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Growth, spectral, and thermal characterization of 2-hydroxy-3-methoxybenzaldehyde semicarbazone

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Abstract 2-Hydroxy-3-methoxybenzaldehyde semicarbazone (HMBS) has been synthesized from 2-hydroxy-3-methoxybenzaldehyde and semicarbazide hydrochloride using sodium acetate as catalyst. Good quality single crystals of HMBS were successfully grown by slow evaporation method at room temperature using a mixture of DMF and ethanol as solvent. Fourier transform infrared and Fourier transform Raman spectral studies have been performed to identify the functional groups. Single-crystal XRD study was conducted to obtain the crystal structure and lattice parameters. The grown crystal was subjected to ^{1}H- and ^{13}C-NMR spectral studies in order to confirm its structure and purity. The compound crystallizes into a monoclinic $P21/c$ space group. Intermolecular hydrogen-bonding interactions facilitate unit cell packing in the crystal lattice. The UV–Vis spectrum confirmed the transparency of the compound between the wavelengths 420 and 1,100 nm, which is a characteristic property of a nonlinear optical (NLO) material. The thermal decomposition of the compound under static air atmosphere was investigated by simultaneous TG–DTG at a heating rate of 10 °C min^{-1}. The NLO property of HMBS was confirmed from the second-harmonic generation by Kurtz–Perry powder test.

Keywords Semicarbazone · Solution technique · X-ray diffraction · NMR · Thermal studies

Introduction

The chemistry of semicarbazones has been receiving considerable attention primarily because of their importance in biological fields [1–5]. These compounds are useful as efficient protecting groups for aldehydes and ketones, and they have been widely used as spectrophotometric agents for the analysis of metal ions [6, 7]. Semicarbazones are extensively used in purification and characterization of carbonyl compounds [8]. In recent decades, organic NLO crystals with good nonlinear properties have attracted the attention of both chemists and physicists owing to their potential applications in the area of laser technology, optical communication, optical information processing, and optical data storage technology [9, 10]. Semicarbazones are well known for their nonlinear optical (NLO) behavior due to the presence of delocalized π-electrons [11, 12]. They are the most important and widely studied class of chelating ligands due to remarkable ligation properties and simple preparation methods. They coordinate as neutral or anionic chelators commonly via their azomethane nitrogen and the oxygen atoms. Aryl semicarbazones can be considered as a new class of compounds with anticonvulsant activity [13]. Gambino et al. [14] reported the physicochemical, structural characterization, and biological activities of gallium(III) complexes of tridentate salicylaldehyde semicarbazone derivatives. The synthesis, characterization, and thermal properties of mixed ligand cobalt(III) complexes with salicylaldehyde semicarbazone and pyridine were investigated by Leovac et al. [15].

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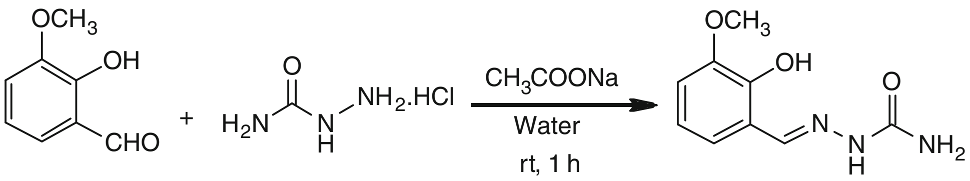
Scheme 1 Synthesis and molecular structure of HMBS



Low-temperature solution growth method is a powerful purification process and the obtained crystals are less defective than those obtained from high-temperature growth methods [16]. In this paper, the synthesis, growth, and thermal properties of a new organic crystal namely 2-hydroxy-3-methoxybenzaldehyde semicarbazone by slow evaporation solution growth technique using a mixture of dimethyl formamide (DMF) and ethanol as solvent are reported. Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectral studies have been performed to identify the functional groups. Single-crystal X-ray diffraction (XRD) study was conducted to obtain the crystal structure and lattice parameters. The grown crystal was subjected to ^{1}H- and ^{13}C-NMR spectral studies in order to confirm its structure and purity. The UV–Vis absorption spectrum was recorded to study the optical transmittance in the range of 200–1,100 nm. The thermal decomposition of the compound under static air atmosphere was investigated by simultaneous TG–DTG at a heating rate of 10 °C min^{-1}.

