

Crystal growth and characterization of 4-nitro-4'-methoxy benzylidene aniline (NMOBA)

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Abstract

We report the crystal growth studies of 4-nitro-4'-methoxy benzylidene aniline (NMOBA). NMOBA was synthesized by the condensation of the corresponding aniline and aldehyde. Formation of the product was confirmed from the FTIR and NMR spectral analyses. Powder second harmonic generation analysis of the crystal showed that its efficiency is 1.24 times than that of KDP. The solubility of NMOBA was determined in toluene at different temperatures. Single crystals were grown from toluene by restricted evaporation and slow cooling methods. The structural characterization of the grown crystal was carried out by X-ray diffraction method and the thermal properties were studied by TGA, DTA and DSC experiments and optical transparency of the sample was determined by UV–VIS–NIR spectroscopy.

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1. Introduction

Conjugated organic molecules have very large second-order optical non-linearities [1]. Organic crystals in terms of non-linear optical property possess advantages when compared to their inorganic counterparts. In addition, they have large structural diversity [2]. Donor–acceptor benzene derivatives are well known to produce high molecular non-linearity. Two energy models and the donor–acceptor π -charge transfer model for hyper-polarizability (β) proposed by Ouder and Chemla [3] paved way for the emergence of numerous NLO-active organic molecules. An organic molecule should possess large second-order hyper-polarizability (β) to exhibit good non-linear optical properties [4]. β can be enhanced

by increasing the intra-molecular charge transfer interaction and by extending the size of π -conjugated system [5]. Benzylidene aniline derivatives are successful examples for high non-linear optically active crystals. One of the well-known benzylidene aniline derivatives used in NLO applications is 4-nitro-4'-methyl benzylidene aniline (NMBA) [6]. NMBA crystallizes in two polymorphic forms, triclinic and monoclinic [7]. In addition to it, NMBA shows different habits from needles to rhombic plates when grown in solvents of different polarities [8,9]. Octahedral crystals having dimension 56 mm \times 22 mm \times 10 mm of NMBA are grown [10].

In this work, we introduce a new benzylidene aniline derivative, NMOBA, which is 4-nitro-4'-methoxy benzylidene aniline. NMOBA is a benzylidene aniline with a charge transfer interaction between the *para*-methoxy donor ($-\text{OCH}_3$) and nitro-acceptor ($-\text{NO}_2$). Benzylidene aniline molecule having a methoxy group as a weaker donor has a

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relatively large β which is about seven times larger than that of *p*-nitro aniline in which the amino group is the donor [4]. In the present study, we report for the first time the synthesis of NMOBA, its structural confirmation, solubility determination, crystal growth and structural, thermal, second harmonic generation and optical characterization studies.

2. Experimental results and discussion

2.1. Synthesis and purification

NMOBA was synthesized by the condensation reaction of 4-nitro benzaldehyde (99.9% of Merck) and 4-methoxy aniline (99.9% of Merck). The synthesized product was recrystallized three times using ethyl acetate. Activated charcoal was added during the recrystallization process for removing colored impurities. The purified sample was shiny reddish yellow in color. The purity of the synthesized compound was ascertained by the determination of its melting point. The structural confirmation was done with the aid of FTIR and NMR spectral methods.

2.2. FTIR spectral analysis

FTIR spectrum was recorded for the purified sample using Perkin Elmer-Paragon-500 (UK), FTIR spectrophotometer for its group confirmation. The spectra were recorded by KBr pellet technique between the range 400 cm^{-1} and 4000 cm^{-1} . From the following observations, the presence of the specific groups is confirmed.

Aromatic nitro compounds can be recognized from two strong bands in the region $1570\text{--}1500\text{ cm}^{-1}$ and $1370\text{--}1300\text{ cm}^{-1}$. The presence of the bands in the above regions is confirmed from the absorptions at 1511 cm^{-1} and 1323 cm^{-1} (Fig. 1). The expected range for methoxy group is $1653\text{--}1639\text{ cm}^{-1}$. In the present case, the absorption is noticed at 1623 cm^{-1} . Benzylidene anilines display their C=N

stretching as a band at 1600 cm^{-1} [11]. The band obtained at 1598 cm^{-1} is a proof for the formation of imine group (C=N) as a result of the condensation reaction between aldehyde and amine.

