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Comparative study on the spectral characterization, nonlinear optical efficiency and thermal characterization of thiosemicarbazone of (e)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide and a-oxodiphenylmethane

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Abstract

The thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide (TSCCB) and Thiosemicarbazone of A-Oxodiphenylmethane (TSCBP) is an interesting of organic compound in the crystalline nature. The quartz glass which is grown slow evaporation method from the solvent methanol. The crystal dimension up to 14X6.5X4mm3 obtained by benzpphenone and both crystal sizes are the same. The harvested crystals were purified by repeated recrystallization. FT-IR spectroscopic study was carried out on the growth, recognize the fundamental function group. Optical absorption studied illustrate the low absorption in the entire UV and visible spectral. The UV-Visible Spectra are confirming the optical transparency. This is more helpful to use these crystals in option applications. The harvested crystals TSCCB and TSCBP were characterized by proton nuclear magnetic resonance and of ^{13}C NMR spectra which show the molecular structure of the crystals. Thermal analysis is a very useful technique for material characterization it provides with various information about the studied materials such as thermal stability, crystallization, Purity and Structure. Its thermal stability for analysis in the crystal by TGA and DSC. The TGA and DSC confirm the decay of TSCCB at 210 °C and it confirms the grown crystal TSCBP is thermally stable up to 184.14 ^{0}C. It further confirms the grown crystal TSCCB and TSCBP is thermally stable up to 210 °C and 184.14 ^{0}C. The frequency was identified in the crystal that enough by dielectric properties. The second harmonic generation efficiency of the powdered TSCCB and TSCBP and was tested using Nd: YAG laser and it is found to be 6.1 and be ~0.8 times time of potassium dihydrogen phosphate and urea. The obtained data support the formation of the expected thiosemicarbazone structures and suggest potential stability for further coordination studies.

Keywords: Solution growth, slow evaporation technique, spectral characterization, thermal analysis, SHG efficiency

Introduction

TSCCB and TSCBP are organic crystals that play important roles in optical computing and optical communication devices due to their unique nonlinear optical properties. In recent year, intense research study has been taken out to identify a limited form of thermally stable optical material. Organic compounds are frequently shaped by very weak Vander walls and hydrogen bonds and possess a high degree of delocalization. Hence, they are optically more nonlinear than inorganic crystals. Recent researches have brought up that organic crystals are bulk in size, strong, 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, stability, optical crystals are being produced by this technique [1-2]. Hence, these crystals are employed in the field of optical communication and optical computing and information process. The harvested crystals were characterized by FT-IR spectral analysis, UV, ^{1}H and ^{13}C Nuclear magnetic resonance spectra, TGA-DSC studies, X-ray diffraction (XRD), Micro hardness analysis, and SHG efficiency studied [3-5].

2. Experimental

An organic crystal of TSCCB and TSCBP was prepared by taking a general procedure [6-8]. All chemicals used in this study were supplied by E.Merk. Aldrich Chemical Co.IR Spectra were recorded in a AVTAR 370 DTGS FT-IR spectrometer using KBr pellets. UV Spectra were recorded using a Lambda 25 UV-Visible spectrometer.^{13}C and ^{1}H NMR spectra were recorded in BRUKER NM-474. Thermal studies have been carried out using on SDTQ 600R 20.9 BUILD 20 Instrument [5-7]. X-ray diffraction patterns of the samples were recorded on a BRUKER D8 ADVANCE POWDER diffract meter with Cu Kα radiation. To a hot solution of Thiosemicarbazone in methanol, a solution of 4-Chlorobenzaldehyde and benzpphenone in methanol was added drop wise during thirty minutes. The mix was stirred and refluxed for 4 hours. It was strained and the filtrate was concentrated to half the mass. 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. The harvested crystals are indicated in figure 1 and 2. These crystals are suitable for characterization studies.

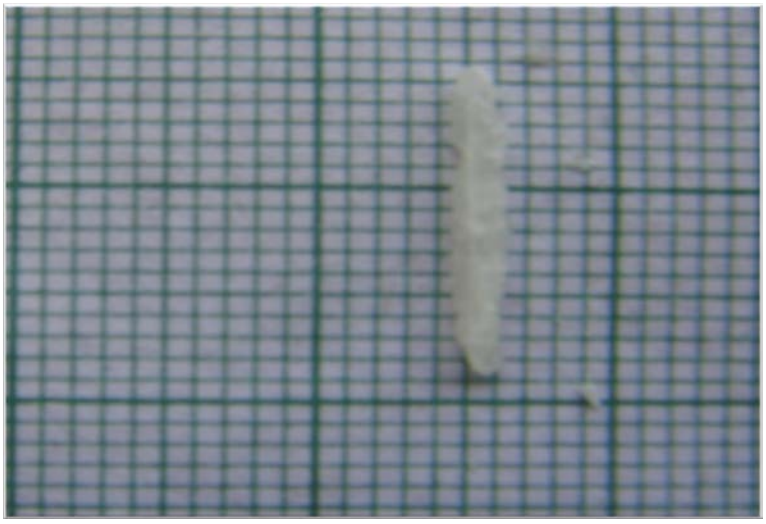

Fig 1: Crystals of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

4-Chlorobenzaldehyde + Thiosemicarbazide → Thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

