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# SYNTHESIS, GROWTH, OPTICAL, THERMAL AND MECHANICAL PROPERITIES OF AN NEW PIPERIDINE DERIVATIVE: 4-CHLORO-N-{[1-(4-CHLOROBENZOYL) PIPERIDIN-4-YL] METHYL} BENZAMIDE HYDRATE (CPMBH)

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**Abstract:-** *Optically transparent single crystals of 4-chloro-N-{[1-(4-chlorobenzoyl) piperidin-4-yl] methyl} benzamide hydrate (CPMBH) (BPMB), an organic nonlinear optical (NLO) material were synthesized successfully by slow evaporation method using ethyl methyl ketone as solvent. The crystal was grown with in a period of 10 to 15 days. The cell dimensions were obtained by single crystal X- ray diffraction (XRD) study. The crystal is crystallized in monoclinic system with space group P21/n. The a, b , c values are given as a = 8.965(5), b = 19.613(5), c = 11.456(5) ; β = 96.989(5). Optical transparency of the grown crystals has been analyzed by UV-visible -NIR spectral analysis and NMR spectral studies. Thermal stability and micro harness measurement was examined by TG-DTA and Vickers microhardness study.*

***Keywords:*** *Piperidine, single crystal X- ray diffraction (XRD), UV-vis, TG/DTA, Microhardness.*

## I. INTRODUCTION

Much of the research has been directed towards materials that are effectively used in second harmonic generation, the frequency doubling of laser light, telecommunication, optical computing, optical data storage and optical information processing[1-2]. In recent years, organic NLO materials are attracting a great deal of attention for possible use in optical devices because of their large optical nonlinearity, low cut-off wavelengths, short response time and high laser damage thresholds [3]. Enormous work has been carried out to understand the microscopic origin of nonlinear behavior of organic materials [4-7]. Organic compounds containing a proton donor (-OH) group and proton acceptor amine ($NH_2$) group are naturally crystallize in non-centrosymmetric space groups, which is the preferred condition for nonlinear optical (NLO) property [8]. Literature knowledge of this class of reported organic compounds for their second harmonic generation, preperidine derivatives are appears to be an effective materials due to their excellent light transmittance and good crystallinality. In this communication we are reporting the synthesis, growth and characterization of a new nonlinear optical peperidine derivative (BPMB).

## II. EXPERIMENTAL PROCEDURE

2.1 Synthesis and Growth

To 4-aminomethylpiperidine (0.02 mol) in a 250 ml round-bottomed flask, 120 ml of ethyl methyl ketone was added and stirred at room temperature. After 5 minutes, triethylamine (0.04mol) was added and the mixture was stirred for 15 minutes. 4-Chlorobenzoyl chloride (0.04mol) was then added and the reaction mixture was stirred at room temperature for about 2 hours. A white precipitate of triethylammonium chloride was formed. It was filtered and the filtrate was evaporated to obtain the crude product which was recrystallized twice from ethyl methyl ketone [Melting Point: 230°C yield: 82%] Figure 1.1 The solution of recrystallized CPMBH was prepared at 30°C using Ethyl Methyl ketone as a solvent. The beaker containing the solution was covered and the solution was housed in a constant temperature bath (0.1°C) and continuously stirred using Teflon coated immiscible magnetic stirrer. Utmost care was taken towards maintenance of temperature because even minor fluctuations in temperature would lead to inclusions and defects in the growing crystals. The temperature was lowered at a rate of 0.5°C/day. After a fortnight, yellow colored transparent and large size crystals were obtained as shown in Figure. 1.2.

 

