Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(12):135-142
(http://derpharmachemica.com/archive.html)

Synthesis, characterization and solvent effect on the optical properties of 2-semicarbazono-1-hydroxy, 1-(2-chlorophenyl)-2-(4'-methoxyphenyl) ethanol single crystal

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ABSTRACT

2-semicarbazono-1-hydroxy, 1-(2-chlorophenyl)-2-(4'-methoxyphenyl) ethanol (abbreviated as 2C4MBS) with chemical formula $C_{16} H_{16} Cl N_3 O_3$ was synthesized and a new organic crystal was grown by slow evaporation technique. Single crystal of 2C4MBS had been subjected to X-ray diffraction analysis to estimate the lattice parameters and the space group. The qualitative analysis on the compound was carried out using Fourier transform infrared (FTIR) measurements. The structure was confirmed by FTIR, Mass spectra, proton and carbon nuclear magnetic resonance (NMR) spectral analyses. Transmission of the compound in the visible and u.v, region was investigated using UV–vis spectroscopy. The thermal stability of the crystal was determined by TG-DTA analysis. The non-linear optical absorption (NOA) properties in the solution state were investigated by the Z-scan technique. 2C4MBS compound exhibited reverse saturable absorption (RSA) under nanosecond pulse irradiation.

Key words: Synthesis, crystal growth, XRD, FTIR, UV, Z scan

INTRODUCTION

Highly nonlinear materials are capable of fast and efficient processing of optical signals in the fast growing development of optical fiber communication systems [1]. The nonlinear crystals have proved to be interesting candidates for a number of applications, such as second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation etc. [2-7]. Due to the technological importance of these nonlinear crystals the need for high quality organic crystals has grown dramatically in the last decade. With rapid progress in the crystal growth technology, crystals having attractive nonlinear properties are being discovered. This has enabled the commercial development of single crystals with promising nonlinear optical properties. An organic molecule with significant nonlinear optical activity generally consists of a π-electron conjugated moiety substituted by an electron donor group at one end of the conjugated structure and an electron acceptor at the other end, forming a "push–pull" conjugated structure. The conjugated π-electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Functionalizing both ends of the conjugated π bonded system with an appropriate electron donor and acceptor group can increase the asymmetric electronic distribution in either or both the ground and excited state, thus leading to increased optical nonlinearity [8]. Organic molecules should have high second order hyperpolarizability (β) to exhibit effective NLO properties in many cases, an order of magnitude smaller than the widely known inorganic materials [9].Our earlier work on 4-methoxy benzoin [10] possess an efficient non-linear property, based on this we synthesized the title compound as one of the derivatives of benzoin [11].

Basically, semicarbazone family crystals exhibit nonlinear optical behavior and also biological activity [12, 13]. We report the synthesis, growth and characterization of a new organic crystal viz. 2-semicarbazono-1-hydroxy, 1-(2-chlorophenyl)-2-(4'-methoxyphenyl) ethanol (2C4MBS) by as slow evaporation technique.