Experimental

Materials and physical measurements

Commercial reagents 2-hydroxy-3-methoxybenzaldehyde (Aldrich) and semicarbazide hydrochloride (Aldrich) were used as such. The carbon, nitrogen, and hydrogen contents of the compounds were determined using Vario EL III CHNS analyzer. The IR spectra were recorded on a Thermo Nicolet Avtar 310 DTGS spectrometer (4,000–400 cm^{-1}) in KBr pellets. The FT-Raman spectrum was obtained on a Bruker IFS 100/S, Germany. For excitation of the spectrum, the emission of Nd:YAG laser was used with excitation wavelength of 1,064 nm and maximal power of 150 mW for the measurement on solid sample. The spectral resolution after apodization was 4 cm^{-1}. ^{1}H- and ^{13}C-NMR spectra of the compound were recorded in dimethyl sulphoxide (DMSO-d_6) on Bruker Avance III, 400 MHz spectrometer. The UV–Vis spectrum of the compound was recorded using Varian Cary 5000 spectrometer in the range 200–1,100 nm. Thermogravimetric analysis (TG–DTG) was carried out in air with a heating rate of 10 °C min^{-1} using Perkin Elmer Diamond TG–DTG analyzer. Single-crystal XRD data of the title compound was collected on Bruker axs kappa apex2 CCD diffractometer with Mo-Kα (λ = 0.71073 Å) at 293 K. Data collection and reduction were performed by APEX2 and SAINT/XPREP programs. The structure was solved and refined using SIR 92 and SHELXL-97 [17, 18]. A crystal with approximate dimension 0.35 × 0.30 × 0.25 mm^{3} was selected and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms are attached to nitrogen was geometrically fixed at calculated positions. Those on nitrogen atoms were refined from Fourier maps. Refinement of F^2 was done against all reflections. The NLO property of HMBS was measured by Kurtz–Perry powder technique. Q-switched quanta PRO-LAB 170 Nd:YAG laser with a fundamental wavelength of 1,064 nm and having a pulse width of 10 ns at a repetition rate of 10 Hz was used as a light source.

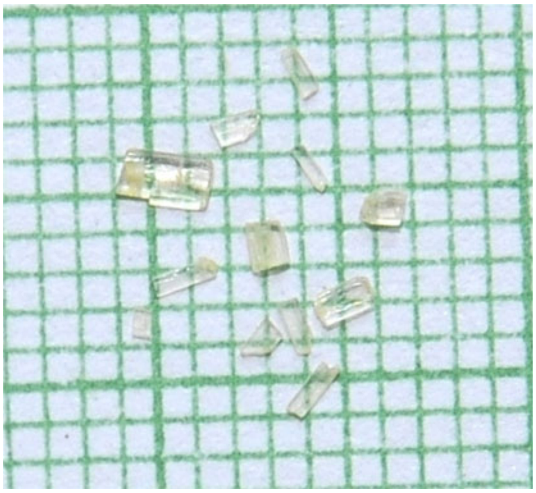


Fig. 1 Grown crystals of HMBS

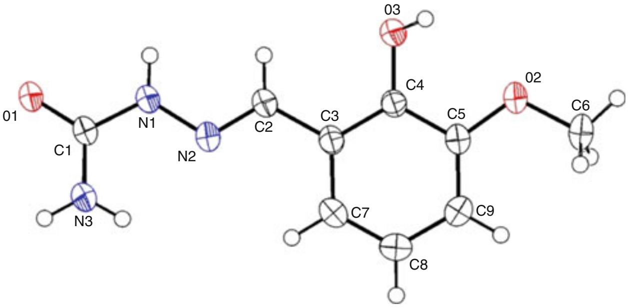
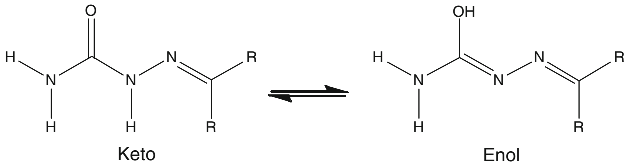


