International Journal of Emerging Trends in Science and Technology
5 (1), June 2019, 17-22
http://www.publishingindia.com/ijetst

Growth and Characterization of P-Chloroanilinepthalic Acid Single Crystals

J. Vidhya[1*] and R. Padmavathi[2]
[1]Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, Tamil Nadu, India.
Email: opilal@gmail.com
[2]Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, Tamil Nadu, India.
*Corresponding Author

Abstract: P-CaP (p-chloroanilinepthalic acid) single crystal was grown by slow evaporation technique. A single Crystal XRD study reveals that the grown crystal belongs to orthorhombic system. Decomposition mechanism and melting point of the sample were deliberated in TGA/ DSC analysis. Transmission ability of the crystal in the visible was tested by recording UV-VIS-NIR spectrum also Mechanical strength of the material is determined by Vickers hardness test. The FTIR Spectrum was recorded in the range of 400 cm^{-1} and 4000 cm^{-1} which is confirmed the formation of p-CaP crystal.

Keywords: Optical analysis, Single crystal, XRD.

I. Introduction

Recently, organic nonlinear optical (NLO) materials receive much importance from the researchers because of its frequency conversion property. NLO materials with high frequency conversion in visible and infrared range are requisite for the fabrication of tunable laser [1-3]. Compare to inorganic materials, these shows good laser damage resistance and has faster response time which attained in the result of the structural flexibility of the materials [1]. Among the available organic materials, Aniline, as bases which are found to be a potential candidate to develop supramolecular structures. Aniline and its organic and inorganic salts can develop supramolecular structures which consists complementary arrays of hydrogen bonding sites. The structure of the nitro groups in aromatic compounds containing NO2 and NH2 group has been the subject of a special interest in materials science. In particular, nitroaniline series forms a special interest, because of its ability to form intermolecular hydrogen bonds between amino and nitro groups [5]. Hence, in the present investigation we have chosen p-chloroanilinepthalic acid (p-CaP) for crystal growth. The structural, vibrational and optical properties of p-CaP were investigated and results are discussed in this manuscript.

II. Experimental

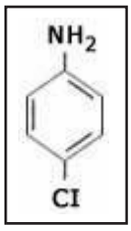
P-Chloroaniline is available commercially from Loba Chemie in extra pure form. Recrystallization of the material was done several times to attain the purity of the material using acetone solutions. Pthalic acid was acquired from Merck. Calculated quantity of p-chloroaniline and pthalic acid was taken and dissolve in acetone and ethanol respectively. The two clear solutions were added and the mixture solution was reflux for two hours. The solution was filtered and the clear solution was kept undisturbed. After few days yellow colour crystals were obtained from the solution.

A. P-Chloro Aniline

Structure of the p-chloro aniline along its physical properties is presented below:

Molecular Formula	C6H6 Cl N
Molecular Weight	127.57 g/mol
Melting Point	69-71 ˚C
Solvent	Acetone, Chloroform, Ethanol

Structure of p-chloro aniline

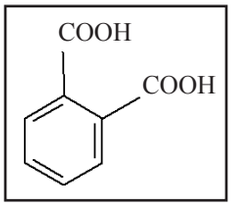


B. Phthalic Acid

Chemical structure of phthalic acid and the other physical properties are given below:

Molecular Formula	C6H4 (CO2H)2
Molecular Weight	166.13 g/mol
Melting Point	205-215 ˚C
Solvent	Ethanol

Structure of Phthalic acid



From the melting point value the purity of the grown crystal was ascertained. The structural conformation was done with the aid of FTIR studies.

C. Product Confirmation

Thin layer chromatography (TLC) is inexpensive and simple which is performed to identify the purity of the products [13]. The purity of the product was checked on TLC (silicagel, ethyl acetate: Hexane, 4:1) by comparison with the starting materials (pthalic acid and p-chloro aniline). The Rf value of 0.6 was observed for the product which proved that the product is a single compound.

D. Melting Point

The melting point of p-CaP was determined using visual observation method and TEMPO make melting point apparatus was employed for this purpose. p-CaP was grinded well using mortar and pestle into fine powder. The powder was filled into the capillary tube. Then the capillary tube was inserted into the melting point apparatus. On slowly raising the temperature, the melting point of p-CaP was observed at 176 ˚C.

