

Preparation, Growth, Spectroscopic and Thermal Characterization of Thiosemicarbazone of 4-Chlorobenzaldehyde and Benzaldehyde

C.JEEVARATHINAM^a G.V.PANDIAN^b

^aDepartment of Chemistry, Arignar Anna Govt. Arts & Science Karaikal

^bDepartment of Chemistry, T.B.M.L College, Porayar.

Abstract

The thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde is an interesting of organic compound in the crystalline nature. The crystal which is grown slow evaporation method from the solvent methanol. The harvested crystals were purified by repeated recrystallization. FT-IR spectroscopic analyze was carried out on the growth recognize the fundamental function group. Optical absorption studied illustrate low absorption in the entire UV and visible spectral. The UV-Visible Spectra are confirms the optical transparency. This is more helpful to use these crystals in option applications. The harvested crystals Thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde was characterized by proton nuclear magnetic resonance and of ¹³C NMR spectra which show the molecular structure of the crystals. Its thermal stability for analysis in the crystal by TGA and DSC. The TGA and DSC confirm the decomposition of the sample at 210°C. It further confirms the grown crystal Thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde is thermally stable up to 210°C. The frequencies was identified in the crystal by dielectric properties. Second harmonic generation efficiency of the powdered Thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde and was tested using Nd: YAG laser and it is found to be **18** times higher than that of urea.

Keywords: solution growth, slow evaporation technique, spectral characterization, Thermal analysis, SHG efficiency

1. Introduction

Thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde is an organic crystal plays an important role in application in optical computing and optical communication devices. In recent year, intense research work has been carried out to identify a special variety of thermally stable optical material. Organic compounds are often formed by very weak Vander walls and hydrogen bonds and possess high degree of delocalization. Hence they are optically more nonlinear than inorganic crystals. Recent researches have mentioned that organic crystals are bulk in size, hard, stable, and large nonlinear optical susceptibilities compared to the inorganic crystals

The slow evaporation solution growth Technique (SESGT) is an important technique because large size, stable, optical crystals are being grown by this technique [1-5]. Hence these crystals are used in the area of optical communication and optical computing and information process. The harvested crystals were

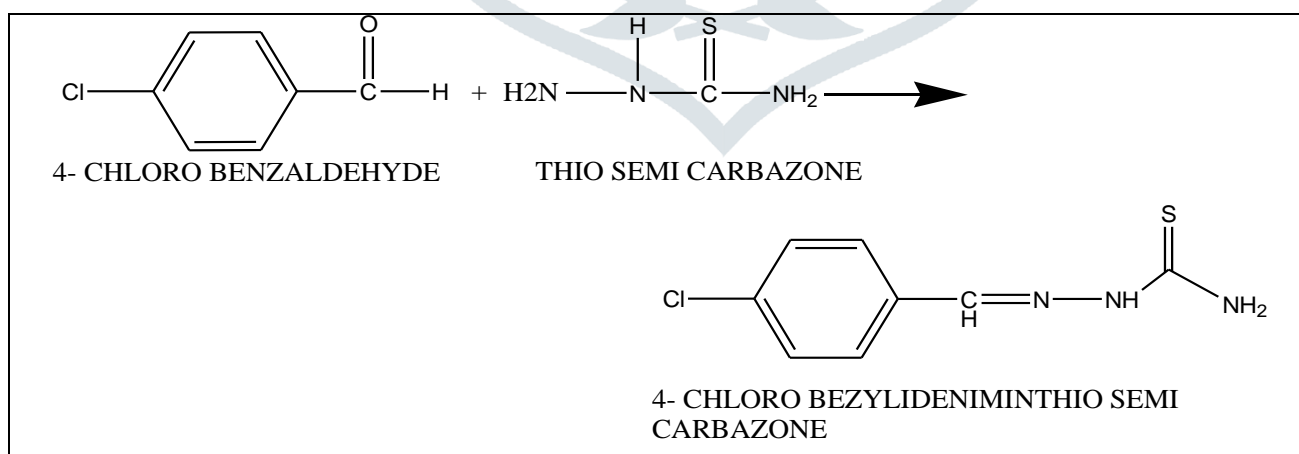
characterized by FT-IR spectral analysis, UV, ^1H and ^{13}C Nuclear magnetic resonance spectra, TGA-DSC studies, X-ray diffraction (XRD), Micro hardness analysis, and SHG efficiency studied [8-10].

2. Experimental

An organic crystal of thiosemicarbazone of 4-Chlorobenzaldehyde and Thiosemicarbazone of benzaldehyde was prepared by adopting general procedure [14-15]. To a hot solution of Thiosemicarbazone in methanol, a solution of benzaldehyde in 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 volume. After a slow evaporation of the concentrate at room temperature, Crystals were collected by filtration, washed with cold ethanol and dried in vacuum. The harvested crystals are shown in figure 1. These crystals are suitable for characterization studies.