Fig 2: Crystals of Thiosemicarbazone of a-Oxodiphenylmethane

Benzophenone + Thiosemicarbazide → Thiosemicarbazone of a-Oxodiphenylmethane

3. Result and Discussion

3.1. FT-IR Spectral analysis

Fourier transformer infrared (FT-IR) spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding to the functional group of the compound. In this technique almost all working groups represent in this molecule absorb characteristic within a definite scope of frequency [8-9]. The concentration of infrared radiation makes the various alliances in a molecule to vibrate stretch and bend with respect to one another. The spectrum was recorded using AVTAR 370 DTGS FT-IR spectrometer in the wave number range from 400-4000cm^{-1} with KBr pellet. The Fourier Infra-red spectrum (FT-IR) of the grown crystal is indicated in figure-3 and 4; the observed frequencies and their corresponding group identification are given in Table 1 and 2. The band obtained at 1600cm-1is due to the establishment of the amine group between (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide and Thiosemicarbazide. Referable to the C=N and N-N stretching vibrations the peaks observed at 1524 cm-1. The peak observed in 1089.23cm^{-1} shows C=S stretching vibration. As expected the top corresponds to aromatic C-H was observed in 1281cm-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-C_l structure.

The band obtained at 1600cm-1 is due to the formation of the amine group between a-Oxodiphenylmethane and thiosemicarbazide. The peak at 3365cm-1 shows the C-H stretching vibration of alkynes. The peak at 1482.02cm-1 shows N-H and S-N stretching vibration [10-11].The peak at 1160.43cm-1 shows C=S stretching vibration. The peak at 1278 cm-1 corresponds to aromatic C-H. The peak at 999.89cm-1 indicates C-N stretching. The peak at 647cm-1 shows N-H bending of 20 amines. The spectral data obtained for the thiosemicarbazone of TSCCB and TSCBP are well in accordance with theoretical and literature values.

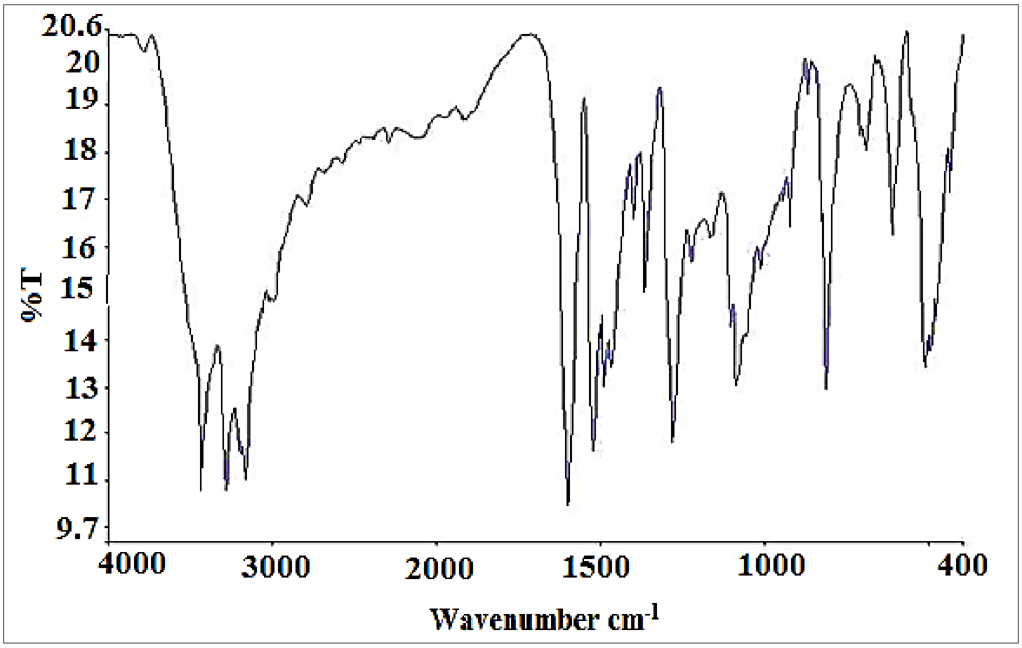

Fig 3: FT-IR Spectrum of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

Table 1: FT-IR Spectral data of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