Fig. 2 Molecular structure of HMBS



Scheme 2 Tautomerism in semicarbazone

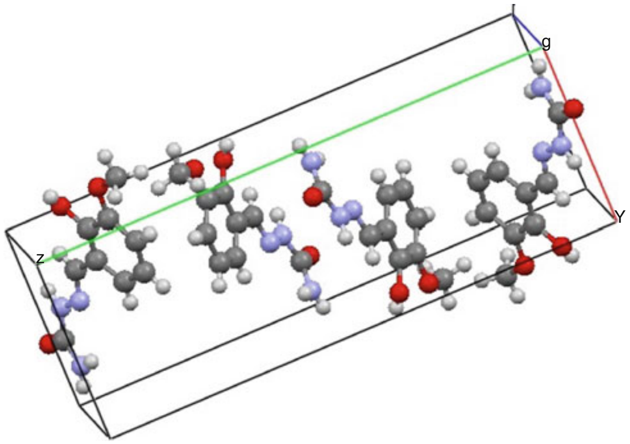


Fig. 3 Molecular packing diagram of HMBS

Synthesis and crystal growth

Semicarbazone of 2-hydroxy-3-methoxybenzaldehyde was synthesized from the starting materials of semicarbazide hydrochloride and 2-hydroxy-3-methoxybenzaldehyde using sodium acetate as catalyst (Scheme 1). Semicarbazide hydrochloride and sodium acetate were dissolved in deionized water in the molar ratio of 1:1.5 and then 0.5 M of 2-hydroxy-3-methoxybenzaldehyde was added to the solution. The mixture was stirred at room temperature for 1 h, and the resultant precipitate was collected, dried, and re-crystallized from absolute ethanol (Yield 70 %, m.p. 182 °C. Elemental analysis, found (calculated): C 51.75(51.67); H 5.44(5.30); N 20.15 (20.09).

Crystal growth experiments were carried out by slow evaporation method. The obtained crystals of HMBS were further purified by repeated recrystallization processes using ethanol as a solvent for three times. The purified product was dissolved in a mixture of dimethyl formamide (DMF)–ethanol (3:1) as solvent. The above solution was taken in an optimally covered container and placed in a constant temperature bath at 35 °C for controlled evaporation. After 15 days, spontaneous nucleation was noticed in the solution. Good transparent single crystals of HMBS were collected in 30 days. The photographs of the harvested crystals are shown in Fig. 1.

Table 1 FT-IR and FT-Raman vibrational frequencies of HMBS and their assignments

IR/cm^{-1}	Raman/cm^{-1}	Assignments
3,466	–	υ_s NH_2
3,279	–	υNH
3,167	3,101	υCH
3,076	3,078	υCH
3,015	3,021	υCH
2,987	2,995	$\upsilon_{as}CH_3$
2,966	2,943	$\upsilon_s CH_3$
1,676	–	υC=O
1,586	1,612	υC=N
–	1,578	δNH_2
1,516	1,504	υPh
1,473	1472	υPh
1,438	1,458	υPh
1,362	1,362	υPh
1,285	1,325	υPh
1,263	1,263 and 1,244	δCH
1,218	1,220	δCH
1,186	1,188	δCH
1,149	1,169 and 1,150	δCH
1,087	1,085	ρNH
1,064	1,046	Ring breathing
1,005	1,017	γCH
963	–	γCH
919	919	τNH_2
880	–	γCH
827	826	γCH
782	772	γCH
762	–	ωNH_2
731	–	ωNH
663	667	γPh
632	614	δC=O
589	580	δCC
568	562	γC=O
516	512	δC=N
421	–	δPh