Figure: 1. Crystals of Thiosemicarbazone of 4-Chlorobenzaldehyde



4-chlorobenzaldehyde + Thiosemicarbazide = Thiosemicarbazone of 4- chlorobenzaldehyde

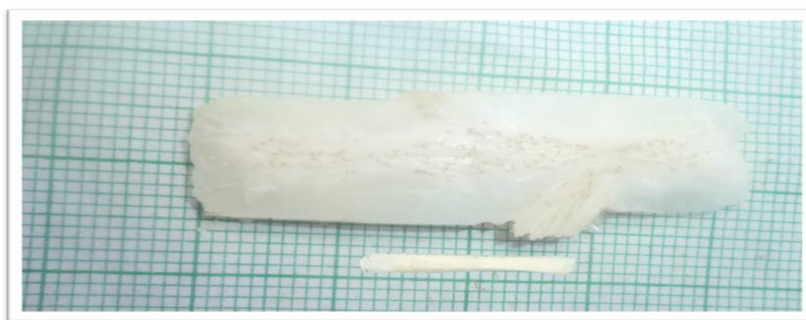
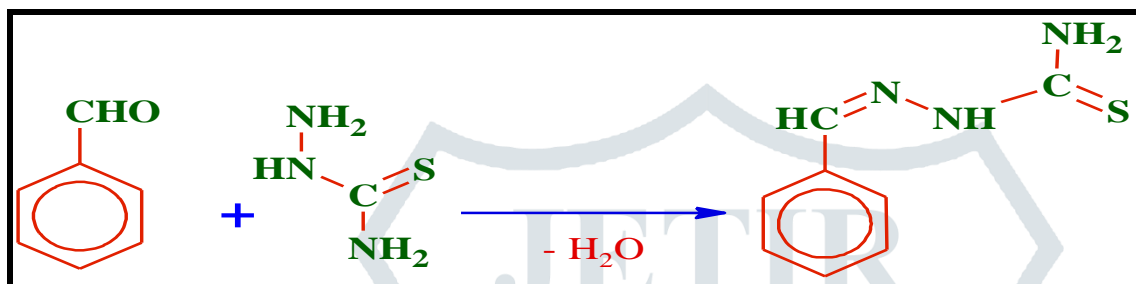


Figure: 2. Crystal of Thiosemicarbazone of benzaldehyde



Benzaldehyde + Thiosemicarbazide = Thiosemicarbazone of benzaldehyde

3. Result and Discussion

3.1. FT-IR Spectral analysis

Fourier transform infrared (FT-IR) spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding to the molecular structure of the compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency [12-13]. The absorption of infrared radiation causes the various bonds in a molecule to vibrate stretch and bend with respect to one another. The spectrum was recorded using AVTAR370 DTGS FT-IR spectrometer in the wave number range from 400-4000 cm^{-1} with KBr pellet. The Fourier Infra-red spectrum (FT-IR) of the grown crystal is shown in figure-1; the observed frequencies and their corresponding group identification are given in Table 1 and 2. The band obtained at 1600 cm^{-1} is due to the formation of the imine group between Benzaldehyde and Thiosemicarbazide. Due to the C=N and N-N stretching vibrations the peaks observed at 1524 cm^{-1} . The peak observed at 1089.23 cm^{-1} shows C=S stretching vibration. As expected the peak corresponds to aromatic C-H was observed at 1281 cm^{-1} . The absence of at 2720 cm^{-1} confirms the presence aldehyde functional group in 4-Chlorobenzaldehyde. The peak observed at 815 cm^{-1} confirms the presence of aryl C-C₁ structure. The Fourier transform Infrared spectrum of thiosemicarbazone of benzaldehyde is shown in figure 2 respectively. The peak at 3365 cm^{-1} shows the N-H stretching vibration. The peak at 1482.02 cm^{-1} shows N-N stretching vibration. The peak at 1160.43 cm^{-1}

shows C=S stretching vibration for thiosemicarbazone of benzaldehyde. The signal at 999.89cm^{-1} indicates C-N stretching. The band obtained at 1590cm^{-1} is due to the formation of the imine group between carbonyl group and thiosemicarbazide. Due to the C=N and N-N stretching vibration the peaks observed at below 1540cm^{-1} . There is no peak observed at 2720cm^{-1} confirms the absence of (CHO) functional group in thiosemicarbazone derivatives.