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

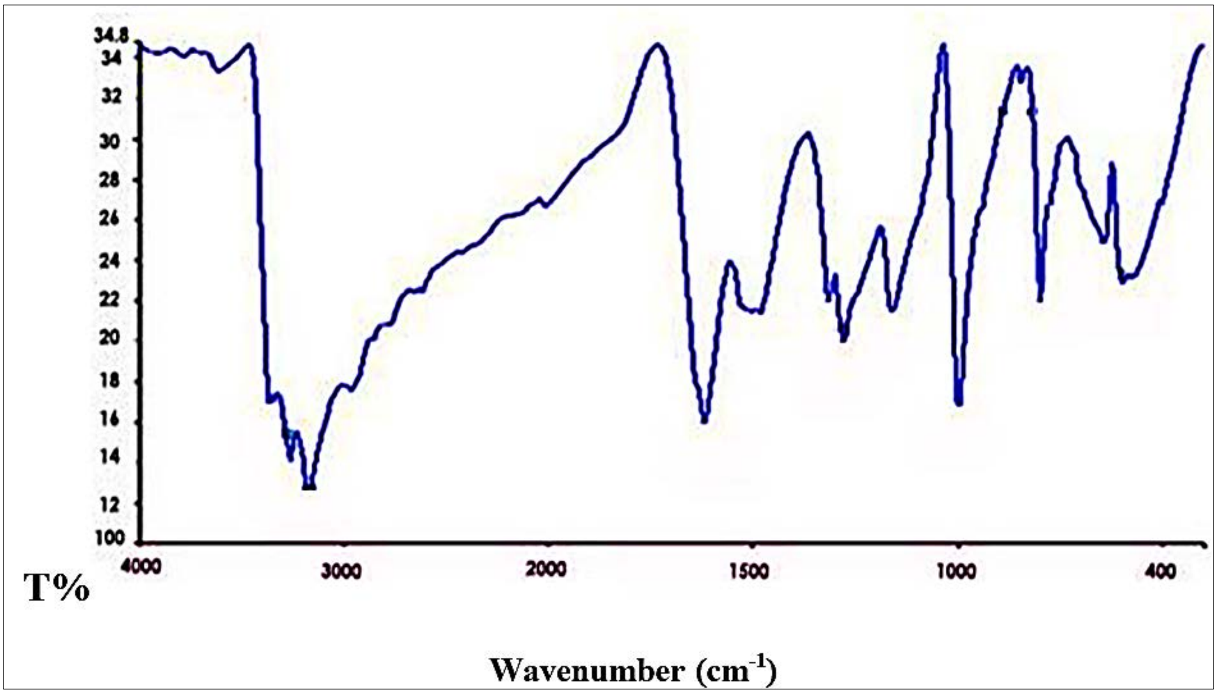

Fig 4: FT-IR Spectrum of thiosemicarbazone of a-Oxodiphenylmethane

Table 2: FT-IR Spectral data of thiosemicarbazone of a-Oxodiphenylmethane

S. No.	Frequency cm-1	Group identification
1	3365	C-H stretching
2	1482.02	N-H and N-N stretching vibration
3	1160.43	C=S stretching vibration
4	1278	C-H Aromatic
5	999.89	C-N Stretching
6	647	N-H bending of 2^0 amines

3.2 UV Visible Spectral studies

UV-Visible Spectral study is very useful technique to determine the optical properties and transparency of a substance. UV Spectra were recorded using a Lambda 25 UV-Visible spectrometer. The molecular absorption in the UV-Visible region depends mainly on the electronic structure of the molecule [12-13]. The UV-Visible spectrum of thiosemicarbazone of TSCCB and TSCBP crystal was recorded using Lambda 25 and 35 spectrometer is shown in figure: 5 and 6. This spectrum shows the characteristic absorption maximum (λ max) of thiosemicarbazone of TSCCB and TSCBP crystal is found between 260-350 nm and 325-950 nm. The recorded UV-Visible spectrum proves the highly transparent nature of TSCCB and TSCBP between 350-800 nm and 325-950 nm. This is one of the important both of characteristic properties of a fabric suitable for visual and optoelectronics applications. Optical properties of crystalline materials give information regarding the composition nature and quality of the crystal.