Four regions of the spectrum are associated with the confidently assignable vibrations of aromatic residues, which are C–H stretching, C=C stretching, C–H deformation and a group of overtone combination bands. C–H stretching absorptions are weak absorptions expected around 3030 cm^{-1} . A weak band is obtained around this region for our sample. C=C stretching absorption is confirmed from the band at 1502 cm^{-1} . An out-of-plane C–H deformation band is a characteristic of aromatic ring with 1,4 substitution. It is confirmed from the band at 856 cm^{-1} . Para-di-substituted benzenes show C–H deformation vibrations in the region $840\text{--}800\text{ cm}^{-1}$. It is evidenced from the C–H deformation vibration at 822 cm^{-1} [12]. Absence of characteristic aldehydic bands at 2720 cm^{-1} and 2820 cm^{-1} indicates that there is no aldehyde group in the final product. Substituted aromatic amines absorb in the region $3470\text{--}3390\text{ cm}^{-1}$. FTIR spectrum does not show any signal corresponding to aldehyde and amine group present in the reactants.

2.3. NMR spectral analysis

Proton NMR spectrum of the purified NMOBA sample was recorded using Jeol:GSX400 instrument in deuterated chloroform with tetramethylsilane (TMS) as the internal standard. Structure of NMOBA containing six different types of protons is shown in Fig. 3. The proton NMR spectrum of NMOBA (Fig. 2) shows six different peaks as expected, at different chemical shift positions from the reference standard [13].

The protons H_a and H_b can see each other as aligned (parallel) or opposed (anti-parallel) and come to resonance twice. Thus, protons H_a and H_b appear as doublet. The proton pairs H_a and $H_{a'}$, H_b and $H_{b'}$, H_c and $H_{c'}$ and H_d and $H_{d'}$ are chemically equivalent by virtue of the symmetry within the molecule and have same electronic environment. So, their signals are indistinguishable, for example, signals of H_a and $H_{a'}$ appear in the same position. Following the same manner, aniline ring protons also give two doublets.

The imine protons have no neighbour proton and it should appear as a singlet. The singlet signal A at δ 8.57 ppm corresponds to the proton of imine group [14]. δ values for the protons of $-\text{CH}_3$ group attached to $-\text{OAr}$ radicals are expected at 3.7 ppm [12]. The singlet signal F at δ 3.85 ppm denotes protons of methoxy group.

Nitro group shift ortho-protons (H_a) by 1 ppm higher from the normal signal for benzene ring protons (δ 7.27 ppm). The doublet B at δ 8.29 ppm can be assigned for the H_a proton. Similarly, $-\text{NO}_2$ group is expected to shift the meta-proton (H_b) signal to δ 7.37 ppm. The doublet D around δ 7.30 ppm can be taken as the peak of H_b proton. The methoxy protons move the ortho-protons to lower frequency by 0.2 ppm.

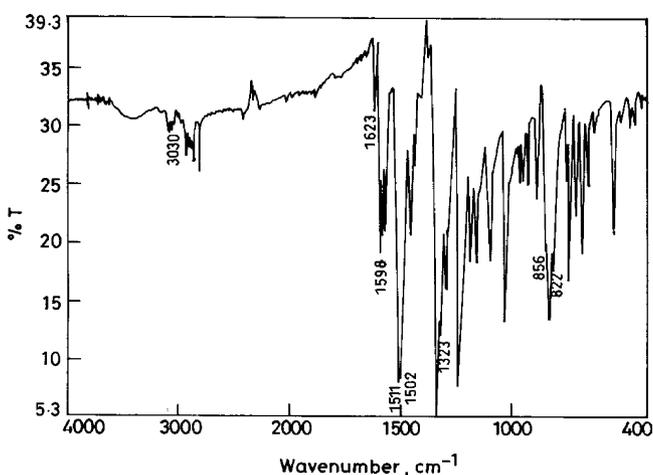


Fig. 1. FTIR spectrum of NMOBA.