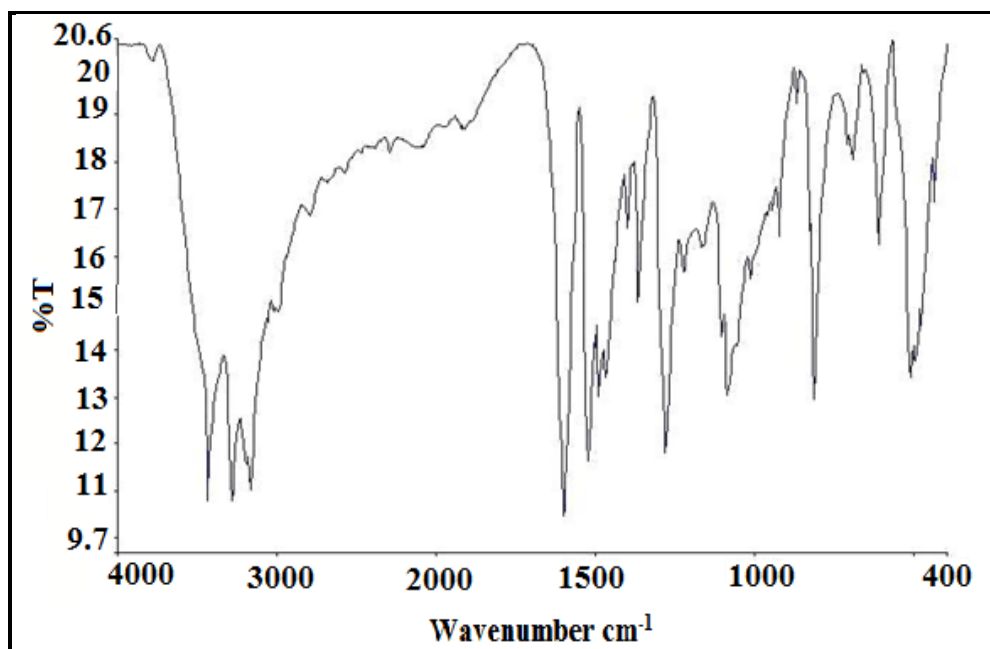


Figure: 3. FT-IR Spectrum of thiosemicarbazone of 4-Chlorobenzaldehyde

Table-1 FT-IR Spectral data of thiosemicarbazone of 4-Chlorobenzaldehyde

S.NO	Frequency cm^{-1}	Group identification
1	1600	C=N imine group
2	1524	N-N Stretching
3	1089	C=S Stretching
4	1281	Aromatic C-H
5	815	Aryl C-C

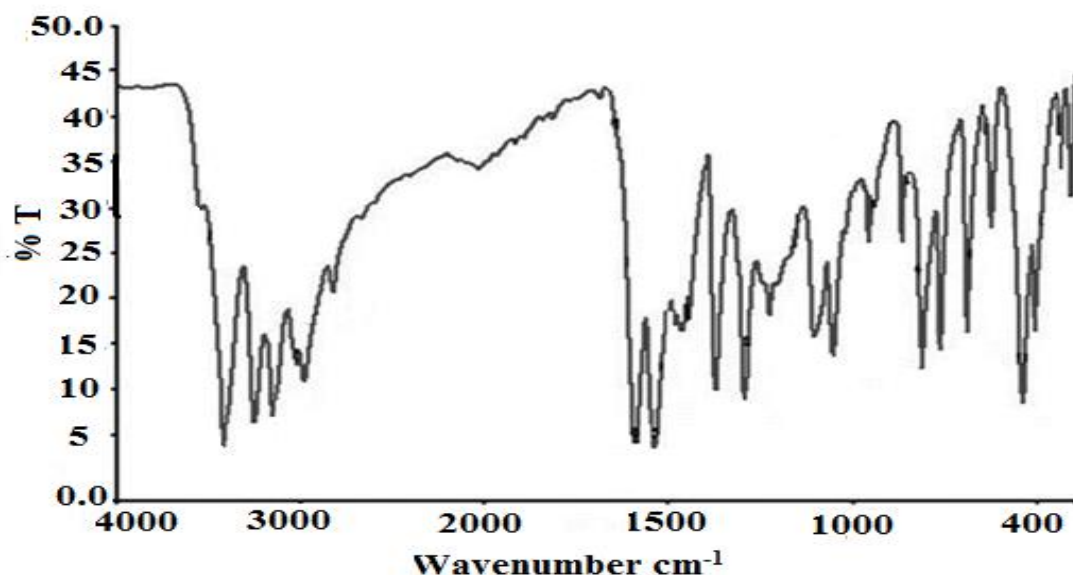


Figure: 4. FT-IR Spectrum of Thiosemicarbazone of Benzaldehyde

Table-2. FT-IR Spectral data of Thiosemicarbazone of Benzaldehyde

S.No	Frequency cm^{-1}	Group identification
1	1590	C=N imine group
2	1482	N-N Stretching
3	1160.43	C=S Stretching
4	1298	C-H Aromatic

