Growth and Characterization of a 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 dimension were obtained by single crystal X- ray diffraction (XRD) study. The crystal is crystallized in monoclinic system with space group P_{21}/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). The functional group and molecular structure are confirmed by 2 UV-Vis, NMR, FT-IR spectral analysis.

Keywords: Piperidine, single crystal X- ray diffraction (XRD), NMR, FT-IR .

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

A. Synthesis of the compound

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

B. Crystal growth

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.

III CHARACTERIZATION

A. 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].

B. UV-VIS-NIR spectral studies

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.

C. FT-IR Spectroscopy

FT-IR Spectroscopy was effectively carried out to investigate the functional groups in the grown crystal. FT-IR spectrum of CPMBH is shown in the Figure 1.4. The N-H stretching vibration of amino group gives rises to an amide band between 3250 and 3500 cm^{-1} [11]. The bending vibration of H-OH of water molecule has been observed at 1682 $cm^{-1}$and 1641cm^{-1}. The presence of chlorine in this compound is indicated by the peaks at 807cm^{-1} and 688cm^{-1}, respectively. The peak 1547 and 1579 cm^{-1} confirms the presence of the nitro group in CPMBH crystal. The sharp peaks at 2919, 2940 and 2995 cm^{-1} indicates the presence of asymmetric CH_3 and CH_2 group, respectively. The absorption peaks present in between 450cm-1 to 525cm-1 are assigned to C-C deformations. FT-IR spectral analysis of the grown crystal reveals the presence of various functional groups c [11, 12].

D. Proton 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 1.5. 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 [10]. 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 [13]. The sharp peak δ 2.52 ppm is assigned to the OH2 proton in the crystal.

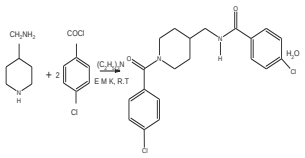

Fig 1.1 chemical scheme

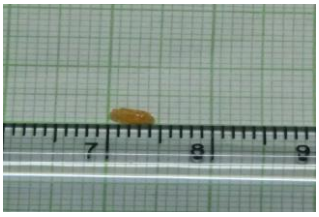

Fig 1.2 Grown crystal

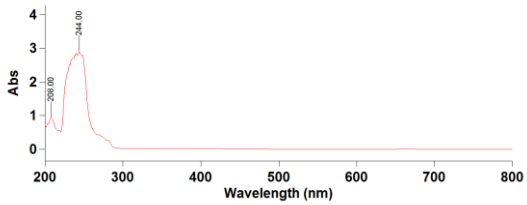

Figure 1.3 UV-VIS-NIR spectrum

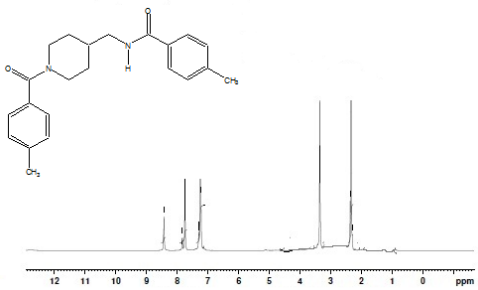

Figure 1.4 FT-IR Spectral studies

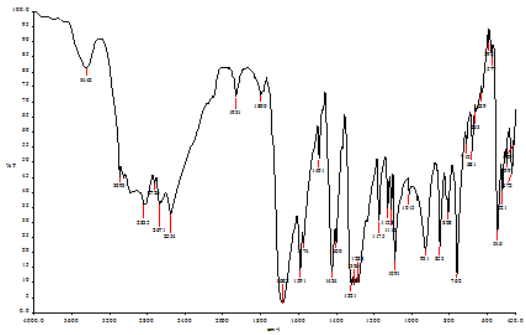

Figure 1.5 Proton NMR Studies

IV 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 FTIR spectra reveal the various functional groups present in grown crystal. 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.

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