E. Solubility

Synthesized material of p-CaP was purified by the process of re-crystallization in acetone. The re-crystallized powdered salt was added in small quantity to a beaker containing 100 ml of acetone at 30 ˚C by stirring the solution continuously. The saturation level of p-CaP at 30 ˚C was estimated. This experiment was repeated and the solubility of p-CaP was estimated for, 30, 35, 40 and 45 ˚C shown in Fig. 1.

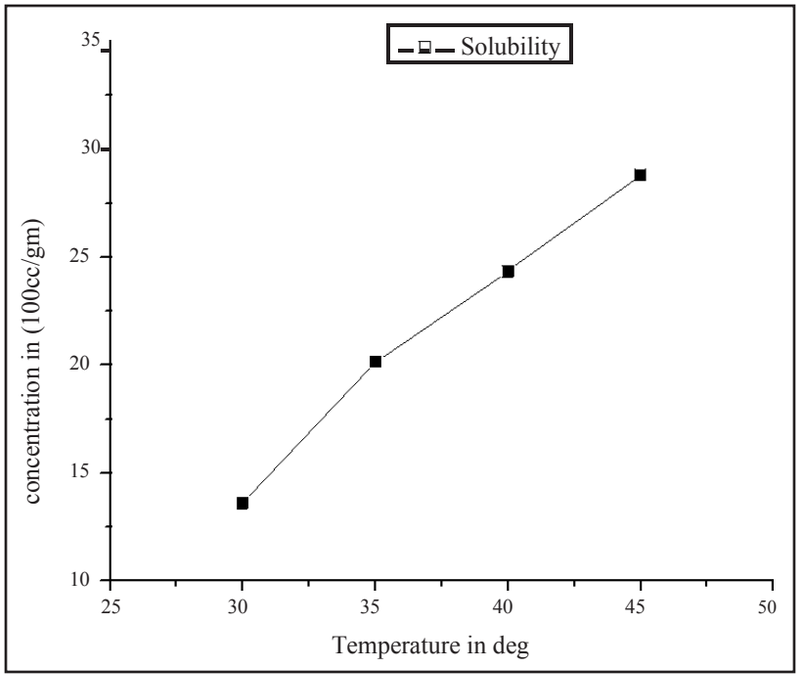


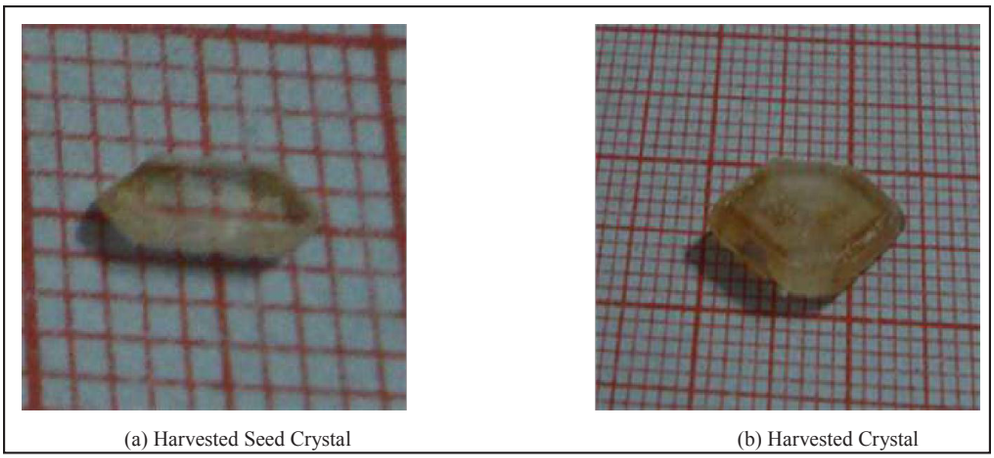
Fig. 1: Solubility Diagram of p-CaP

F. Choice of the Solvent

Solvents play a vital role for the growth of organic crystals having well developed good optical quality crystals. Solvents offering moderate solubility-temperature gradient for a material and yielding prismatic growth habit will be considered as suitable solvents for growing crystal of that material. Another important factor that influences the habit of growing crystal is the polarity of the solvents [14, 15]. Hence, in this study a few organic solvents were employed to identify the reasonable solvent. From this test acetone and methanol were found to yield prismatic growth. Since the crystals obtained from acetone were found to be relatively transparent, acetone was selected as the suitable solvent to grow p-chloro aniline pthalic acid.