3.2 UV Visible Spectral studies

UV-Visible Spectral study is very useful technique to determine the optical properties and transparency of a substance. The molecular absorption in the UV-Visible region depends mainly on the electronic structure of the molecule; [23-28]. The UV-Visible spectrum of thiosemicarbazone of 4-Chlorobenzaldehyde and thiosemicarbazone of benzaldehyde crystal was recorded using Lambda 25 spectrometer is shown in figure-5. This spectrum shows the characteristic absorption of thiosemicarbazone of 4-Chlorobenzaldehyde crystal is found at 260-350 nm. The recorded UV-Visible spectrum proves the highly transparent nature of thiosemicarbazone of 4-Chlorobenzaldehyde between 350-800 nm which is one of the important characteristic properties of a material suitable for optical applications. The UV-Visible spectrum of thiosemicarbazone of benzaldehyde crystals were recorded using a Lambda 25 spectrometer. UV-Visible spectrum is shown in figure 6. The spectrum shows the characteristic absorbance band between 260-380 nm. There is no characteristic absorbance band

between 380-800 nm. Because of these properties thiosemicarbazone of benzaldehyde may find applications in opto electronics.

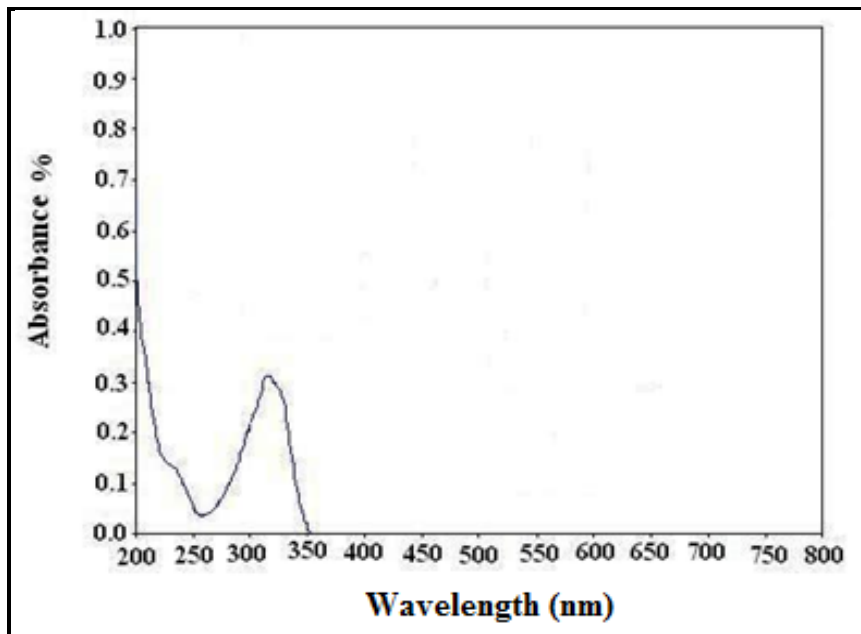


Figure: 5. UV-Visible Spectrum of Thiosemicarbazone of 4- Chlorobenzaldehyde

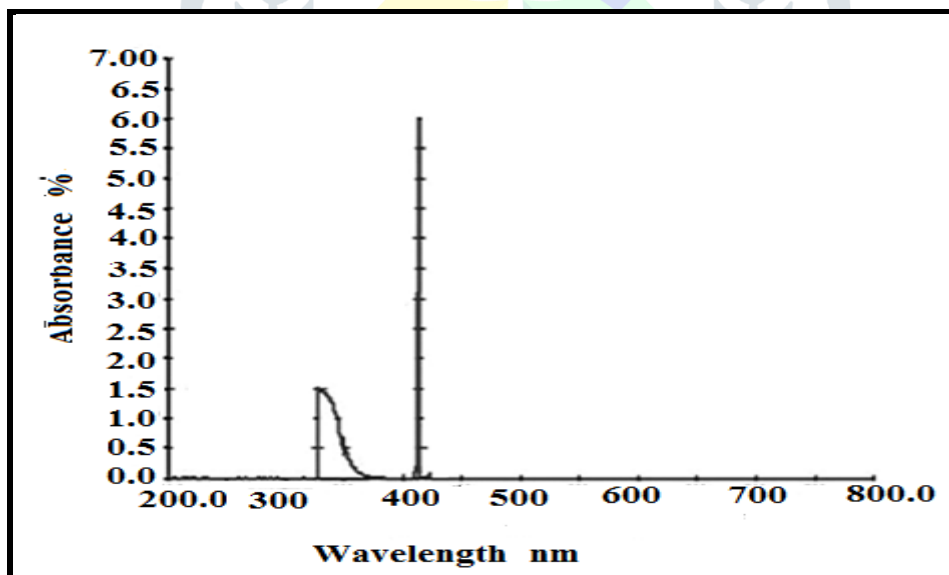


Figure: 6. UV-Visible Spectrum of Thiosemicarbazone of Benzaldehyde

3.3 NMR Spectral analysis

(a).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., Based on the chemical environment of the magnetic nuclei proton NMR and Carbon-13 NMR Spectral studies is used to determine molecular structure [26-28]. The ^1H NMR spectral analysis was carried out on the thiosemicarbazone