υ stretching, δ in-plane bending, ρ rocking, γ out-of-plane bending, ω wagging, τ twist, *Ph* phenyl, *sh* shoulder, *as* asymmetric, *s* symmetric

Result and discussion

Crystal structure

The molecular structure of HMBS along with the atom numbering scheme is given in Fig. 2. The compound crystallizes in the space group *P*21/*c* with one molecule in the asymmetric unit. The obtained lattice parameters revealed that the crystal belongs to monoclinic system with $a = 7.0792$ Å, $b = 20.5122$ Å, $c = 6.5686$ Å and $\alpha = 90°$, $\beta = 99.2°$,

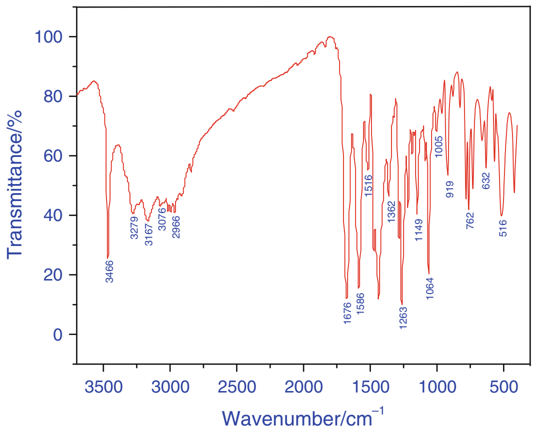


Fig. 4 FT-IR spectrum of HMBS

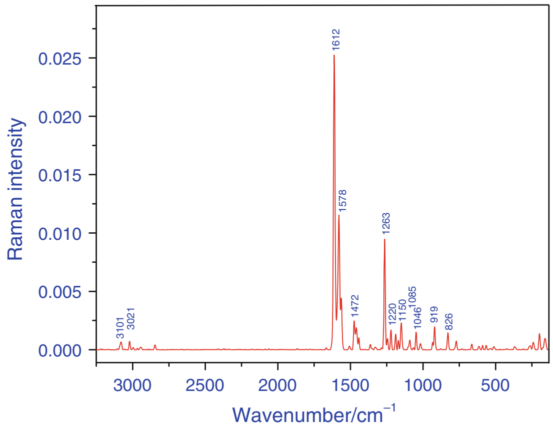


Fig. 5 FT-Raman spectrum of HMBS

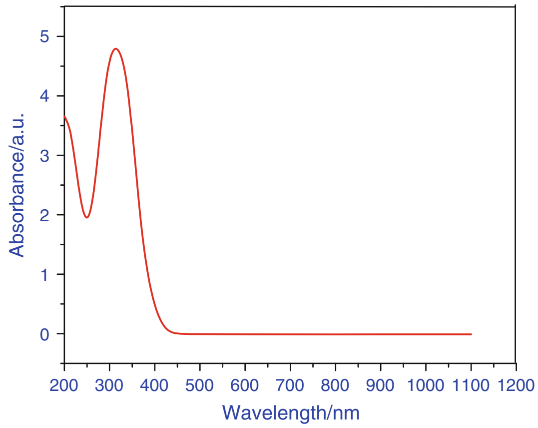


Fig. 6 UV–Vis spectrum of HMBS

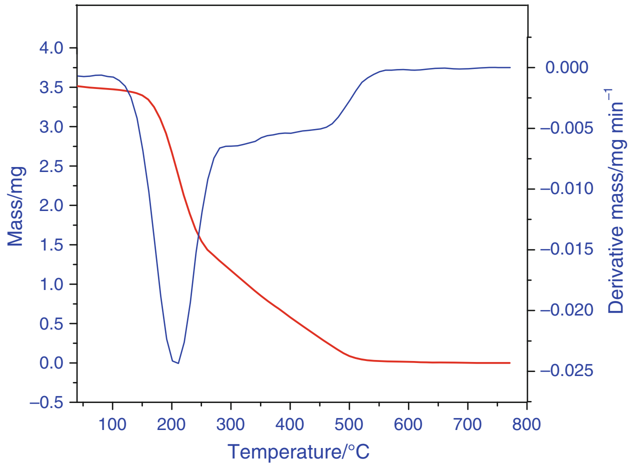


Fig. 7 TG–DTG curves of HMBS

$\gamma = 90°$, and cell volume $V = 941.61$ Å^3. The adjacent units are interconnected through intermolecular hydrogen-bonding interactions which plays a major role in the packing arrangement of these molecules in the unit cell. The C_2–N_2 bond distance 1.2725 Å is appreciably close to that of C=N double bond distance 1.28 Å confirming the azomethane bond formation. Semicarbazones generally exists in two tautomeric forms namely keto and enol forms (Scheme 2).The existence of semicarbazone in keto form in the solid state is evidenced by the C_1–O_1 bond distance of 1.2447 Å, which is very close to the formal C=O bond length 1.21 Å. However, the N_1–N_2 (1.3632) and N_1–C_1 (1.3535) Å bond distance are intermediate between the ideal values of corresponding single (N–N; 1.45 and C–N; 1.47) and double bonds (N=N; 1.25 and C=N; 1.28), which is a support of an extended π-delocalization along the semicarbazone chain [19] (Fig. 3).