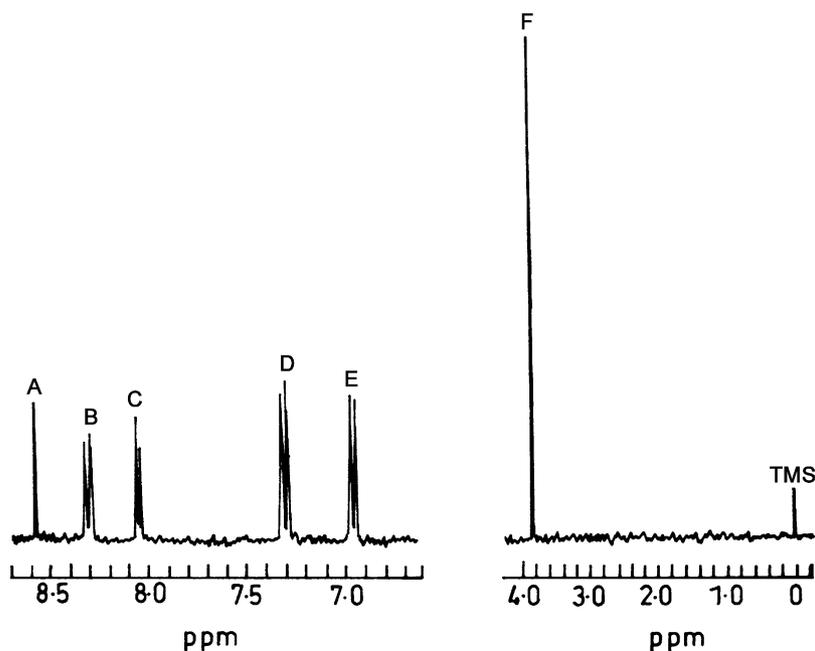


Fig. 2. NMR spectrum of NMOBA.

Thus, the H_d protons probably come to resonance around δ 7.07 ppm. It is worthy to assign signal E at δ 6.97 ppm for H_d proton. The other signal C at δ 8.04 ppm can be taken as the signal for H_c protons. Though there is little variation in the intensities of the neighbouring lines in the doublets, the coupling constant is same ($J = 8.79$) for all the cases. The protons of benzylidene aniline give signals at higher frequencies (down-field) while methoxy group protons resonate at lower frequency (up-field). The lowest and the highest frequencies are in the range 1537.60 Hz and 3425.78 Hz. Molecular structure of NMOBA is thus confirmed from the NMR spectrum.

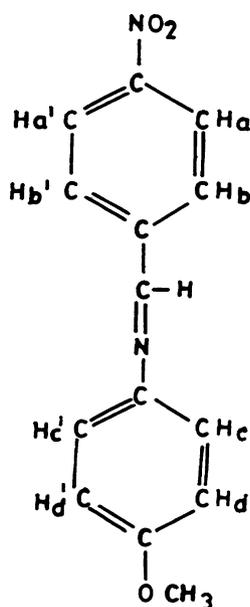


Fig. 3. Molecular structure of NMOBA.

2.4. Solubility studies

Solubility of NMOBA in the organic solvent toluene was determined at temperatures 25 °C, 30 °C, 35 °C, 40 °C and 45 °C by gravimetric method. Thermostatically controlled constant temperature bath (CTB) with an accuracy of ± 0.01 °C coupled with a cryostat was used for the study. The purified NMOBA sample was added in excess to the solvent taken in stoppered bottles kept in the CTB and maintained at the temperature of interest. The solution was stirred for 2 h and thereafter, a fixed amount of the supernatant solution was pipetted out and weighed. The volume of the solution was calculated from the weight. The solution was then evaporated to dryness. From the weight of solute left after the evaporation of solvent and the volume of the solvent calculated, the solubility of NMOBA per 100 ml of the solvent at each temperature was determined.

Solubility of NMOBA in toluene increases with the increase of temperature (Fig. 4). Solubility coefficient is an important parameter for studying the solubility diagrams. The solubility coefficient at a particular temperature can be calculated from the solubility diagram using the formula, $(dS/dT)/S_0$, where S is the solubility (g/100 ml) and T is the temperature. S_0 is the solubility in g/100 ml corresponding to T_0 , the temperature for which solubility coefficient is determined [8]. Solubility coefficients per degree Celsius at T_0 values 25 °C, 30 °C, 35 °C, 40 °C and 45 °C were calculated. The solubility co-efficient is 0.04 per °C at 35 °C and 40 °C and 0.05 per °C for all other temperatures studied. This regular behaviour in the solubility diagram makes NMOBA suitable for the growth by temperature lowering and slow evaporation techniques using toluene as the solvent.