of 4-chloro benzaldehyde and of thiosemicarbazone of benzaldehyde crystals in BRUKER NM-474 spectrometer. The ^1H NMR spectra of thiosemicarbazone of 4-chlorobenzaldehyde is shown in figure 7. Four different environment of proton present in the crystal .both aromatic and aliphatic proton are present in the crystal, The chemical shift value (δ) around 7.8 exhibits a multiplet indicates the aromatic ring protons present in the 4-chlorobenzaldehydue to the high electron negative electron donating group chlorine substituent ortho and meta protons environments are slightly varied between the 7.4 to 8.2 ppm .The delocalization of π electron in the aromatic ring also influence the (δ) value. A Peak arised near down filled expiates three aliphatic proton environments are present in crystal. The chemical shift value of aliphatic proton is always below 7 ppm chemical shift value. A Peak at 0.039 ppm indicates the aliphatic CH proton. A peak at 3.394 ppm indicates the NH proton and a triplet around 2.5 ppm therefore exculpated proton environment were found exactly by this proton NMR spectroscopy. The ^1H NMR spectral analysis was carried out on the thiosemicarbazone of benzaldehyde crystals in BRUKER 300 NMR spectrometer at 300 MHz using DMSO as solvent. The ^1H NMR spectra of thiosemicarbazone of benzaldehyde is shown in figure.8. The ^1H NMR spectrum revealed the presence of an aromatic system. There is a multiplet at $\delta=7.370-7.801$ ppm indicates the presence of aromatic protons. The NH_2 proton of hydrazide is observed at 8.658 ppm as broad singlet. The $-\text{NH}$ proton is observed at 7.219 ppm. The spectral data obtained for the thiosemicarbazone of benzaldehyde were well in accordance with theoretical and standard spectrum.