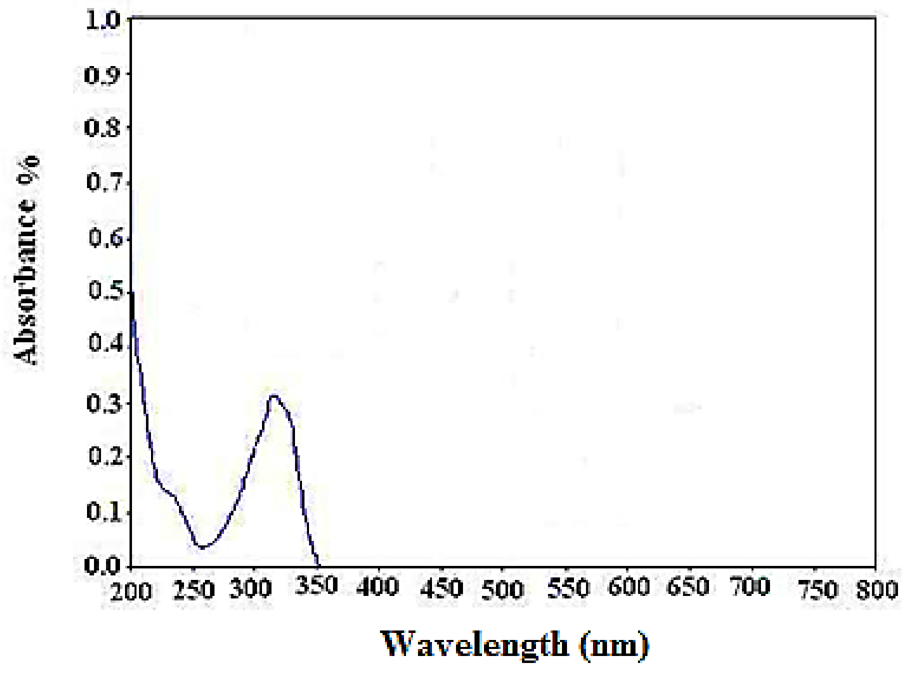

Fig 5: UV-Visible Spectrum of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

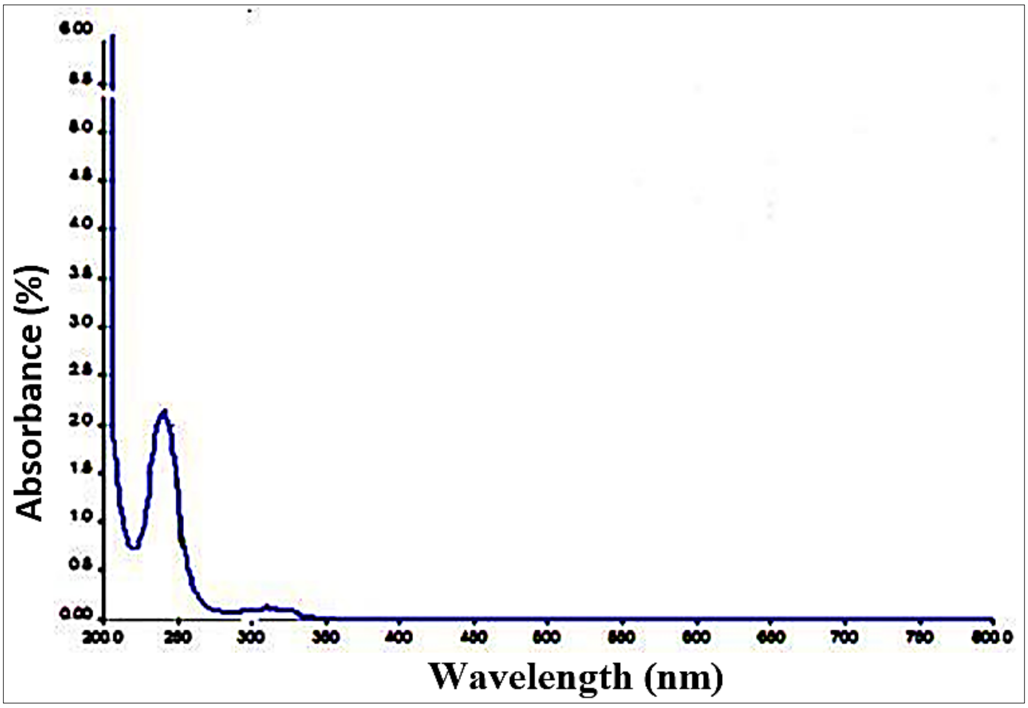

Fig 6: UV-Visible Spectrum of thiosemicarbazone of a-Oxodiphenylmethane

3.3 NMR Spectral analysis

3.3.1. (a). ^{1}H 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., Based on the chemical environment of the magnetic nuclei proton NMR and Carbon-13 NMR spectral studies are used to determine molecular structure [14].The ^{1}H NMR spectral analysis was carried out on the TSCCB and TSCBP crystal in BRUKER NM-474 spectrometer using DMSO as solvent.^{1}H NMR spectrum of TSCCB and TSCBP shows. The observed and their corresponding group identification are given in Table (3.4). The (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide 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 (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide 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 drown 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 spectrum of thiosemicarbazone of a-Oxodiphenylmethane revealed an aromatic system at δ= 7.721ppm.There is a multiplet at δ=7.721 ppm indicates the presence of aromatic group. The NH2 proportion of hydrazide is observed at 8.658 as broad singlet. The hetero atom sulphur observed at 7-8 ppm with 1.29Hz. The -NH proton is observed at 7.219 ppm, Because of the results the presence of hydazide group which confirmed by NMR spectral analysis.