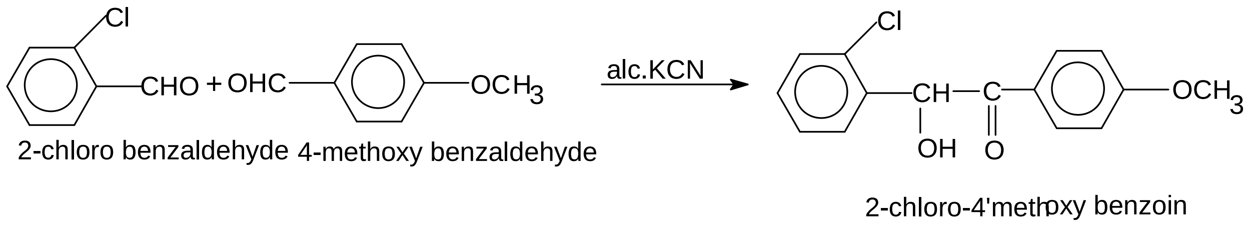
MATERIALS AND METHODS

2.1. Synthesis

The starting material for the title compound was 2-chloro-4’-methoxy benzoin (2C4MB), which has been prepared by benzoin condensation using 4 g of KCN dissolved in 75cc of water in a one litre flask**.**To this was added 6.8g (0.05moles) of anisaldehyde, 7g (0.05moles) of 2-chloro benzaldeyde and 75cc of 95% ethanol [14]. On refluxing for about half an hour, crude mixture was obtained. The crude mixture was dissolved in hot alcohol and allowed to crystallise slowly. The 2C4MB crystallized out as colourless, hexagonal crystals. The structure was confirmed through IR, NMR, Mass spectra and single XRD analysis.

Scheme 1

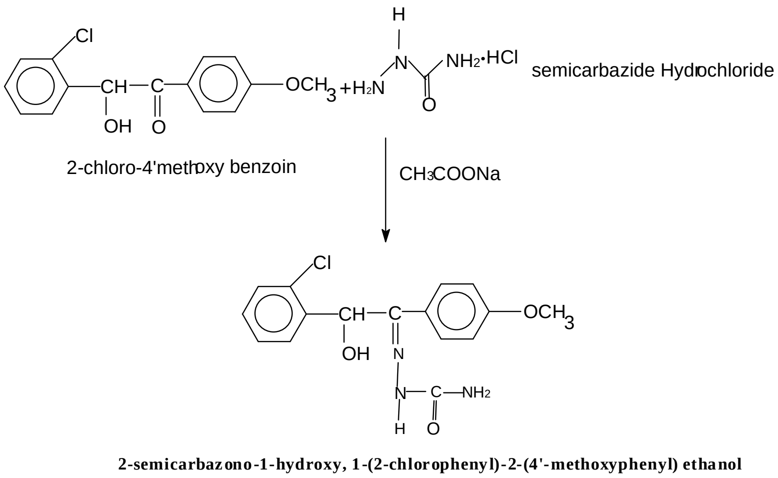
Schematic representation of 2-chloro-4’-methoxy benzoin



Semicarbazide hydrochloride, sodium acetate and 2C4MB were mixed in the mole ratio 2:4:1, respectively. The prepared solution was found to be turbid. Hence, ethanol was added and stirred well, and the solution was gently warmed till a clear solution was obtained [15]. The obtained product was washed with hexane and purified by repeated recrystallization using ethanol. Single crystal of 2C4MBS was obtained by slow evaporation technique. The melting point of the compound was found to be 76.5±1°C.

Scheme 2

Schematic representation of 2-semicarbazono-1-hydroxy, 1-(2-chlorophenyl)-2-(4'-methoxyphenyl) ethanol



2.2.Characterisation studies

Single crystal X-ray diffraction data recorded using a BRUKER AXS KAPPA APEX (II) CCD X-ray diffractometer with MoKα radiation (λ=0.71073 Å) to identify the structure of the grown crystal . The structure was solved by a direct method and refined by the full matrix least square technique using the SHELXL program. It is observed from the XRD analysis that the 2C4MBS crystal has as Triclinic, with the space group P-1. FTIR spectrum was recorded for 2C4MBS on a BRUKER 66 V FTIR spectrometer by the KBr pellet technique in the range 400–4000cm^{-1} for the identification of the functional groups.^{1}H NMR spectrum was recorded in a BRUCKER spectrometer of frequency 300MHz using MeOD as a solvent (Aldrich) and TMS (0.03%) as an internal standard. The optical absorption spectrum of 2C4MBS was recorded in a VARIAN CARY 5E spectrophotometer. Optical limiting properties were investigated from open aperture Z-Scan experiments with 7ns laser pulses at 532nm from a frequency doubled, Q switched Nd:YAG laser. Thermal analyses were carried out simultaneously in a NETZSCH STA 409 C thermal analyser from 28 to 1200^{o}C at a heating rate of 2^{0}C per min in nitrogen atmosphere.