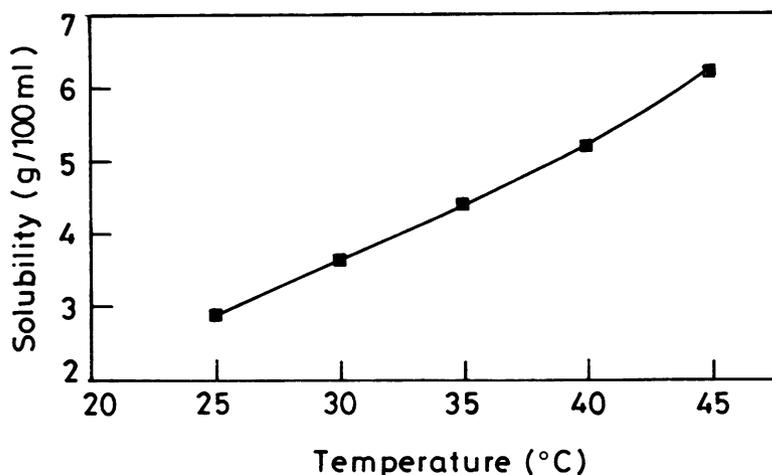


Fig. 4. Solubility curve of NMOBA in toluene.

2.5. Crystal growth

Crystal growth experiments were performed by slow evaporation and slow cooling methods. The following procedure was adopted for the growth by slow evaporation. Saturated solutions of NMOBA were prepared at 35 °C with reference to the solubility data. The solutions were heated 5 °C above their saturation temperature to remove any un-dissolved crystallites. The crystallizer was then placed in the constant temperature bath and cooled to the predefined saturation temperature, 35 °C. Few perforations were made for the evaporation of solvent. On the fourth day, nucleation was noticed and it was allowed to grow for a period of 40 days. The harvested crystal has the dimension 23 mm × 20 mm × 1 mm.

For the growth by slow cooling method, the crystallizer was filled with NMOBA saturated in toluene at 40 °C. The solution was then heated for an hour at higher temperature to remove any un-dissolved nuclei. Then, the solution was kept at 40 °C in thermostatically controlled constant temper-

ature baths. A defect-free seed crystal of dimension 4 mm × 3 mm × 0.4 mm was tied using a nylon thread and suspended in the solution. Growth begins as the operating temperature was slowly reduced in the order of 0.1 °C per day for the first three days. Then, the temperature decrement was increased to 0.2 °C per day till it reached to room temperature. The growth continued for 40 days and growth rate is estimated as 33 mg per day. The dimension of the crystal grown from toluene by slow cooling method is 27 mm × 25 mm × 2 mm.

The photographs of the grown crystals are shown in Fig. 5. The habit of the crystals obtained from toluene either by slow cooling or slow evaporation is three-dimensional and platy. The growth along 'a' direction that is normal to the flat surface (1 0 0) is minimum when compared with the growth along b-axis and c-axis. In slow cooling method, the growth rate is high and the crystal obtained is also more transparent. Slow cooling method can be a better method for growing bulk single crystals of NMOBA. Further efforts towards obtaining

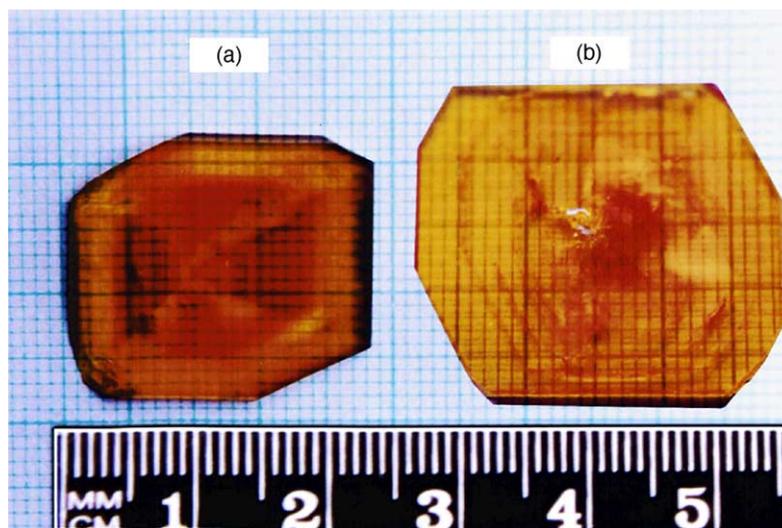


Fig. 5. NMOBA crystal grown from toluene: (a) restricted evaporation method, and (b) slow cooling method.

Table 1
Experimental details of single-crystal X-ray diffraction

Molecular formula	$C_{14}H_9N_2O_3$
Formula weight	256.28 g mol ⁻¹
Crystal color	Reddish yellow
Shape	Rectangular plate
Size	1 mm × 0.4 mm × 0.15 mm
Symmetry	Monoclinic
Space group	P2 ₁
Unit cell parameters	$a = 12.89 \text{ \AA}$ $b = 7.12 \text{ \AA}$ $c = 14.05 \text{ \AA}$ $\beta = 102^\circ 43'$
Volume	1258 Å ³
Diffractometer	CAD4 Enraf-Nonius 4-circle automatic diffractometer
Radiation	Mo K α
Wavelength	0.7107 Å
Temperature	293 K

large-size single crystals and their detailed characterization are in progress.

