(IJIRSE) International Journal of Innovative Research in Science & Engineering
ISSN (Online) 2347-3207

Growth, Thermal and Optical properties of organic NLO crystal of novel N-nitroso r-2,c-6-bis(4-methoxyphenyl)-c-3,t-3-dimethylpiperidin-4-one

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Abstract: - Non linear optical material of *N-nitroso-r-2,c-6*-bis(4-methoxyphenyl)-*c-3,t-3*-dimethylpiperidin-4-one (NPM3DMPO) was grown by the slow evaporation technique using methanol as the solvent. The absorption spectrum range of grown crystals was identified by UV- VIS spectroscopy. The presence of functional groups and modes of vibrations were identified by FT-IR Spectroscopy. The thermal stability of the crystal was established by TGA/DT analysis. The nonlinear optical property of the grown crystal was confirmed by second harmonic generation test which shows the suitability of this crystal for NLO applications.

I. INTRODUCTION

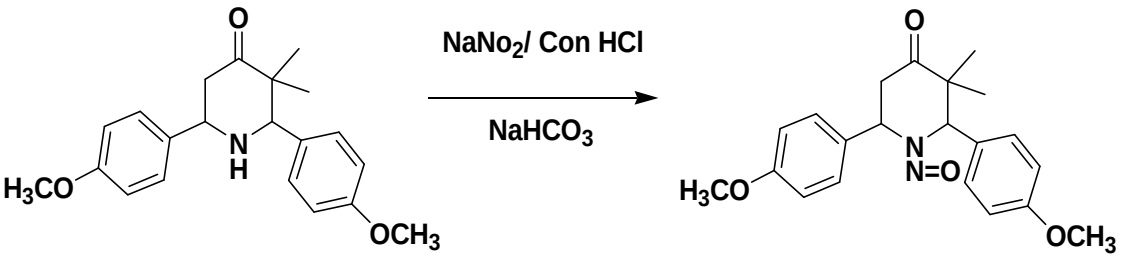
Non linear optical crystals have been a great deal of interest in recent years due to their potential use in the fields like laser technology, optical communication, optical data storage and optical signal processing [1–3]. It is also contributing number of applications in the domain of optoelectronics and photonic technologies [4,5]. This induces the physicists, chemists, material scientists and crystal engineers to identify a new class of NLO materials which should fulfill the needs of the above fields. The search for finding the new and better NLO materials with high transparent window in visible region, high optical damage threshold and good optical frequency conversion efficiency have been engaged by several scientists. In this context, variety of organic and inorganic NLO materials has been proposed [6-9]. Normally organic chromophores exhibit high and fast nonlinearities than their inorganic counter parts. The SHG or frequency doubling of light requires the materials with a noncentrosymmetric structure which in turn gives rise to large second order nonlinear optical susceptibility. For molecular materials, it is widely assumed that the molecular structure as well as the packing arrangement must also be noncentrosymmetric [10-15].

In this present work, we report the growth of NLO organic crystals of N-nitroso-r-2,c-6-bis(4-methoxyphenyl)-c-3,t-3-dimethylpiperidin-4-one (NPM3DMPO, Fig.1) [16, 17]. The absorption spectrum range of grown crystals was identified by UV- VIS technique. The presences of functional groups and modes of vibrations were identified by FT-IR Spectroscopy. The thermal stability of the crystal was established by TGA/DT analysis. The nonlinear optical property of the grown crystal was confirmed by second harmonic generation using Nd:YAG laser.

II. EXPERIMENTAL STUDIES

A. Synthesis and Crystal Growth of NPM3DMPO

To a solution of c-3,t-3-dimethyl-r-2,c-6-bis(4-methoxyphenyl)piperidin-4-one (1.69g 5 mmol) in chloroform (10 ml) was added con.HCl (1.5) and water(1.5 ml) and while stirring, solid NaNO2(0.84g, 12 mmol) was added in portion during 0.5 hr. The solution was stirred at room temperature for another 0.5 hr. The organic layer was washed with water, saturated aquous NaHCO3 and dried over anhydrous Na2SO4. The resulting solution was concentrated and the residue was crystallized from ethanol.