RESULTS AND DISCUSSION

3.1. Mass spectral analysis of 2C4MBS

Mass spectral data and elemental analysis were in good agreement with the assigned formula [Fig. 1].

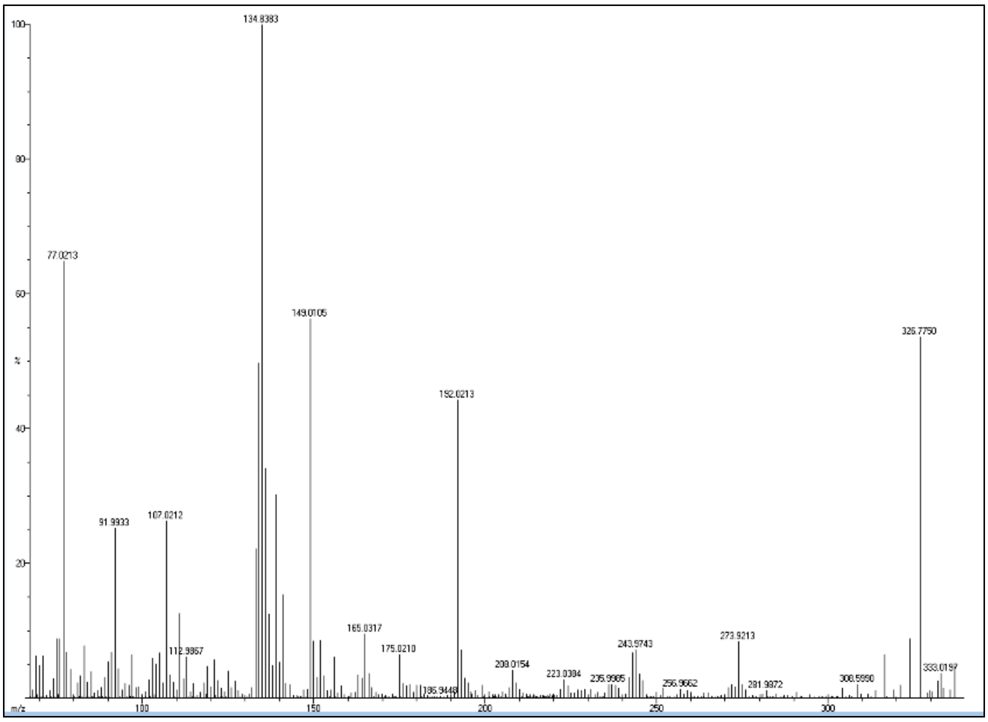


Fig. 1 Mass spectra of 2C4MBS

3.2. FTIR Spectral Analysis of 2C4MBS

In the FTIR spectrum of 2C4MBS the O–H and –NH stretching modes merge and found between 3572-3450 cm^{-1}. The bands around 2840 cm^{-1} are assigned to the aromatic

C–H stretching modes. The aliphatic -CH stretching vibration is assigned to the band at 2315 cm^{-1} and 2055 cm^{-1} in FTIR with weak intensity. The symmetric stretching mode of the carbonyl group and C=N appears as broad band around at1667 cm^{-1} with very strong intensity. The aromatic C = C symmetric stretching vibrations appear at 1604 cm^{-1} as a very strong intensity. The inplane deformation of C–OH appears around 1297- 1250 cm^{-1} as a medium band in spectrum. The OH out of plane deformation is observed as strong band around 1000 cm^{-1} in FTIR .The band at 1086 cm^{-1} and 1052 cm^{-1} is assigned to the benzene ring deformation.   The band at 729 cm^{-1} is establishes the presence of disubstituted benzene ring [Fig. 2].