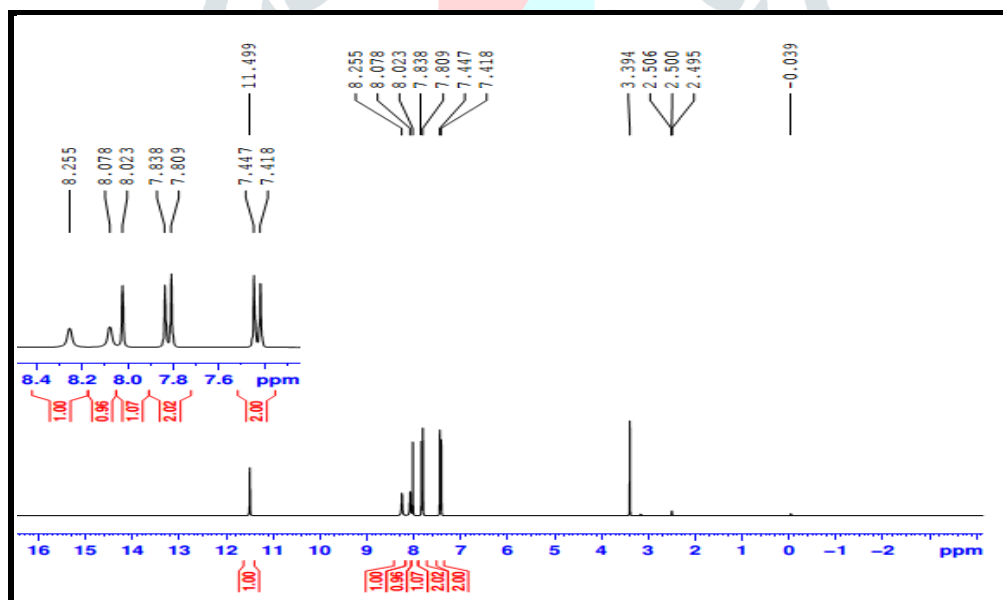


Figure.7. ^1H -NMR Spectrum of Thiosemicarbazone of 4-Chlorobenzaldehyde

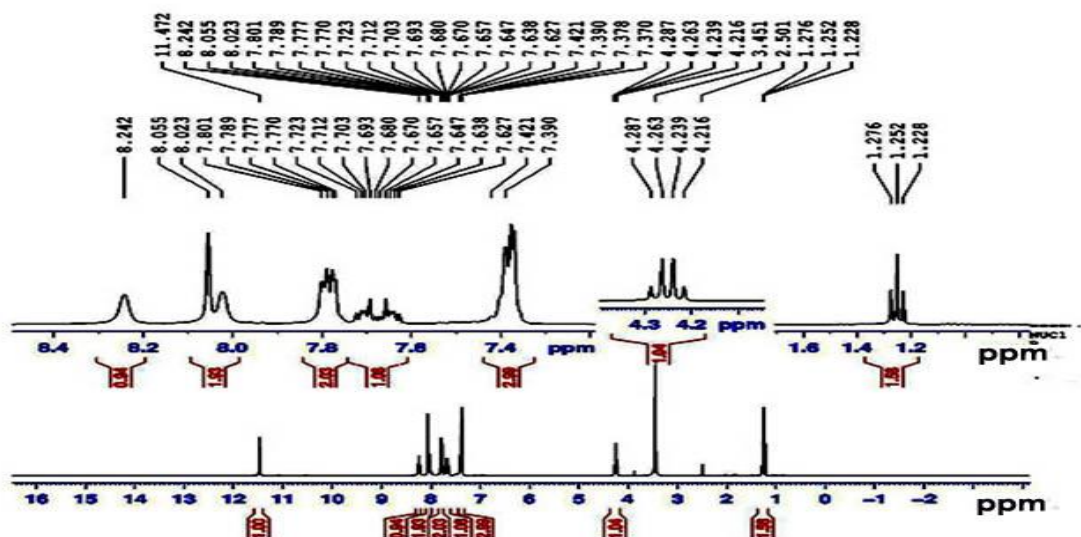


Figure: 8. $^1\text{H-NMR}$ Spectrum of Thiosemicarbazone of Benzaldehyde

7. Thermal analysis

Thermal analysis is a very useful technique for material characterization it provide with various information about the studied materials such as thermal stability, crystallization, purity and structure. Thermal study of Thiosemicarbazone of 4-chlorobenzaldehyde was analyzed using SDT Q 600V 20.9 BUILD20 instrument between the temperatures 0°C to 600°C at a heating rate of $10^\circ\text{C}/\text{minutes}$ under nitrogen atmosphere. The thermal analysis is a very useful technique in the characterization and thermal stability of the crystal [32-34]. The thermogram of thiosemicarbazone of 4-Chlorobenzaldehyde shown in figure.7. The sample weight is 14.9860 mg sample was taken for the measurement the thermogram shows the endothermic peak at 218.74°C . Further shows the grown crystal has crystalline nature and thermal stability. The grown crystal begins to attain an endothermic transition and begins decompose. The sharpness of this endothermic peak shows the good degree of crystallinity and purity. In TGA there are three weight losses noted in the thermogram. The First and second major weight loss is observed just above 200°C and 300°C