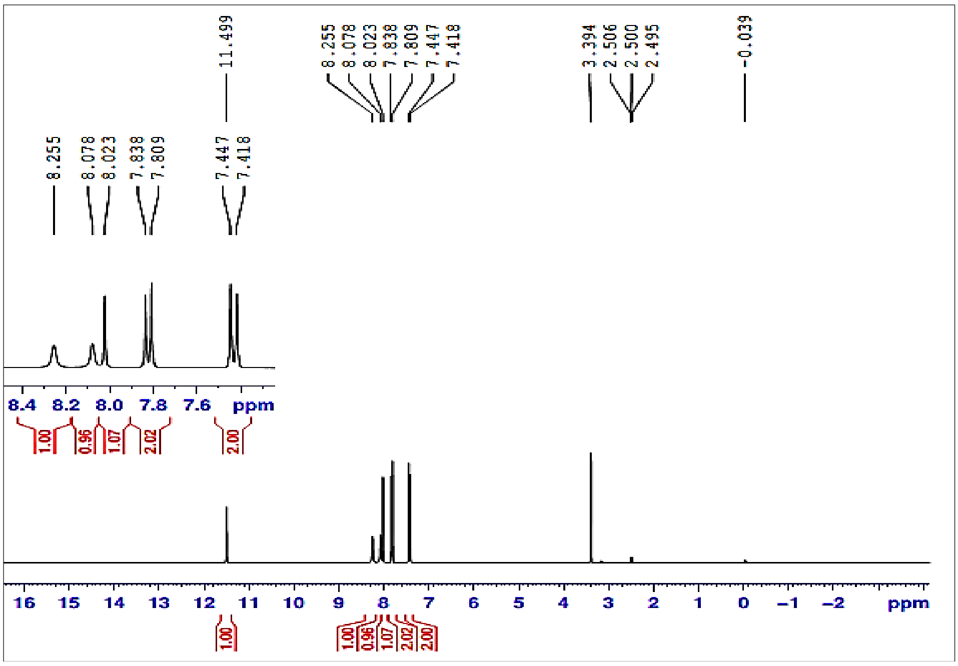

Fig 7: ^{1}H-NMR Spectrum of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

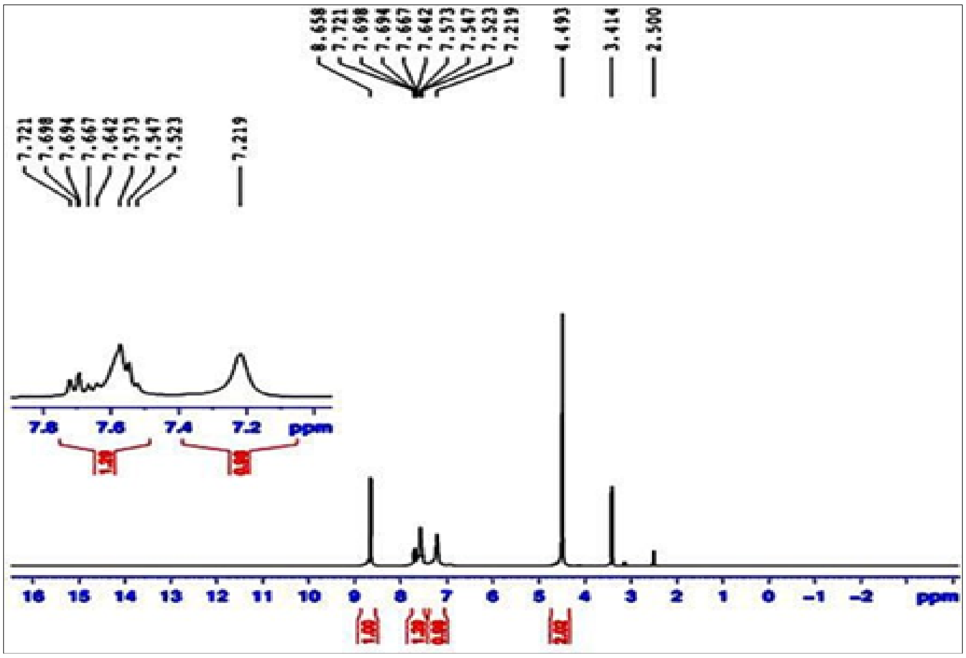

Fig 8: ^{1}H-NMR Spectrum of thiosemicarbazone of a-Oxodiphenylmethane

3.3.2. (b) ^{13}C NMR spectral analysis

The^{13}C NMR spectral analysis was carried out on the TSCCB and TSCBP Crystal in BRUKER NM 474 NMR spectrometer using DMSO as solvent.The^{13}C NMR Spectra of TSCCB and TSCBP are shown in figure: 9 &10 from the ^{13}C NMR spectral studies environment of carbon present in the TSCCB and TSCBP were analyzed [15]. The TSCCB there are six environment of carbon were found among this six two carbons are aliphatic carbon C=S and C=N the C=S peak was found at 178.04ppm chemical shift value and C=N carbon attached to the 4 th carbon of aromatic ring was found 140.58 ppm chemical shift value there are 6 carbon in the aromatic ring chemical shift value of two ortho carbon is around 129 ppm the two meta carbon chemical shift value are found at the128 ppm chemical shift value the carbon attached to the chlorine as found 134.21 ppm chemical shift value the carbon linked with thiosemicarbazone chain as found at the 126 ppm chemical shift value one more unrelevent multiplies found between 38.62 to 40.26 ppm indicates the present of hetro atom sulphur conformed the present of thio group the spin spin splitting accuse between C-neutron and S-neutron lead to the completely around 40ppm. 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. In the ^{13}C NMR spectral of TSCBP studies also used to determine the molecular structure of the compound [16]. The singlet observed at δ=196.03 ppm shows the presence of non-chelated ketone carbon. The peak observed at δ= 137.04 ppm confirms the sp2 hybridized carbon atom. The singlet at δ=132.88 methine sp2 hybridized carbon atom. The methoxy carbon proves the peak observed at δ= 129.73 ppm and δ= 128.73 ppm.The multiplet observed at δ =40.36 ppm shows the presence of methyl group and sulphur atom.