Scheme – 1 The schematic representation for the preparation of NPM3DMPO

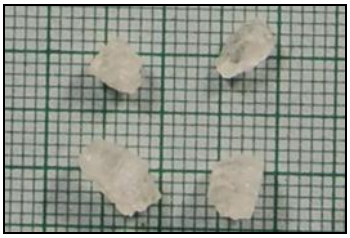


Fig 1 N-nitroso r-2,c-6-bis(4-methoxyphenyl)-c-3,t-3-dimethylpiperidin-4-one **(NPM3DMPO)**

B. Solubility

The solubility measurement of a material in any solvent gives indication about the nucleation and availability of the solute material for crystal growth and cooling rate during the crystal growth. Super saturation is the driving force for the crystallization and it also affects the crystal quality. The solubility of NPM3DMPO has been determined for various temperatures. The recrystallized crystal was used for these studies. The solubility for NPM3DMPO in benzene and ethanol was determined by dissolving the solute in an airtight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility curve is shown in fig 2.

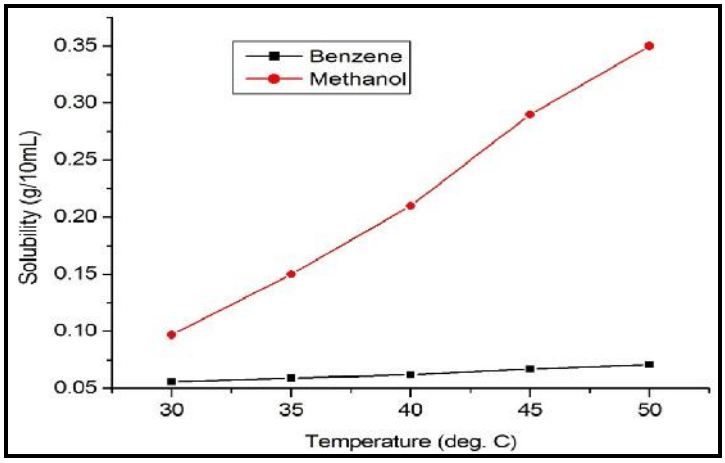


Fig 2 Solubility test for **NPM3DMPO**

III. RESULTS AND DISCUSSION

A. UV-VIS Spectroscopy

The UV-Vis spectrum of NPM3DMPO was reproduced in Fig 3. The spectrum exhibits strong absorption bands due to π-π* and n-π* transitions in the near UV-region of the spectrum. The crystal does not exhibit any absorption band in the entire visible region up to 800 nm. This transparency of the spectrum strongly suggests that the grown crystals of the title material are suitable for various optical and NLO applications.

B. FT-IR spectrum

The FTIR spectrum of NPM3DMPO single crystals is depicted in Fig.4. The aromatic C–H symmetric stretching vibration is observed at 3027 cm-1 and the corresponding symmetric stretching vibration is observed at 2977 cm-1. The bunch of frequencies appearing around 2800 cm-1 has been assigned to the C–H asymmetric and symmetric stretching vibrations of methyl and methylene groups in the molecule. The strong and sharp band appeared at 1702 cm-1 is assigned to the carbonyl (>C=O) stretching vibration. Ther stron absorption at 1511 and 1333 cm-1 were due to NO stretching vibrations.

C. Thermal Properties

The TG/DTA spectrum of NPM3DMPO is shown in Fig.5. Thermogravimetric curve illustrate a weight loss of 0.66 % between 25 and 170ºC due to loss of water of crystallization. The sudden changes in the weight loss of 21.90% starting nearly 200 to 260ºC and again gradually weight loss of 16.27 % between 350 to 450ºC and the residual mass is 26.17 % at 498.1ºC. The sharp endothermic peak at 151.6º C is found to be matching with the first weight loss of this crystallization. The exothermic peak appearing close to 245.3º C matching with the major weight loss in TGA. From this analysis, it is understandable that the material can be exploited for NLO applications up to 151.6 º C. The sharpness of the endothermic peak illustrates the good degree of crystalline and purity of the crystal.

D. Powder SHG efficiency measurements

In continuation of our work on the discovery of piperidin-4-one based new organic NLO materials [18, 19], in the present work, we tested the SHG efficiency of NPM3DMPO. A Q-switched Nd: YAG laser was used as light source. A laser beam of fundamental wavelength 1064, 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample cell. Potassium dehydrogenate orthophosphate (KDP) crystal was powdered and was used as reference materials in the SHG measurement. The input laser energy incident on it be 8.1 mj/pulse. The NPM3DMPO second harmonic signal of 5.1 mv was obtained when compared to KDP for which 11 mv was obtained for the same input beam of energy.