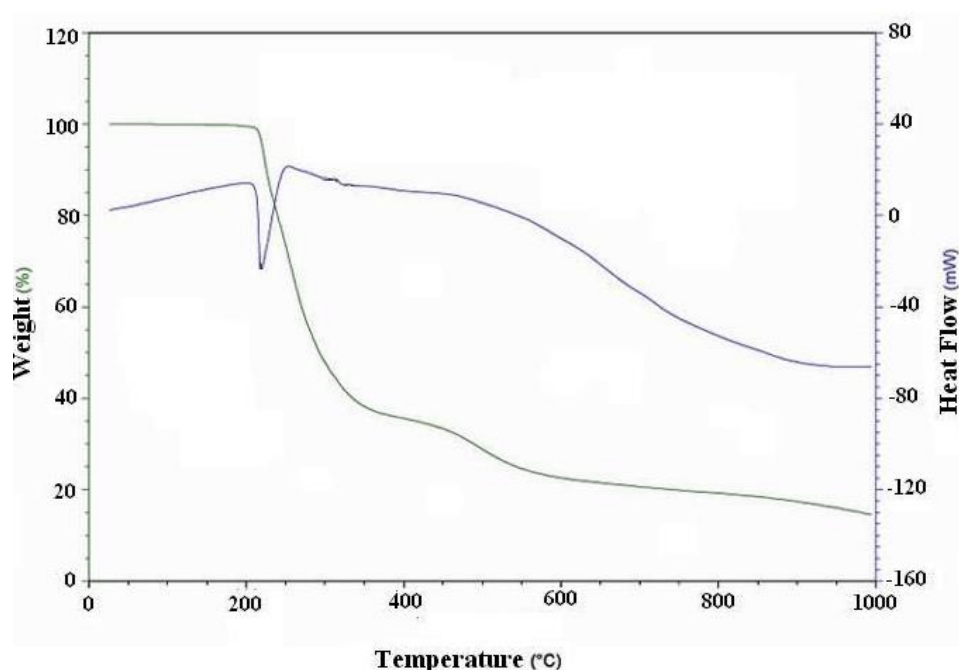


Figure.9. Thermogram of thiosemicarbazone of 4-Chlorobenzaldehyde

Thermal properties of harvested crystal of Thiosemicarbazone of Benzaldehyde were studied in powder form by recording TGA and DSC response curve in the temperature range between 0°C to 500°C. Thermal studies have been carried out using on SDTQ 600R 20.9 BUILD 20 Instrument at a heating rate of 10 °C /min under nitrogen atmosphere. The thermogram of Thiosemicarbazone of Benzaldehyde is shown in figure.9. In Thiosemicarbazone of Benzaldehyde the sample taken for the measurement is 10.9750 mg. There is an endothermic peak at 153.50 °C shows its melting point. Thermal analysis clearly depicts the thermal stability and crystalline nature of the grown crystal [19]. Thermal and spectral analyses are very useful technique for material characterization [21-22].The thermogram further shows the thermal stability and crystalline nature of the grown crystal. The other endothermic peak shows the further decomposition .In TGA there is a sharp weight loss is observed just above 200°C and 300°C.

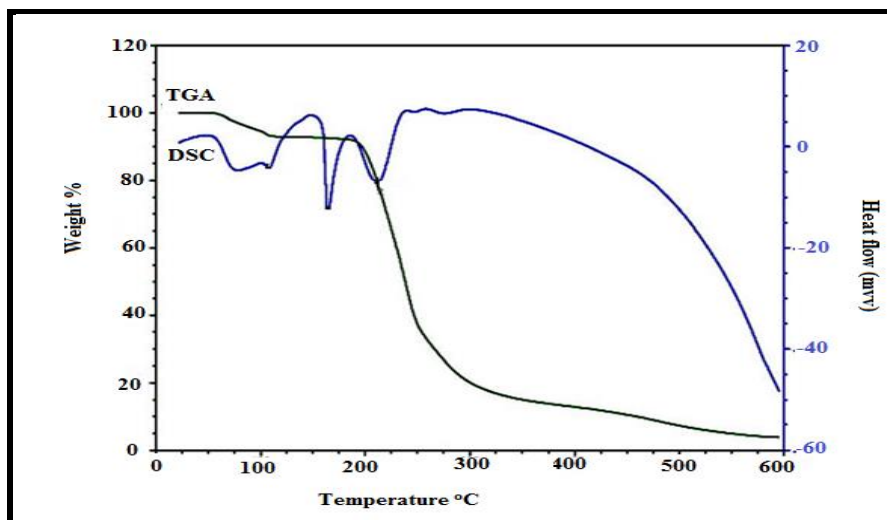


Figure.10. Thermogram of thiosemicarbazone of benzaldehyde

3.6 Nonlinear optical studies

A Kurt's and Perry second harmonic generation (SHG) test [42] was performed to determine the NLO efficiency of Thiosemicarbazone of 4-Chlorobenzaldehyde and thiosemicarbazone of benzaldehyde crystal. The grown crystal was powdered with a uniform particle size and packed in a micro capillary of uniform bore and was illuminated using spectra physics quanta rayDHS2.Nd:YAG laser is used to test second harmonic generation (SHG) of grown crystal, The SHG efficiency obtained for Thiosemicarbazone of 4-chlorobenzaldehyde thiosemicarbazone of benzaldehyde and is about 18 times that of Urea.

Conclusion

Thiosemicarbazone of 4-Chlorobenzaldehyde and thiosemicarbazone of benzaldehyde was prepared by using methanol solution by adopting standard procedure. The crystal was grown by slow evaporation solution growth technique (SESGT). The presence of benzaldehyde group and the nature of the protons were identified by FT-IR and ^{13}C ; ^1H NMR Spectral analysis. The UV-Visible spectrum reveals that the grown crystal is transparent in the wavelength region. Thermal stability of the crystal was confirmed by TGA/DSC studies. The NLO test confirms the SHG efficiency of Thiosemicarbazone of 4-Chlorobenzaldehyde and thiosemicarbazone of benzaldehyde.

Acknowledgement

One of the authors (GVP) thank University Grant Commission, New Delhi for the award of UGC: minor project [File No. 4- 1/2008 (BSR)]. The authors thank the management and principal of T.B.M.L.College for their support. Authors are grateful to Dr. Brindha Department of Center for Advanced Research in Indian System of Medicine (CARISM).