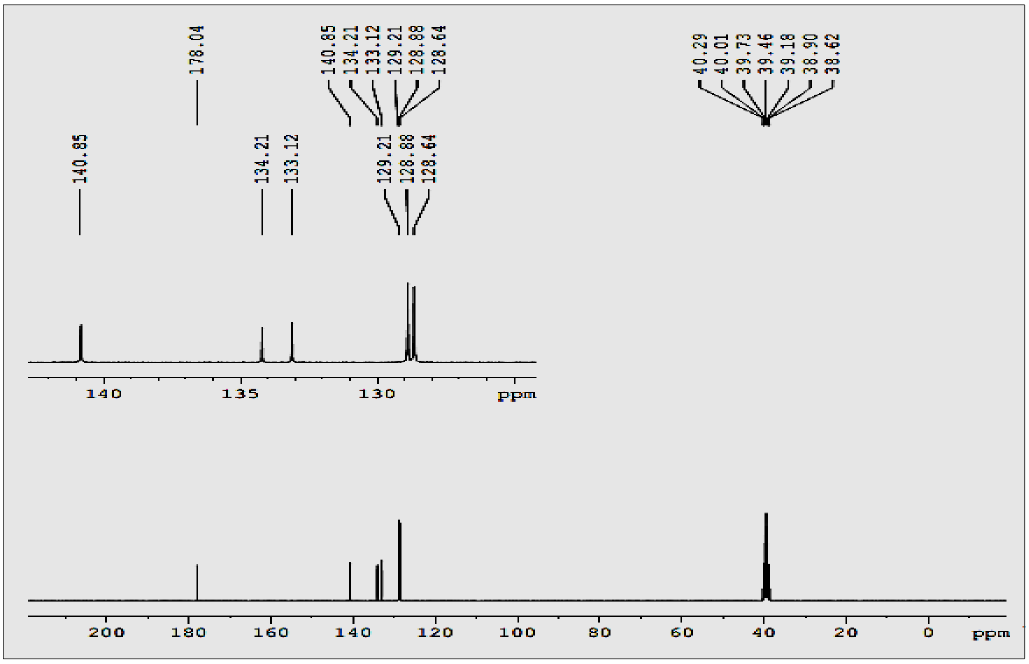

Fig 9: ^{13}C -NMR Spectrum of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

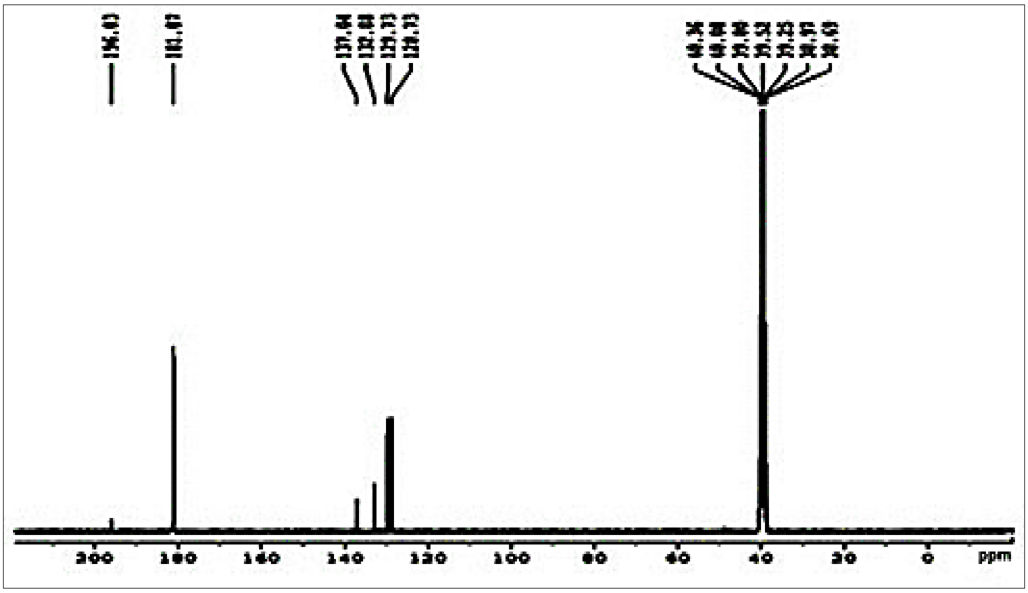

Fig 10: ^{13}C -NMR Spectrum thiosemicarbazone of a-Oxodiphenylmethane

Table 3: Spectral data thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide (^{1}H &^{13}C)