FT-IR and FT-Raman spectral analyses

The characteristic frequencies of HMBS were assigned and the absorptions are compared with similar compounds [20–24]. The assigned frequencies are tabulated in Table 1. The NH symmetric stretching vibration appears as a strong broad band at 3,466 cm^{-1} in the FT-IR spectrum. The bands at 1,087 cm^{-1} in IR and 1,085 cm^{-1} in Raman spectrum are assigned to NH rocking vibration. The out-of-plane twist τ-NH_2 is observed at 919 cm^{-1} in both IR and Raman spectra. The wagging mode ωNH_2 is observed at 762 cm^{-1} in the IR spectrum and it is usually easy to recognize by its broad structure. The medium bands in the range 3,170–3,010 cm^{-1} are ascribed to the aromatic C–H stretching vibrations. The bands at 2,987 and 2,966 cm^{-1} in the IR spectrum and bands at 2,995 and 2,943 cm^{-1} in the Raman spectrum are assigned to the C–H asymmetric and symmetric stretching vibrations of the methoxy group. The presence of a band at 1,676 cm^{-1} in the IR spectrum is assigned to υ(C=O) stretching vibration which reveals the presence of only keto form of the molecule in the solid state. The peak at 1,586 cm^{-1} in the IR spectrum is assigned to characteristic C=N stretching vibration of the Schiff base [25].The aromatic ring skeletal vibration is

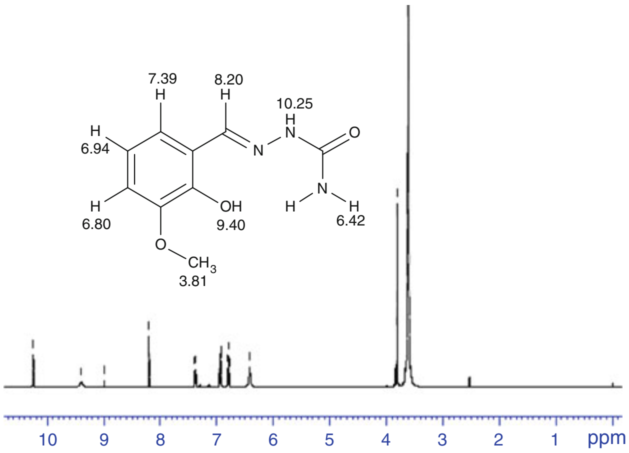


Fig. 8 ^{1}H-NMR spectrum and assignments for HMBS

observed around at 1,450 cm^{-1}. The ring breathing mode appears as a weak band at 1,046 cm^{-1} in Raman spectrum, at 1,064 cm^{-1} in the IR spectrum. The peaks lying below 1,500 cm^{-1} could be due to C–H and the N–H bending vibrations. The bands in the region 950–550 cm^{-1} are due to the out-of-plane bending of the C–H protons and C–C bonds of the aromatic ring (Figs. 4, 5).