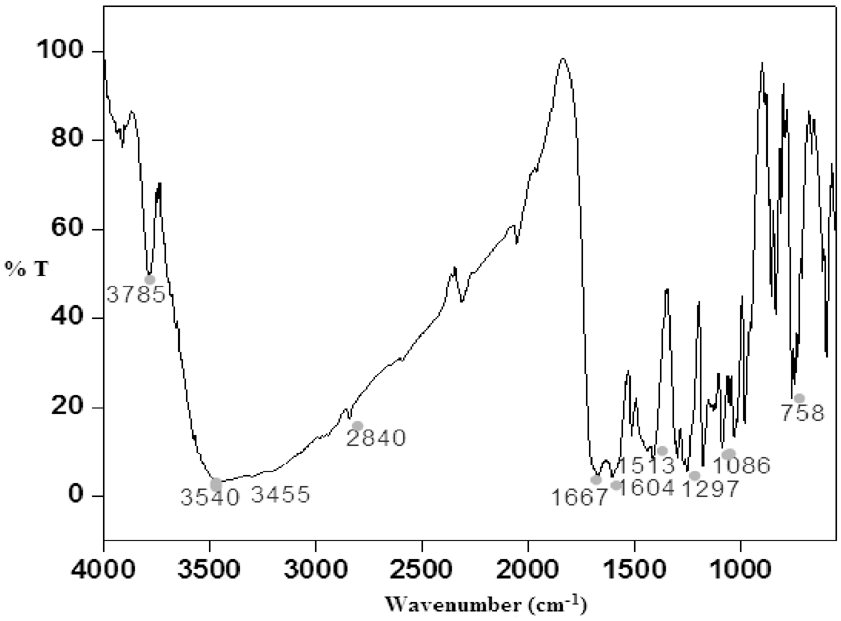


Fig. 2 IR spectra of 2C4MBS in KBr

3.3. FT NMR Spectral Analysis of 2C4MBS

The signals observed in the ^{1}H NMR and ^{13}C NMR spectra of the 2C4MBS studied and the data Fig.3 & 4. The spectra exhibit a multiplet at 6.8-7.8 ppm for the hydrogens of the aromatic rings. The -CHOH hydrogen leads to a singlet of intensity equivalent to one hydrogen at 3.3 ppm. The signals at 3.8 ppm due to the hydrogens of the -OCH_3 and signal at 6.3 ppm for –$CONH_2$ groups. The spectra show a singlet with an integration equivalent to one hydrogen at 5.9 ppm corresponding to the hydrogen of the N–NH group.

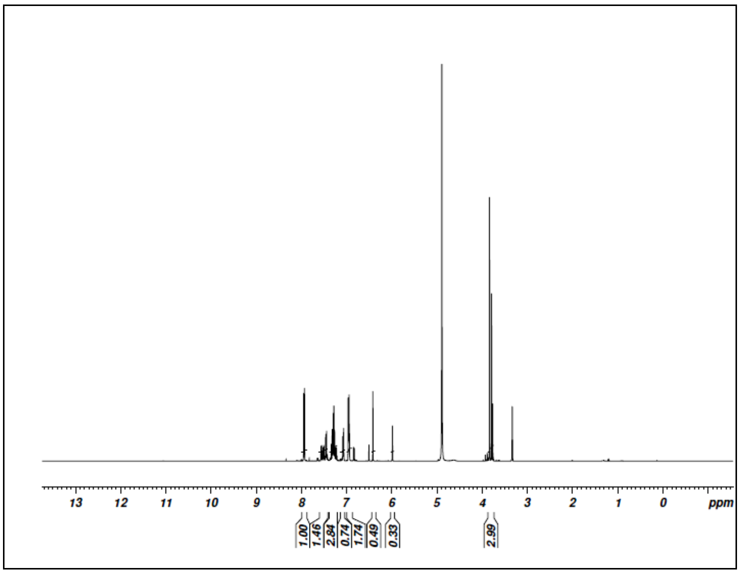


Fig. 3 ^{1}HNMR of 2C4MBS in acetone d_6

3.4.Bond Geometry (2C4MBS)