G. Crystal Growth

Recrystallized salt of p-CaP was used to prepare saturated solution of acetone at room temperature. Controlled slow evaporation of the solvent yielded transparent seed crystals. One of the selected good quality crystals was used as a seed to grow single crystal at room temperature. Single crystal of size 14x10x2 mm was obtained in a period of 12 days by employing slow evaporation method and is shown in Fig. 2(a) and Fig. 2(b)



(a) Harvested Seed Crystal (b) Harvested Crystal

Fig. 2

H. Structural Studies

i) FTIR Spectral Analysis

Infrared spectrum is an important record, which provides more information about the formation and the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency [16]. FTIR spectrum was recorded for the purified sample using Perkin Elmer- paragon - 500, FTIR spectrometer. The spectra were recorded by KBr pellet technique between the range 400 cm^{-1} and 4000 cm^{-1}, which confirmed the formation of p-CaP.

P-CaP display their C-N stretching as a band at 1289 cm^{-1} C=C stretching absorption is confirmed from the band at 1525 cm^{-1} (Aromatic). Para di substituted benzenes show C-H deformation vibrations in the region 840-800 cm^{-1}. From the C-H deformation frequency at 829 cm^{-1} the formation of C-H bond was confirmed [17]. FTIR spectrum was shown in Fig. 3. Tentative frequency assignment of p-CaP is given in Table I.

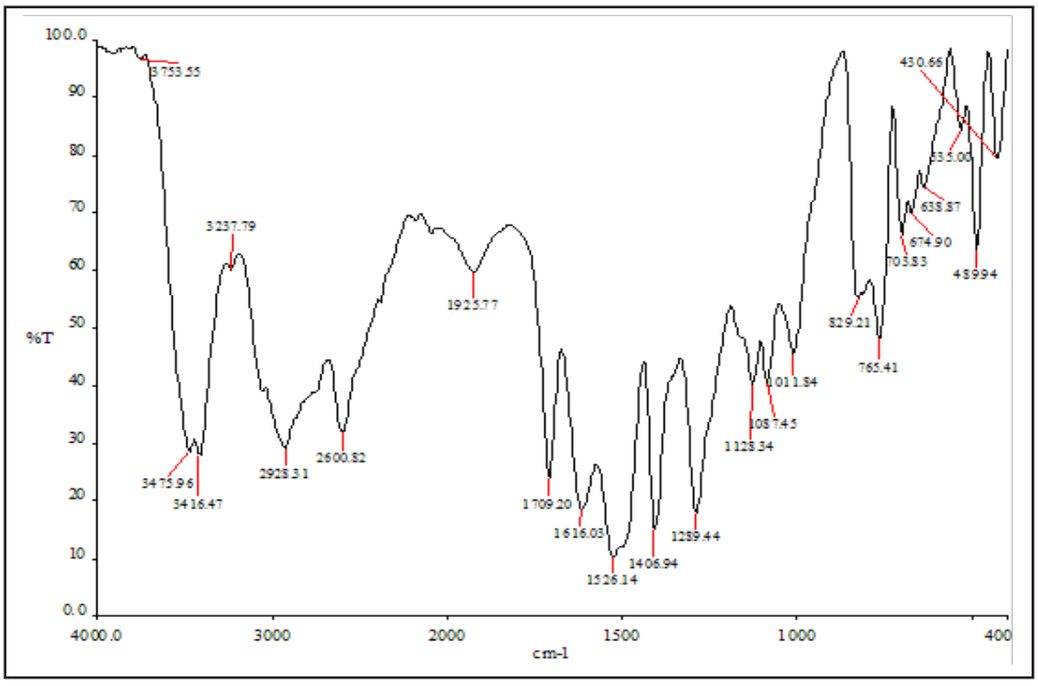


Fig. 3: FTIR Spectrum of p-CaP

Table I: Vibration Frequency Assignment of p-CaP

S. No	Frequency	Assessment
1.	3475.9	NH group
	3416.4	
2.	2928.3	C-H Stretch (Aromatic)
	2600.8	
3.	1289	C-N Stretch
4.	1525	C=C Stretch (Aromatic)
5.	829	C-Cl