UV–Vis spectral analysis

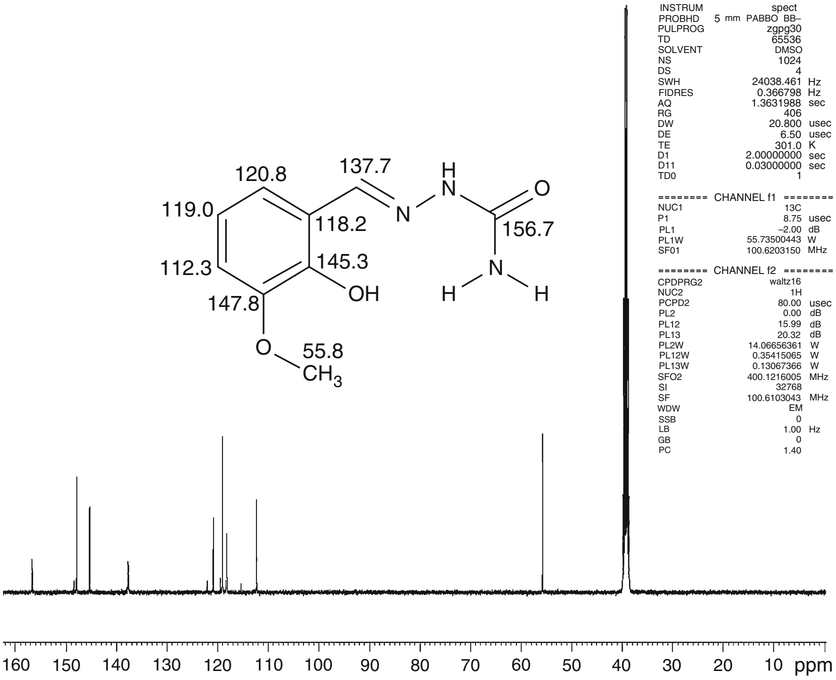
The UV–Vis spectrum of HMBS was scanned between 200 and 900 nm (Fig. 6). The spectrum of the compound exhibits an absorption band at 314 nm is due to $\pi \rightarrow \pi^*$ transitions. The UV–Vis spectrum of HMBS also shows clearly that there is no absorption band between 420 and 1,100 nm. This illustrates that HMBS has good transparency in the visible and near-IR regions. From the UV–Vis absorption studies, it can be said that HMBS has good transparency in the visible region and this material can be used for NLO applications [26].

Thermal analysis

The TG analysis for the compound was carried out within the temperature ranges from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. The TG and DTG curves of HMBS (Fig. 7) indicate that the sample is stable up to 180 °C and shows two decomposition stages. They were denoted by the DTG peaks at 204 and 450 °C, respectively. The first stage of decomposition started at about 180 °C and completed at 240 °C, and second stage of decomposition started at about 250 °C and completed at 530 °C. The thermal analysis confirms the purity and single-crystalline nature of solution grown 2-hydroxy-3-methoxybenzaldehyde semicarbazone crystals. The crystal is stable up to the melting point without any phase transition and hence it may be useful for making the NLO devices below its melting point.