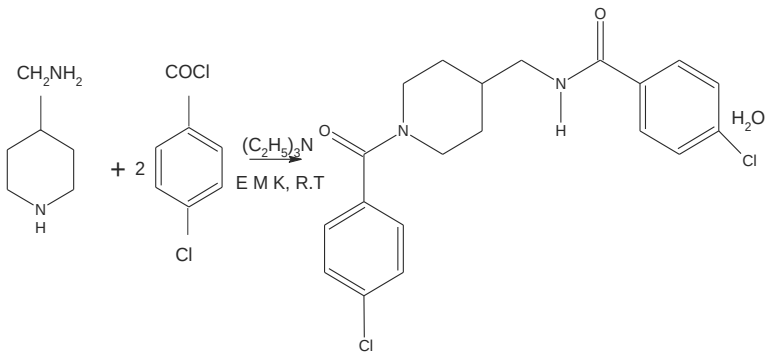


***Figure 1.1 Chemical Scheme***

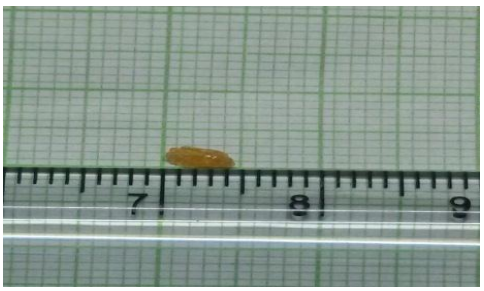

***Figure 1.2 Grown crystal***

## III. RESULTS AND DISCUSSIONS

### 3.1. Single crystal X-ray diffraction (XRD)

The XRD studies have been carried out to determine the 3D crystal structure Fig. 3. The title compound is crystallized in triclinic space group Pī with unit cell parameters a = 8.965(5), b = 19.613(5) ,c = 11.456(5) ; β = 96.989(5). and V= 1999.3(2)Å$^3$. The structure was solved by direct methods using the program SHELXS97 and refined by SHELXL97 with full-matrix least-squares procedure and the crystallographic results were published [9].

### 3.2. UV-Visible spectral analysis

The UV-Vis-NIR spectrum gives information about the structure of the molecules because the absorption of UV and Visible light involves promotion of the electron in the π orbital to the high energy π* orbital [10]. The percentage of transmission enables the suitability of materials for optoelectronic applications. The absorption spectrums of the grown crystal grown crystal was recorded using T90+ UV/Vis spectrometer and is shown in Figure 1.3. From the absorption spectra of CPMBH single crystal, it is observed that there is no absorption in the region of 300–800 nm. The cutoff wavelength of the grown crystals CPMBH is measured as λc = 244nm respectively. The band gap is calculated using the formula, Eg = [hc/λ]eV = 12.4237/λc eV. The calculated band gap value of CPMBH crystal is found to be 5.091eV respectively.

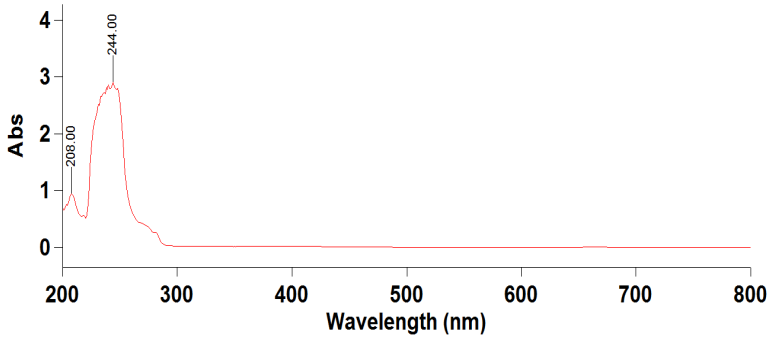


***Figure 1.3 UV-VIS-NIspectrum***

 

### 3.3. NMR Spectral Analysis

$_1H^1$NMR spectrum of the grown crystal was recorded using a Bruker Advance III 500 MHz NMR spectrometer and DMSO-d6 as internal standard, which is shown in Figure 1.4. The presence of strong and sharp peaks centered at δ 7.93ppm and at δ 7.56ppm is assigned to the ArH and RCH2R of piperidine moiety [11]. The appearance of broad and small signal at δ13.19 ppm corresponds to the strongly deshielded NH proton. The small and narrow peak at δ3.40 ppm is due the NCH2R ethylene proton of the compound [12]. The sharp peak δ 2.52 ppm is assigned to the OH2 proton in the crystal.