2.6. X-ray diffraction studies

Single-crystal X-ray diffraction analysis was performed for NMOBA crystal using CAD4 Enraf-Nonius 4-circle automatic diffractometer. From this, it is found that the structure of the grown crystal is monoclinic and the lattice parameter values are presented in Table 1.

2.7. Thermal studies

Thermogravimetric and differential thermal analyses (TGA/DTA) were recorded for NMOBA using S.T.A.–1500 Simultaneous Thermo Analytical system (UK) in the temperature region 30–400 °C. Assessment of the thermal properties of organic crystals is necessary while using them in NLO devices [15]. Thermo gravimetric analysis shows (Fig. 6) that NMOBA is stable up to 296.63 °C and the weight loss starts above this temperature. At 296.63 °C, decomposition of NMOBA starts. It is observed from DTA curve that an

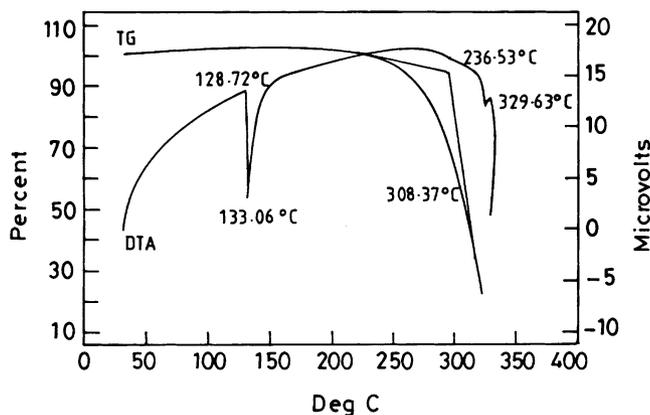


Fig. 6. TGA, DTA trace of NMOBA.

endothermic event starts at 128.72 °C and then a sharp peak appears at 133.06 °C. The sample temperature remains constant at this temperature until the event is completed. The endothermic event in the sample at 133.06 °C corresponds to the experimentally determined melting point. As TGA implies NMOBA is stable up to 296.63 °C and decomposition is not expected below this temperature. Other than solid–liquid transformation, no other phase transformations are noticed from the DTA curve. We thus conclude that polymorphism is not exhibited in NMOBA, contrary to NMBA. NMOBA is stable above its melting point and it suggests that it has favorable crystal growth properties that allow the growth directly from the melt.

Differential scanning calorimetric (DSC) experiment was performed using T.A. Instruments, Model 2010 (USA). The DSC spectrum was recorded in the temperature range 30–200 °C at a scanning rate of 10 °C per min, using indium specimens to verify the instrument calibration. A broad DSC peak was detected between 121 °C and 141 °C and from the peak, melting point is confirmed as 133 °C (Fig. 7). The enthalpy of melting is 145.7 J g⁻¹. Growth in a faceted manner is a characteristic of high Jackson α factor, $\alpha = \Delta H_m/RT_m$, where ΔH_m is the enthalpy of melting and T_m , the melting point [16]. Using the above expression, α is calculated as 11. It can be deduced from the high Jackson α factor value that NMOBA can be crystallized from the melt in a faceted manner and the crystals thus prepared are expected to be structurally perfect.

2.8. Second harmonic generation experiment

Second harmonic generation experiment was performed using Nd:YAG laser instrument, Model: DCR-3G SPECTRA PHYSICS following Kurtz powder method [17]. The crystal was ground into a fine powder and sandwiched between two quartz slides, which serve as sample cell. When Nd:YAG laser beam of wavelength 1.06 μm with pulse duration 18 ns and beam radius 1.6 mm was allowed to fall normally on the NMOBA sample cell, it was converted into green light of wavelength 0.532 μm . SHG intensity of NMOBA is 1.27 times higher than that of KDP. Comparative account of the experimental result is given in Table 2.