From the single crystal analysis, it was observed that the crystal belongs to triclinic system with centro symmetric space group, P_1. Lattice parameters have been determined as *a* = 7.8275(3) Å, *b* = 9.8202(3) Å, c = 11.3731(4) Å and α = 66.439(2) (2)° , β= 89.297(2)°, γ= 83.176(2)° and the volume of the unit cells is found to be 795.07(5)Å^3. The molecular structure consists of two phenyl rings linked by -CHOH and -C=N group [Fig.4].

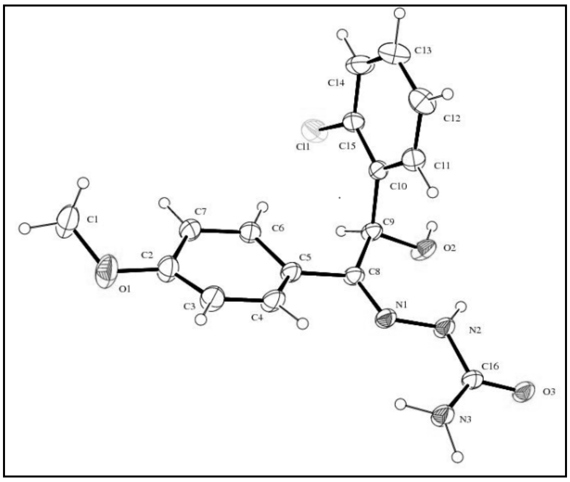


Fig. 4.Ortep diagram of 2C4MBS

3.5.Intermolecular Features (2C4MBS)

Intra molecular hydrogen bonding stabilizes the lattice structure [Fig. 5].

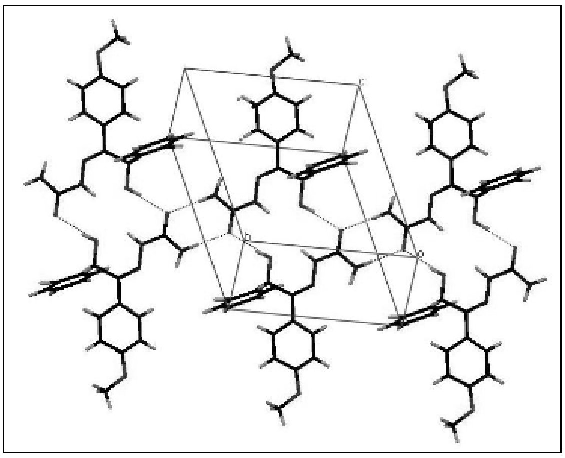


Fig. 5 Packing structure of 2C4MBS

3.6. Optical absorption

The optical absorption spectrum of a good quality grown crystal was recorded in the wavelength range 200–1000nm using a Cary 5E UV-vis-NIR spectrometer using ethanol. The obtained absorption spectrum is shown in Fig.6, where the lower cut off region is obtained at 240nm. The UV spectra show the presence of a wide transparency window lying between 400nm and 800nm with λ_{max} = 400nm. Hence, from the analysis of the absorption spectrum, it is evident that the grown crystal is transparent in the entire visible region without any absorption peak within the range, which is the key requirement for any nonlinear optical crystal. [16-17]