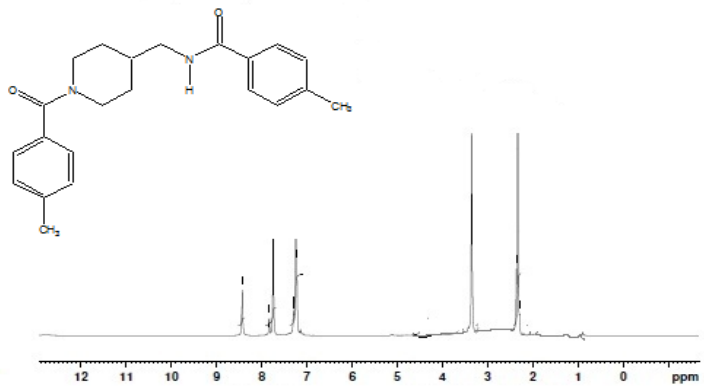


***Figure 1.4 Proton NMR Studies***

### 3.4. Thermal Analysis

Thermogram provides information about decomposition patterns of materials and weight loss [13]. Thermal analyses have been performed on the sample of the grown crystals to study the thermal stability, and the melting point. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) response curves for the powder sample of CPMBH crystal were recorded using NETZSCH STA 409PC/PG thermal analyzer between the temperature 32 and 600˚C at a heating rate of 10 ºC/min in nitrogen atmosphere and is shown in Figure 1.5. The TG and DTA plots of CPMBH exhibits broad endothermic peak at 245.2˚C which represents the melting point of the compounds. This melting point value is found to be very close to the value (230.8˚C) obtained from the melting point apparatus. The broad endothermic peak indicates that the crystals are not pure but with impurity (solvent water). From the TG thermogram curve of CPMBH, it is observed that the single stage complete weight loss is approximately between 250˚Cand 350˚C

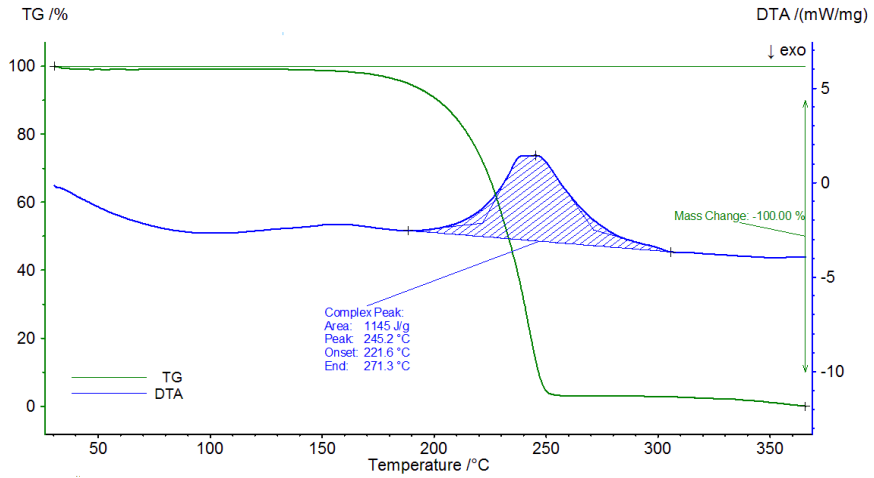


***Figure 1.5 T G-DTA Thermograms***

### 3.5. Microhardness Studies

Measurement of hardness is a useful nondestructive testing method to determine the hardness of the material. The hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing [14,15]. From the Vicker's microhardness studies, it is observed that the hardness value increases up to a load of 50g and cracking occurs at this point which may be due to release of internal stress generated by indentation. The work hardening coefficient n, a measure of the strength of the crystal is computed from the log P vs log d plot Figure 1.6 and it is found to be 2.22CPMBH crystal. From the calculated values for 'n', it may be concluded that the grown crystal belongs to soft material.

 