Spectrum	Signal at δ ppm	Group identification
^{1}H	7.8	Aromatic & Aliphatic Proton
	7.4 to 8.2	Ortho & Meta Proton
	0.039	CH Proton
	3.394	NH protons
	2.5	NH_2
^{13}C	178.04	Imine group
	129	Two ortho carbon
	128	Two meta carbon
	140.58	Substituted aromatic compound
	38.62 & 40.26	Hetero sulphur atom

Table 4: NMR Spectral data thiosemicarbazone of a-Oxodiphenylmethane (^{1}H &^{13}C)

Spectrum	Signal at δ ppm	Group identification
1H	7.721	Aromatic system
	8.658	The NH_2 proportion of hydrazide group
	7-8	Hetero sulphur atom
	7.219	-NH proton
13C	196.03	Non chelated ketone carbon
	137.04	Sp2 hybridised carbon atom
	132.88	Methine sp2carbon atom
	129.73&128.73	Methoxy carbon
	40.36	Methyl and sulphur atom

7. Thermal Analysis

The thermal properties of TSCCB and TSCBP were analyzed using a SDT Q600 V20.9 Build 20 instrument over a temperature range of 0 °C to 500 °C, with a heating rate of 10 °C/min, under a nitrogen atmosphere. Thermal analysis is a valuable technique for characterizing materials and assessing the thermal stability of crystals [16].The thermograms of TSCCB and TSCBP are presented in Figures 9 and 10. Sample weights of 14.9860 mg (TSCCB) and 16.6580 mg (TSCBP) were used. The thermograms display endothermic peaks at 218.74 °C (TSCCB) and 184.14 °C (TSCBP), indicating the onset of thermal decomposition. These sharp endothermic transitions suggest a good degree of crystallinity and purity in the grown crystals. Thermo gravimetric analysis (TGA) reveals three distinct weight losses in the thermograms. The first and second major weight losses occur around 200 °C and 300 °C, more precisely at 246.09 °C and 283.93 °C, respectively. These losses are attributed to the decomposition of the crystal lattice and the release of volatile components. Overall, the thermal analysis confirms that the TSCCB and TSCBP crystals exhibit significant thermal stability and crystalline purity.

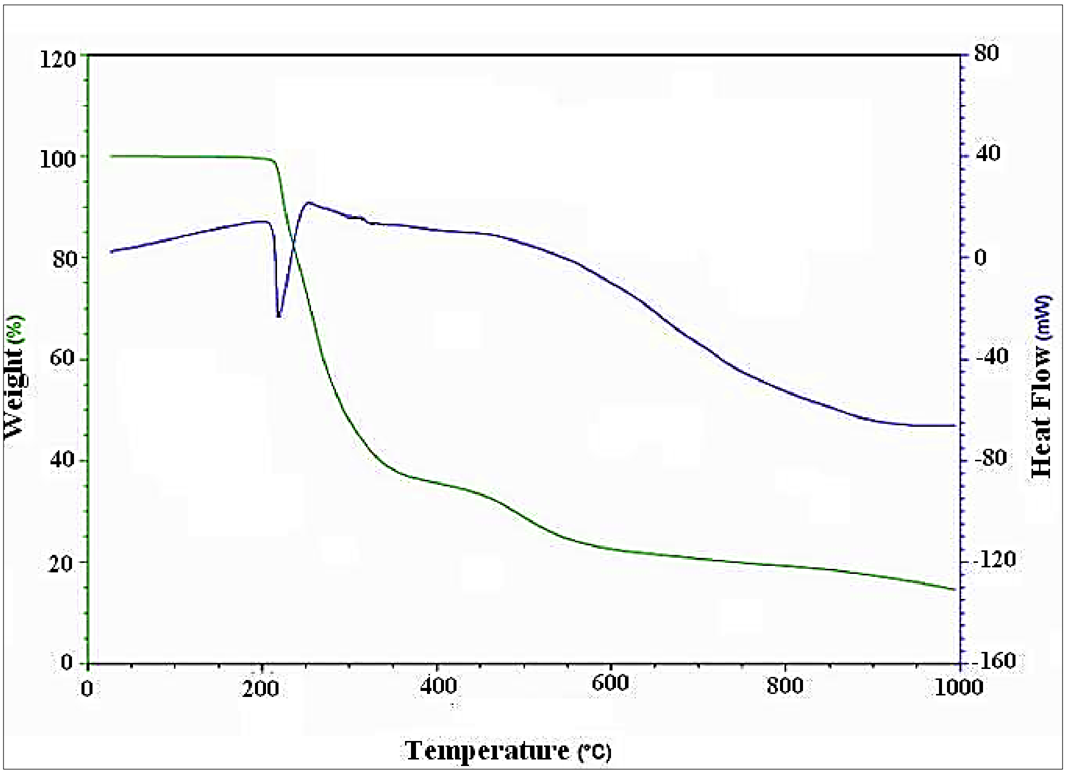

Fig 11: Thermogram of thiosemicarbazone of (E)-2-(4-chlorobenzylidene) hydrazine-1-carbothioamide