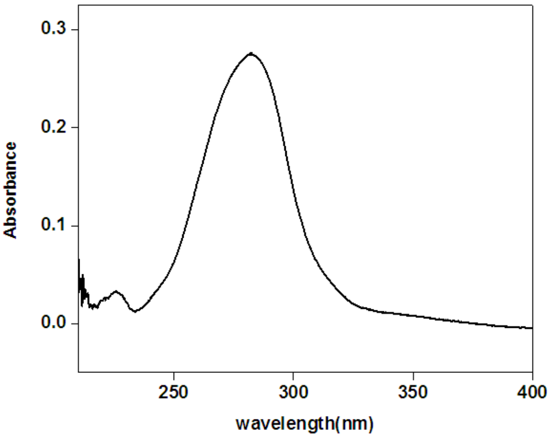


Fig. 6 UV spectra of 2C4MBS in acetonitrile

3.7. Z-Scan studies

Nonlinear optical absorption measurements can give information about photo-excited structure of state and carrier dynamics. The Z-scan technique has been used to measure the third order non-linear optical properties of semiconductors [18] dielectrics [19] organic or carbon-based molecules [20] and liquid crystals [21].

Nonlinear optical absorption (NOA) measurements of the compound 2C4MBS were carried out at nanosecond scale by open aperture Z-scan technique. Fig.7 exhibits the normalized Z-scan transmittance of 2x10^{-4} mol/L solutions of compound 2C4MBS in DMF. The nanosecond laser source was a Q-switch locked Nd:YAG (1064 nm) with a second harmonic generation of 532 nm, pulse width of 12 ns, repeat frequency of 10 Hz, average pulse energy of 0.114 mJ and peak irradiance of 0.670 GW/cm^2. As the sample was moved away from the focus point, the transmittances of both compounds were nearly a flat line, which displayed the linear absorption under weak light irradiation. As the samples were moved close to the focus point, the transmittances decreased as the laser irradiance increased. At the focus point (Z¼0) where the laser irradiance reached maximum, the normalized transmittance decreased to a minimum. These results indicated that 2C4MBS was of obvious reverse saturation absorption (RSA). For conjugated donar-acceptor systems, the distortion of molecular cloud under strong laser irradiation was the reason for nonlinear phenomena. For conjugated π systems of organic compounds, the conjugation behavior of the molecular bone can be easily characterized by UV–Vis spectroscopy. For this purpose, the UV–Vis absorption spectra of compound 2C4MBS were measured. It was obvious that the λ_{max} of 2C4MBS appeared in the UV region, and the λ_{max} of compound at 290nm.

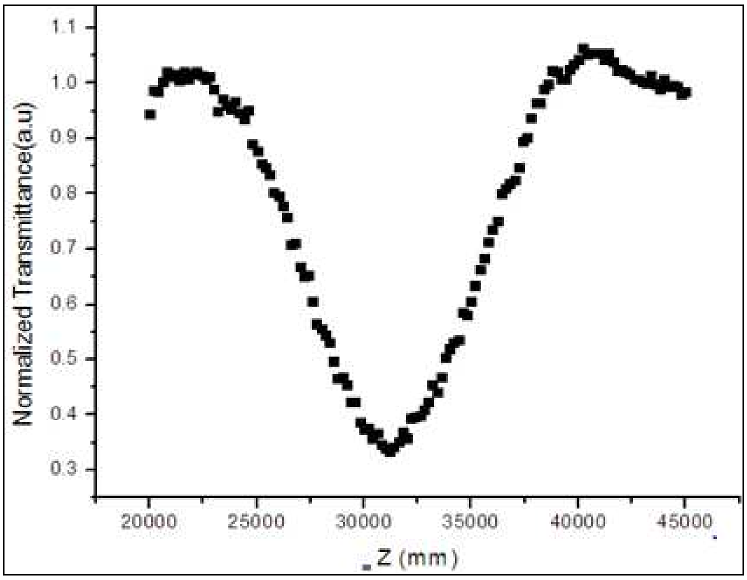


Fig. 7 Non linear absorption coefficient of compound 2C4MBS

3.8. Thermal studies

Thermo gravimetric (TG) and differential thermal analysis (DTA) were carried out simultaneously by a thermal analyzer TGA Q500 V20.10 Build 36. A ceramic crucible was used for heating the sample and the analysis were carried out in an atmosphere of nitrogen at a heating rate of 20 ◦C per minute for the temperature range 50–450 ◦C and are illustrated in Fig. 8 .The endothermic peak at 76.5°C corresponds to the melting point of the compound. An exothermic peak appears at 210°C, which is associated with weight loss as observed from TGA curve. Thus, the compound undergoes exothermic decomposition that results in weight loss of 75% up to 400°C.Prolonged heating beyond 250°C shows complete weight loss of 89.7% due to elimination of volatile substances. Thermal stability of the compound was found to be appreciably high; hence the compound can be used as a drug.