ii) Single Crystal X-Ray Analysis

Single crystal X-ray diffraction study was carried out on the as grown single crystal. The present study shows that p-CaP crystallizes in orthorombic system. The unit cell parameters calculated are a = 6.261 Å, b = 8.890 Å, c = 12.727 Å with V = 708 $Å^3$. The present values compare well with the corresponding values of the parent components shown in Table II.

Table II: Comparison of Cell Parameters with Parent Compounds

Cell Parameter	p-Ca	PA	p-CaP
a (Å)	8.66	5.0	6.261
b (Å)	7.397	14.2	8.890
c (Å)	9.281	9.6	12.727
V $(Å)^3$	594	681.6	708
β°	-	93.5	-

I. Optical Studies

UV-Vis-NIR Spectral Analysis

The optical transparency spectrum of p-CaP was recorded using Shimadzu model 1601 spectrometer. The spectrum recorded in the range of 300-1100 nm is shown in Fig. 4. There is good transmittance between 550 and 1000 nm. The short wavelength cutoff at 369 nm and transparency in the range of 550-1000 nm, illustrate that the crystal has good optical quality. The UV-Vis-NIR transparency range shows that the p-CaP may be a potential candidate for NLO applications evident for that it may use as NLO applications.

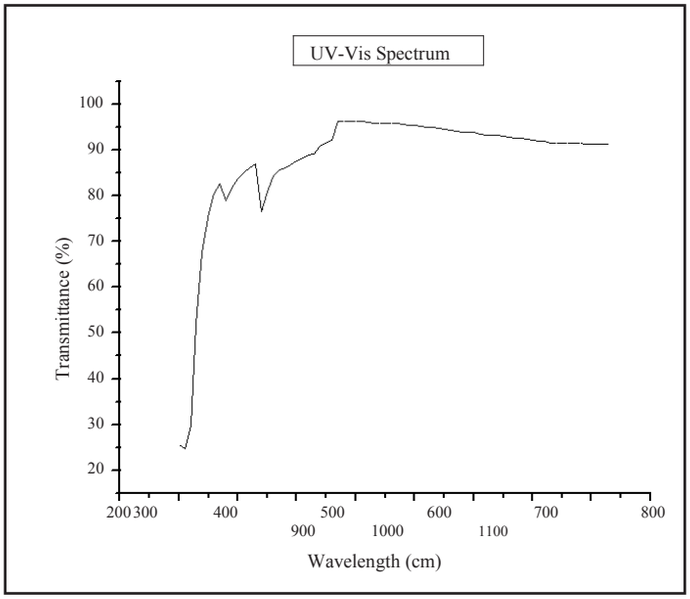


Fig. 4: UV-Vis-NIR Spectrum of p-CaP

J. Thermal Analysis

Thermogravimetry complemented with differential thermal and differential scanning studies provides valuable information about decomposition patterns of materials and weight loss [18]. Thermogram and differential thermogram analyses on p-CaP were recorded using NETZSCH- Geratebau GmbH Thermal analysis (STA 409PC) at a heating rate of 20.0 K/min in nitrogen atmosphere. From the figure it is observed that the material is stable upto 178 ºC, it is agree with the melting point of the p-CaP is 176 ºC shown in Fig. 5.

Thermogravimetric (TG) and differential thermal analysis (DTA) of p-CaP recorded at heating rate of 10 ºC/min under nitrogen atmosphere is shown in Fig. 5. The final residue weight 0.01% after 600 ºC. The peak at 220 ºC for p-CaP is due to the release of the water molecule from the crystal structure [19]. The melting point of the substance measured using 'GUNA make' melting point apparatus was 176 ºC. TGA curve shows that there is a sharp weight loss at 178 ºC and sample undergoes gradual weight loss till 600 ºC.