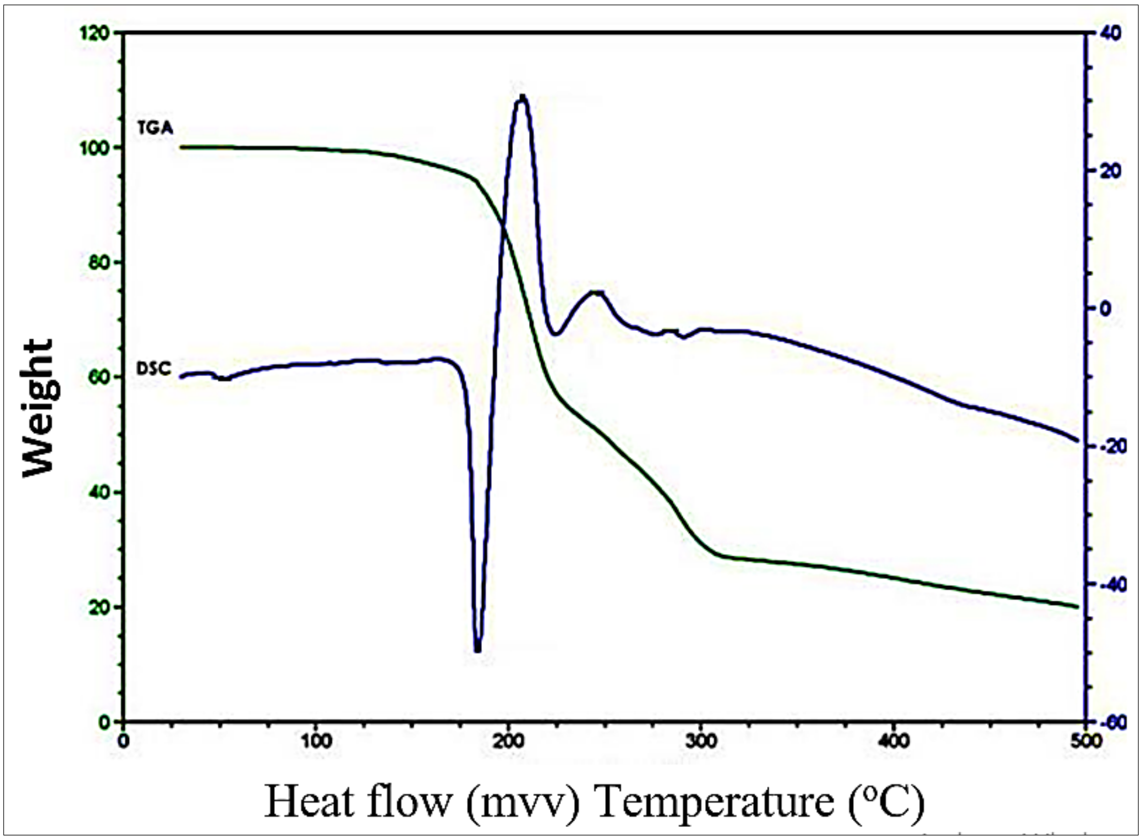

Fig 10: Thermogram of Thiosemicarbazone of a-Oxodiphenylmethane

3.6 Nonlinear Optical Studies

A Kurtz and Perry second harmonic generation (SHG) test [18] was performed to evaluate the nonlinear optical (NLO) efficiency of the TSCCB and TSCBP crystals. The grown crystals were ground into powder with uniform particle size and packed into microcapillaries of uniform bore. These samples were then illuminated using a Spectra-Physics Quanta-Ray DHS2 Nd:YAG laser. The SHG efficiency of the TSCCB and TSCBP crystals was found to be approximately 6.1 and 0.8 times that of standard reference materials, urea and potassium dihydrogen phosphate (KDP), respectively.

Conclusion

The TSCCB and TSCBP crystals were synthesized using methanol as a solvent, following a standard preparation procedure. The crystals were grown by the slow evaporation solution growth technique (SESGT). The presence of functional groups and the nature of the protons were confirmed through FT-IR, as well as ^13C and ^1H NMR spectral analyses. UV-Visible spectroscopy revealed that the crystals exhibit good transparency in the relevant wavelength region. Thermal stability was assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Nonlinear optical (NLO) studies confirmed the second harmonic generation (SHG) efficiency of the TSCCB and TSCBP crystals.

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