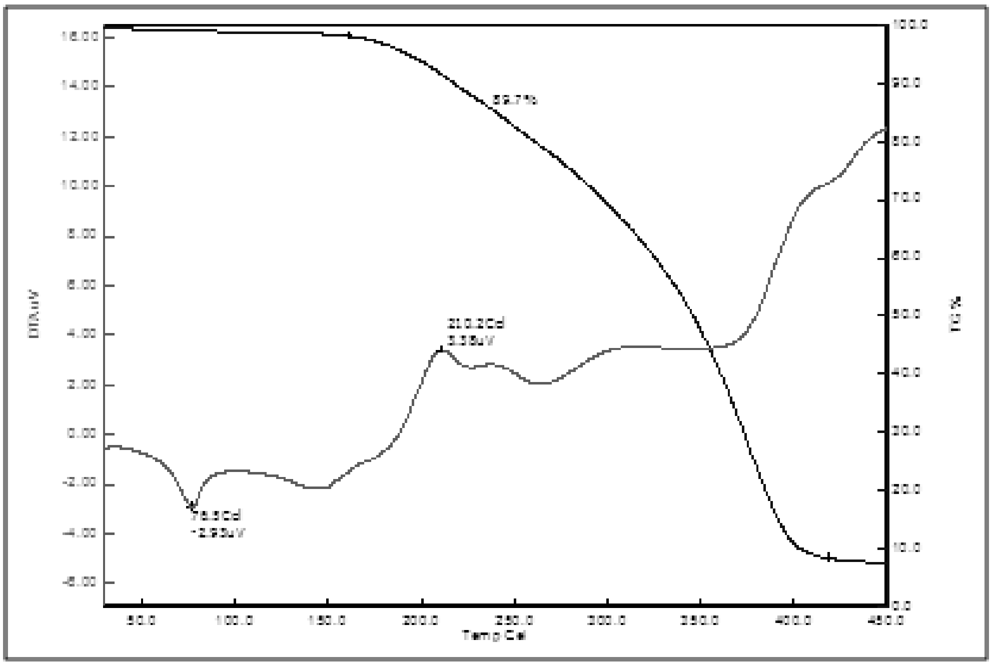


Fig.8 TGA-DTA curve of 2C4MBS

CONCLUSION

The 2C4MBS single crystal was grown by the slow evaporation method. XRD, FTIR, Mass, ^{1}H NMR, and UV absorption studies were carried out for characterization of the synthesized crystal. Single crystal XRD confirmed the crystal structure. Optical studies showed that the crystal had a wide transparency window in the entire visible region, making it an ideal candidate for NLO device applications. Z-Scan technique reveals that 2C4MBS possesses saturable absorption, respectively. The measured third-order non-linear properties confirm its suitability for optical limiting and switching application. Thus the complete study of various properties suggested that the studied compound may be a potential candidate for applications in nonlinear optical area. The decomposition temperature and percentage weight loss of the material were found out from the TG/DTA analysis. The degree of crystallinity and purity was also confirmed from a sharp endothermic peak in the DTA.

Supplementary Material

CCDC 847765 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK (0) 1223-336033;e-mail:deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors are grateful to acknowledge SAIF, IIT-Madras for Supporting in all the spectroscopic studies. The authors also acknowledge SRM Valliammai Engineering College and Sairam Engineering College for continuous support to carry our work.

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