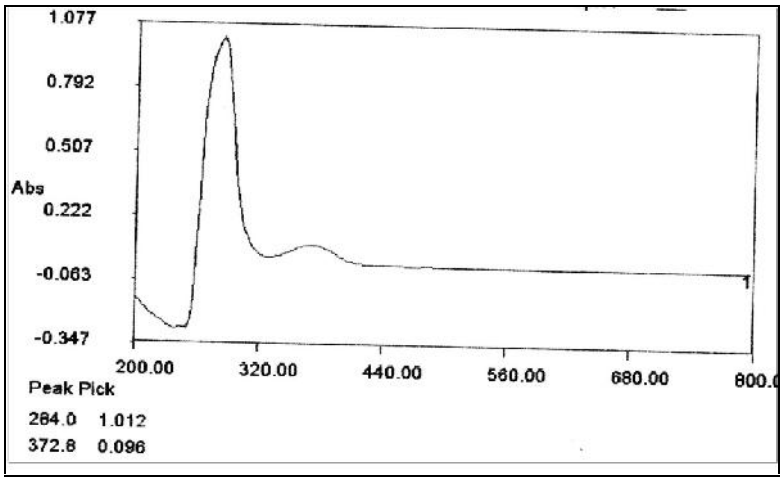


Fig 3 UV-Vis absorption spectrum of **NPM3DMPO**

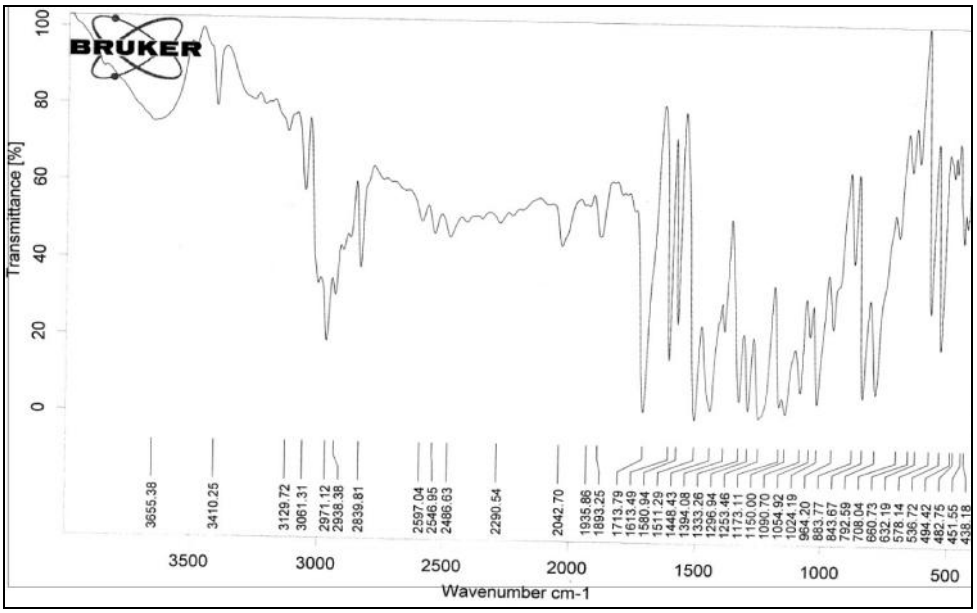


Fig 4 FT-IR spectrum of **NPM3DMPO**

Table-1 FTIR spectral Data of 2C3DMPO

Wave number(cm^{-1})	**Assignments**
3410	N-H Stretching Vibration
3129	N-H Stretching Vibration(bonded) cis&trans secondary amine
2042-3061	CH_3-C-O & CH_2-CO Stretching vibration
1713	>C=O Stretching Vibration
1448	CH_2 bending vibration
1511 & 1333	NO stretching vibrations
1295	Asymmetric C-O-C Stretching
1054	Aromatic Stretching Vibration
964	Asymmetric Stretching of ring

IV. CONCLUSION

The single crystals of NPM3DMPO materials with good optical quality have been grown from the ethanol solution by slow evaporation technique at ambient temperature. The characterization of the crystal has been carried out using UV-Visible spectrum, FT-IR spectrum, thermal and SHG studies. The compound showed a significant SHG efficiency.

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