenone single crystal from solution at ambient temperature. J crystal growth 292 (2006)445-448.
10. Arulchakararavthi A, Jayavel P, santhanaragavan P, Ramasamy P, Growth of organic molecular single crystal trans-stilbene by selective self-seeding from vertical Bridgman technique JCrystal Growth 2002( 234) 159-163.
11. Subashini A, Bhavannarayana G, Ramamurthy K, Investigation on growth and crystalline perfection of an organic Schiff base material: 4-chloro-4” bromobenzylidene aniline, Spectrochimica Acta part A 96 (2012)716-722.
12. Srinivasan P, Gunasekaran M, Ganagasekaran T, Gobalakrishnan R, Ramasamy P, 2, 4, 6-trinitrophenol (TNP); an organic material for nonlinear optical applications, J Crystal Growth 2006 (289) 639-646.
13. Wiliredo Hernandez, Juanpaz, Abraham Viaseb, Evgenia Spodine, Rainer Richter and Lothar Beyer, Synthesis, Characterization and in Vitro Cytoxic Activities of Benzaldehyde Thiosemicarbazone Derivatives and their Palladium (II) complexes against various Human Tumor cell lines, Bioinorgchem Appl-v 2008, 2008, PMC2615113.
14. Santhakumari R, Ramamurthy K Structural, Thermal and optical characterization of an organic NLO material– Benzaldehyde Thiosemicarbazone monohydrate single crystals, Spectro chemical Acta part A: 78 (2011) 653-659.
15. Formation characterization and structural studies of novel thiosemicarbazone Palladium (II) complexes. Vila JM, Pereira Mat, Ortigueira JM, etal. Chemicalsociety, Dalton Transactions 1999 (23) 4193-4201.
16. Sethuraman K, Ramesh Babu K, Vijayan N, Gobalakrishnan R, Ramasamy P, Synthesis, growth of organic nonlinear optical crystal; Semicarbazone of 2-amino -5-chloro –benzophenone (S2A5CB) and its characterization. Crystal growth 2006 (290) 539-543.
17. Janarthanan S, Rajan Y.C, Umarani P.R, Selvakumar S, Pandi S Synthesis and characterization of Semicarbazone p-Hydroxy-3-Methoxy acetophenone (SPH3MA) Single crystal.Physica.B-condenced matter 2011 (406) 135-138.
18. Mojumdar SC. Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with heterocyclic ligands. J Therm Anal Calorim.2001 (64) 629-36.
19. Madhurambal G, Mojumdar SC, Hariharan S, Ramasamy P, TG, DTC, FT-IR and Raman spectral analysis of ZnN3Mg, Ammoniumsulphate mixed crystals; J Therm Anal Calorim 2004 (78) 125-33.
20. Preema. C Thomas, Langabhushankumar, A. Anuradha. S. Aruna, Ginsonp. Joseph, P.Sagayaraj, Growth and characterization of nonlinear optical single crystals of L-argininediiodate, J.crystal growth 2006(290) 560-564.
21. Sweta M, Tamusree K, Growth and characterization of nonlinear optical crystal Zinc tris (thiourea) sulphate in presence of L-arginate. Optical mat 2007; 30: 508-512.
22. Jayalakshmi D, Kumar J. Growth and characterization of bistiourea Zinc acetate, Cryst Res Technol, 2006;41, 37-40.
23. Narayananmoolaya B, Dharma Prakash S.M. Synthesis, growth and characterization of nonlinear optical crystal L-tyrosine hydro bromide. J Crystal growth 290 (2006) 498-503.
24. Balakrishnan, T, Ramamurthi K, Crystal growth. Structural, optical, mechanical and thermal properties of a new nonlinear optical single crystal L-Ornithine monohydrochloride, Spectrochimica Acta part A 72 (2009) 269-273.
25. Mojumdar SC, Mikovic J, Krutosikova A, Valigura D, Stewart J M. Furopyridine-Ni (II) complexes-Synthesis, Thermal and spectral characterization. J Therm Anal Calorim. 2005(81) 211-215.
26. William Kemp, Organic spectroscopy-Third edition-1991.
27. Ramesh Babu R, Ramesh R, Gopalakrishnan R, Ramamurthi K, Bhagavannarayana G, Growth, Structural, optical, mechanical and optical properties of pure and metal ions doped sulphamic acid single crystals. Spectrochimica Acta part A 76 (2010) 498-503.
28. Sangeetha K, Ramesh Babu R, Bhagavannarayana G, Ramamurthi K, Structural, Spectral, and dielectric properties of copper and Glycine doped LAHCL single crystals, Spectrochimica Acta part A 79(2011)1017-1023.
29. Dos Santos M.H, Nagem T.J, Braz-Filho R, ILuta I.S and Speziali N.L Complete assignment of the $^1$H and $^{13}$C NMR spectra of the tetraaisoprenylated benzophenone 15-epicusianone Magn. Reson.Chem. (2001); 39:155158.
30. Sudha S Belgur, Ravindra R, Kamble and Sheena shashikanth, A convinent preparation of novel benzophenonederivatives J,Serb, Chem,Chem;(2008) 73(3)261-269.
31. Myoung-chongsong, FikruNigussie, Hye-Joung Yang and Nam-In Back, A New benzophenone from Linderafruticosa, Bull,Korean Chem, Soc.(2007) 28(7) 1209.
32. Kurtz S.K, Perry T.T, J.Appl.Phys.39 (1968) 3798-3813.
33. Porob RA, Khan SZ, Mojumdar SC, Verankar VMS ,Synthesis, TG, SDC and infra-red spectral study of NiMn2(C2H4O4)36N2H4-A precursor for NiMn2O4 nanoparticles; J Therm Anal Calorim 2006 (86) 605-612.
34. Meera. K, Muralitharan R, Tripathi AK, Dhanasekaran R. Growth of Thiourea doped TGS crystals and their characterization, J. Crystal Growth 2004-260:414-421.
35. Mojumdar SC. Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with hetrocyclic ligands J Therm Anal Calorim. 2001 (64) 629-636.XRD
36. Sawant SY, Verenkar VMS, Mojumdar SC. Preparation, Thermal, XRD, chemical and FT-IR spectral analysis of NiMn2O4 nanoparticles and respective precursor; J Therm Anal Calorim 2007 (90) 669-672.
37. Vila JM, Pereira Mat, Ortigueira JM, et al, Formation characterization and structural studies of novel thiosemicarbazone Palladium (II) complexes. J. Chemicalsocity, Dalton Transitions 1999 (23) 4,193-4201.
38. Uma Devi T, Lawrence N, RameshBabu R, Ramamurthi K, Growth and characterization of Glycine picrate single crystal:Spectrochimica Acta part A 71 (2008) 340-343.
39. Leela S, Hema R, Helenstoeckli Evans, Ramamurthi K, Bhagavannarayana. G, Design, Synthesis, growth and characterization of 4-Methoxy-4” dimethylamino-benzylidine aniline (MDMABA): A novel third order nonlinear optical material, Spectrochimica Acta part A 77 (2010)927-932.
40. Ravindrachary V, Bajantri R F, Richard Goncalves, Growth and characterization of an organic NLO Crystals 1-(4-methyl phenyl) -3-(4- methoxy phenyl) -2-propene -3-one.J. Crystal growth, 2004 (267) 129-133.
41. Renoylds G.F, in D. Fox. A. Weiss Berger M.M. Labes (Eds) Physics and Chemistry of the organic Solid States Vol.1.Wileley Inter science new York1963 pp. 223-286.