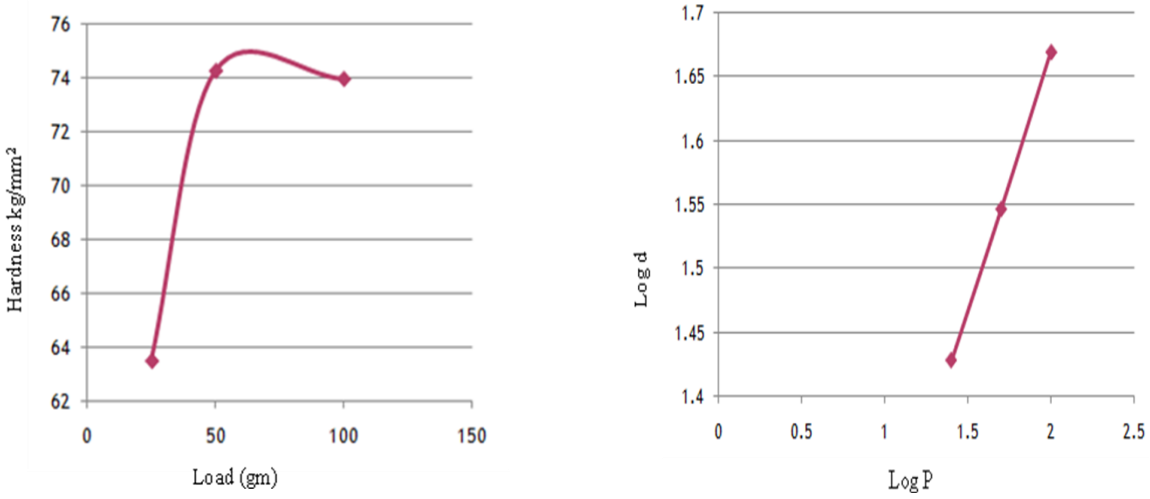


***Figure 1.6 Microhardness Studies***

**4.conclusion**

Optically good quality transparent CPMBH single crystals have been grown by slow evaporation method at room temperature. The cell parameters have been determined by single crystal XRD analysis. The absence of absorption in the region between 300 and 800 nm in the UV-VIS-NIR spectrum shows that the grown crystal is good material for optoelectronic applications. The NMR Spectral Analysis the sharp peak δ 2.52 ppm is assigned to the OH2 proton in the crystals as functional group and molecular structure are confirmed by NMR spectral analysis. The melting point of CPMBH was found to be 245.2˚C from the DTA curve. From the microhardness it is found that crystal belongs to soft material.

**Reference**

[1] R.B Lal ,H. W Zhang, W.S.Wang , Aggarwal M.D., Howard W.H. Lee and Penn B.G., *J. Cryst Growth*, 174, 393-397 (1997)
[2] Periyasamy B.K., Jebes R.S., Gopalakrishnan N. and Balasubramaniam T., Development of NLO tunable band gap organic devices for optoelectronic applications, *Mater. Lett.*, 61(21), 4246-4249 (2007)
[3] M. Narayan Bhat and S. M. Dharmaprakash, *J. Cryst Growth*, Vol. 236, 2002, pp. 376-380.
[4] T. Suthan and N. P. Rajesh, *J. Cryst. Growth*, Vol. 312, 2010, pp. 3156-3160.
[5] Huaihong Zhang, Yu Sun, Xiaodan Chen, Xin Yan and Baiwang Sun, J. Cryst. Growth, Vol. 324, 2011, pp. 196-200.
[6] C.M. Earnet, Anal. Chem . 59 (1984) 1471–1475.
[7] Huaihong Zhang, Yu Sun, Xiaodan Chen, Xin Yan and Baiwang Sun, *J. Cryst. Growth*, Vol. 324, 2011, pp. 196-200.
[8] Natalia Zaitseva, Leslie Carman, Andrew Glenn, Jason Newby, Michelle Faust, Sebastien Hamel, Nerine Cherepy and Stephen Payne, *J. Cryst. Growth*, Vol. 314, 2011, pp. 163-170.
[9] K. Prathebha, D. Reuben Jonathan, Sathya Shanmugam and G. Usha, Acta Cryst. (2014). E70, o771
[10] Ramesh Rajendran, Thangammal Harris Freeda, Udaya Lakshmi Kalasekar, Rajesh Narayana Peruma. Advances in Materials Physics and Chemistry, 2011, 1, 39-43.
[11] M. Anbuchezhian, S. Ponnusamy, C. Muthamizhchelvan J. Optoelec. and Adv. Mat. -Rapid communications 2009, 3, 1161- 1167.
[12] G. AnandhaBabu , S.Sreedhar , S.VenugopalRao , P.Ramasamy JournalofCrystalGrowth312(2010)1957–1962.
[13] Natalia Zaitseva, Leslie Carman, Andrew Glenn, Jason Newby, Michelle Faust, Sebastien Hamel, Nerine Cherepy and Stephen Payne, J. Cryst. Growth, Vol. 314, 2011, pp. 163-170.
[14] T. Kishore Kumar, S. Janarthanan, S. Pandi, M. Victor Antony Raj, J.Kanagalakshmi, D. Prem Anand. Journal of Minerals & Materials Characterization & Engineering, Vol. 9, No.11, pp.961-972, 2010.
[15] T. Pal, T. Kar, G. Bocelli, and L. Rigi, "Synthesis, growth, and characterization of L-arginine acetate crystal: a potential NLO material," Crystal Growth and Design, vol. 3, no. 1, pp. 13–16,2003.

 