^{1}H-NMR spectrum

The ^{1}H-NMR spectrum of the compound taken in DMSO-d_6 along with the spectral assignments is given in Fig. 8. The signal for N–H proton is observed at $\delta = 10.25$ ppm. These protons are shifted to downfield because they are attached to heteroatoms and are decoupled by electrical



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INSTRUM              spect
PROBHD    5 mm  PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1024
DS                       4
SWH              24038.461  Hz
FIDRES            0.366798  Hz
AQ               1.3631988  sec
RG                     406
DW                  20.800  usec
DE                    6.50  usec
TE                   301.0  K
D1              2.00000000  sec
D11             0.03000000  sec
TD0                      1

========  CHANNEL f1  ========
NUC1                   13C
P1                    8.75  usec
PL1                  -2.00  dB
PL1W           55.73500443  W
SF01           100.6203150  MHz

========  CHANNEL f2  ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00  usec
PL2                   0.00  dB
PL12                 15.99  dB
PL13                 20.32  dB
PL2W           14.06656361  W
PL12W           0.35415065  W
PL13W           0.13067366  W
SFO2           400.1216005  MHz
SI                   32768
SF             100.6103043  MHz
WDW                     EM
SSB                      0
LB                    1.00  Hz
GB                       0
PC                    1.40
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Fig. 9 ^{13}C-NMR spectrum and assignments for HMBS quadrupole effects. The resonance due to –OH signal has appeared as a broad peak at 9.40 ppm. The $-NH_2$ protons produce a broad signal at 6.42 ppm. Absence of any coupling interactions at olefinic C–H protons is due to the unavailability of protons on neighboring atoms rendering singlet peak at $\delta = 8.20$ ppm. A sharp singlet at $\delta = 3.81$ ppm is attributed to the methoxy protons which are chemically and magnetically equivalent. The three aromatic ring protons produce characteristic signals in between 6.80 and 7.39 ppm.

^{13}C-NMR spectrum

^{13}C-NMR spectrum of HMBS was recorded in DMSO-d_6. Assignments of different resonating peaks to respective carbon atoms are presented in Fig. 9. The proton-decoupled ^{13}C spectrum of the compound contains nine peaks corresponding to nine sets of carbon atoms. The signal at 156.7 ppm represents the carbonyl carbon (C=O). The signal at 55.8 ppm represents the carbon atom of the methoxy group attached to the benzene ring. The appearance of a peak at 137.7 ppm can be assigned to the azomethane (–C=N) carbon atom. The remaining signals ranging from 118.2 to 147.8 ppm are due to aromatic carbons. From this, it is understood that the product formed is free from solvent and reactant impurity.

NLO test

The crystals were ground to a fine powder and packed tightly in a microcapillary tube. Then the sample was exposed to the Nd:YAG laser beam having a pulse width of 10 ns. Potassium dihydrogen phosphate (KDP) was used as a reference material for the measurement. The second-harmonic radiation generated by the randomly oriented microcrystal was focused by a lens and detected by a photomultiplier tube. The NLO property of HMBS was confirmed by the emission of green radiation ($\lambda = 532$ nm) from the sample [27, 28]. The second-harmonic efficiency of HMBS is found to be 3.1 times that of KDP.

Conclusions

In summary, single crystals of semicarbazone of 2-hydroxy-3-methoxybenzaldehyde have been grown by slow evaporation and are characterized by elemental analysis, FT-IR, FT-Raman, UV–Vis, ^{1}H-NMR, ^{13}C-NMR, and XRD studies. The XRD results confirmed the single-crystalline nature of the solution grown HMBS. The compound crystallizes into monoclinic $P21/c$ space group. The UV–Vis spectrum confirmed the transparency of the compound between the wavelengths 420 and 1,100 nm, which is characteristic to property of an NLO material. Thermal studies confirmed the purity and single-crystalline nature of the solution grown HMBS. The sample is stable up to 180 °C and shows two decomposition stages in the temperature ranges 180–240 °C and 250–530 °C. Kurtz powder second-harmonic generation test confirms the frequency doubling of the grown crystal and its efficiency is 3.1 times as large as KDP. Hence, it is concluded that the grown crystals may find potential applications in optoelectronic applications.

Supplementary materials

Full crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 873657 for the compound 2-hydroxy-3-methoxybenzaldehyde semicarbazone. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033; email: deposit@ccdc.cam.uk or at www: http://www.ccdc.cam.ac.uk).

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