2.9. UV–VIS–NIR spectral analysis

Internal transmittance of NMOBA crystal was recorded using Varian Cary 500 scan double-beam UV–vis–NIR spectrophotometer in the wavelength region 185–2750 nm (Fig. 8). A small (100) plate of thickness 0.5 mm was

Table 2
Powder SHG intensity data of NMOBA

S. no.	Sample	Signal (mV, 532 nm)	SHG intensity $I_{2\omega}/I_{\omega}$ of KDP
1	KDP	200	1
2	NMOBA	254	1.27

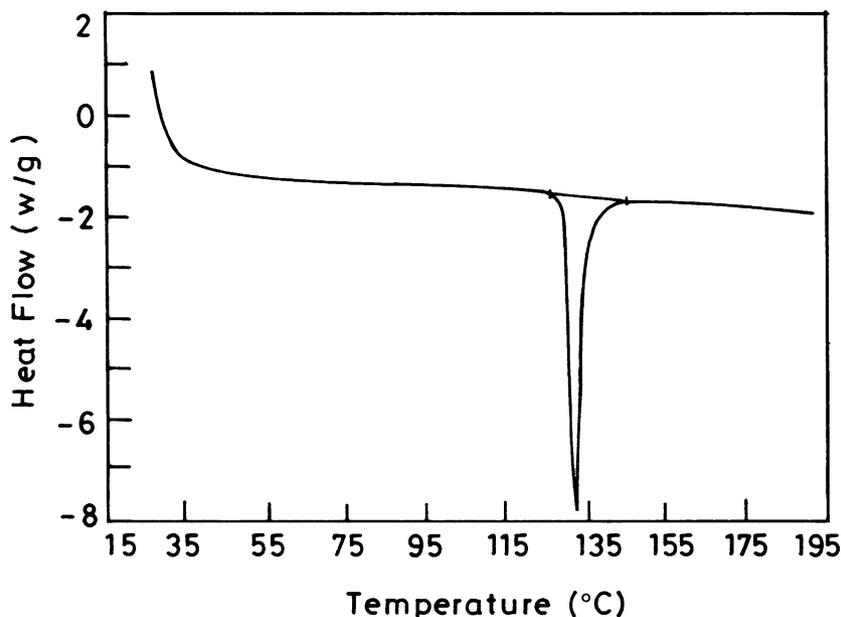


Fig. 7. DSC trace of NMOBA.

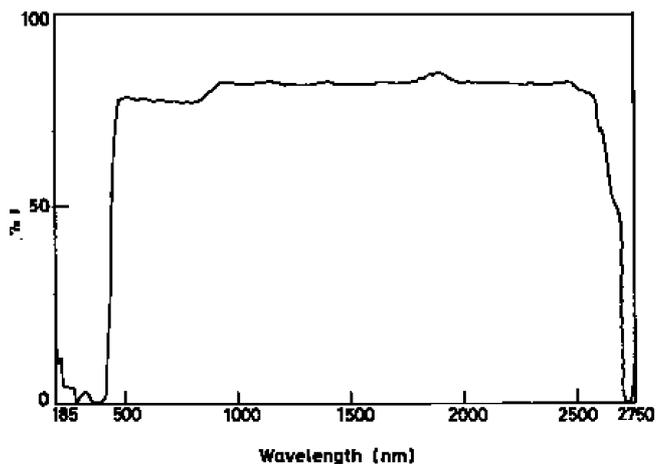


Fig. 8. UV-vis-NIR spectrum of NMOBA.

subjected to the analysis with toluene as the internal standard. At 410 nm, the percentage of transmittance starts increasing, which shoots to 79% at 500 nm. Further, there is no remarkable change in percentage of transmittance other than a hike at 1894 nm. At 2478 nm, the percentage of transmittance starts decreasing and comes to 50% at 2694 nm and finally touches zero at 2724 nm. Thus, we infer that NMOBA crystal is transparent in the visible and near-infrared regions ranging between 410 nm and 2724 nm.

3. Conclusion

The NLO material 4-nitro-4'-methoxy benzylidene aniline was successfully synthesized. Formation of the product was confirmed from FTIR and NMR spectral analyses. Crys-

tals were grown from the purified material by slow evaporation and slow cooling methods. Growth rate and transparency level are high for the crystals grown by slow cooling method. The grown crystals were characterized for their structural features and thermal properties. Structure is found to be monoclinic, $P2_1$. The endothermic event at 133.06 °C corresponds to the melting point of NMOBA and no other phase transformations were noticed. NMOBA is stable above its melting point up to 296.63 °C. Jackson α factor calculated from the DSC studies is also high and it implies that NMOBA can also be grown by melt techniques. Powdered sample of the crystal generates optical second harmonic frequency. Optical transparency of the crystal lies in the region 410 nm and 2724 nm.

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