Reference

1. RamachandraRaja C, Ramamoorthi K, R. Manimekalai, Growth and spectroscopic characterization of ethylene diamine tetra acetic acid (EDTA) doped Zinc sulphate hepta hydrate-A semi organic NLO material, *Spectrochimica Acta Part A* 99(2012) 23-26.
2. Narayanamoolaya. B, Dharmaprakash. SM, Synthesis, growth and characterization of nonlinear optical crystal L-tyrosine hydrobromide. *J Crystal Growth* 290(2006) 498-503.
3. Madhurambal G, Ramasamy P, Anbusrinivasan P, Vasudevan G, Kavitha S, Majumdar SC, Growth and characterization studies of 2-bromo-4'-chloro-acetophenone (BCAP) crystals. *J Therm Anal calorim* 2008; 94:59-62.
4. 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.
5. 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-bromoacetophenone was – HF and DFT calculations; *Spectrochimica Acta part A* 2011(78) 826-834.
6. Manivannan S, Danuskodi S. Growth and characterization of a new organic nonlinear crystals: Semicarbazone of N-dimethylamine benzaldehyde. *J Crystal growth* 257 (2003) 305-308.
7. Yun-zhang, Yonggangwang, Yunxiache, Jiminezheng Growth and properties of two new organic nonlinear optical crystals; Hydroxyethylammonium-l-tartrate monohydrate and Hydroxyethylammonium-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 crystallization of large diameter benzophenone single crystal from solution at ambient temperature. *J crystal growth* 292 (2006) 445-448.
10. Arulchakkaravarthi A, Jayavel P, santhanaragavan P, Ramasamy P. Growth of organic molecular single crystal trans-stilbene by selective self-seeding from vertical Bridgman technique. *J Crystal Growth* 2002(234) 159-163.
11. Subashini A, Bhavannarayana G, Ramamurthi 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. R. M. Silverstein and G. C. Bassler, Spectrometric identification of organic compounds, Wiley, New York (1964).
14. Y. R. Sharma Elementary organic spectroscopy. Reprint (2003).
15. C. N. R. Rao, Ultraviolet and Visible Spectroscopy, Butterworths, London, UK, 3rd edition, 1975. Press 1975.
16. William Kemp, Organic spectroscopy-Third edition-1991.

17. Dos Santos M.H, Nagem T.J, Braz-Filho R, ILuta I.S and Speziali N.L Complete assignment of the ^1H and ^{13}C NMR spectra of the tetraaisoprenylatedbenzophenone15-epiclusianone *Magn. Reson.Chem.* 39 (2001) :155158.
18. Mojumdar SC. Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with hetrocyclic ligands .*J Therm Anal Calorim.*2001 (64) 629-36.
19. 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.
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, TamusreeK, 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 bithiourea Zinc acetate, *Cryst Res Technol*, 2006;41, 37-40.
23. William Kemp, *Organic spectroscopy-Third edition-1991.*
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, Miklovic 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. Narayanamoolaya B.Dharmaprakash S.M. Synthesis, growth and characterization of nonlinear optical crystal L-tyrosine hydro bromide.*J Crystal growth* 290 (2006) 498-503.
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) 470-475.
28. Sangeetha K, Ramesh Babu R, Bhagavannarayana G, Ramamurthi K, Structural, Spectral, optical 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 ^1H and ^{13}C NMR spectra of the tetraaisoprenylatedbenzophenone15-epiclusianone *Magn. Reson.Chem.* (2001); 39:155158.
30. Sudha S Belgur, Ravindra R. Kamble and Sheena shashikanth, A convinent preparation of novel benzophenonederivaties *J,Serb, Chem,Chem;*(2008) 73(3)261-269.
31. Myoung-chongsong, FikruNigussie, Hye-Joung Yang and Nam-In Back, A New benzophenone from Linderافرuticosa, *Bull,Koream Chem, Soc,*(2007) 28(7) 1209.
32. Balakrishnan T, Ramamurthi K, "Crystal growth, Structural, optical, mechanical and thermal properties of a new non linear optical single crystal L-Ornithine monohydrochloride", *Spectrochimica Acta part A* 72 (2009) 269-273

33. Porob RA, Khan SZ, Mojumdar SC, Verankar VMS, Synthesis, TG, SDC and infra-red spectral study of $\text{NiMn}_2(\text{C}_2\text{H}_4\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ precursor for NiMn_2O_4 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. Cryst Growth* 2004-260:414-421.
35. Mojumdar SC. Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with heterocyclic ligands. *J Therm Anal Calorim.* 2001(64) 629-636. XRD
36. Sawant SY, Verankar VMS, Mojumdar SC. Preparation, Thermal, XRD, chemical and FT-IR spectral analysis of NiMn_2O_4 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. Chemicalsociety, Dalton Transitions* 1999 (23) 4,193-4201.
38. Uma Devi T, Lawrence N, Ramesh Babu R, Ramamurthi K, Growth and characterization of Glycine picrate single crystal; *Spectrochimical 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-benzylidene 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. *Wiley Inter science* New York 1963 pp. 223-286.
42. Jaikumar.D, Kalainathan. Bhagavanarayana.G "Synthesis, growth, thermal, optical and mechanical properties of new organic NLO crystal: L-alanine DL-malic acid ," *J. Cryst. Growth*, 312(2009) 120-124.