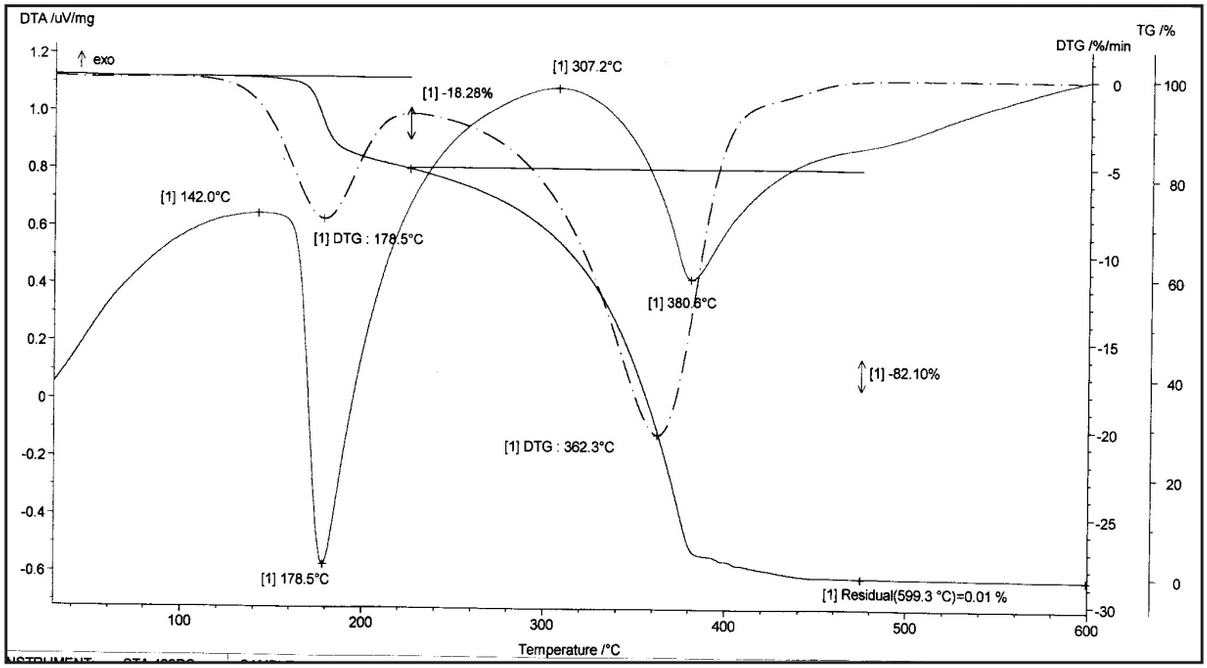


Fig. 5: TGA-DTA Spectrum of p-CaP

K. Hardness

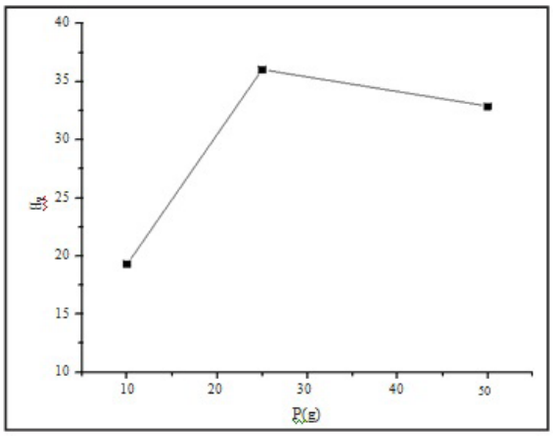


Fig. 6: Vicker Hardness of p-CaP

Microhardness testing is one of the best methods of understanding the mechanical properties of materials. The mechanical strength of the p-CaP crystal was measured using a Leitz hardness tester fitted with a diamond indenter attached to Leitz incident light microscope. Indentations were made for various loads from 5 g to 50 g. The Vickers hardness number (Hv) of the crystal was calculated using the relation $HV = 1.8544\ P/d^2$ where P is the applied load in kg and d is the average diagonal length of impression in mm. Fig. 6 shows the variation of Vickers hardness number with load for p-CaP. Cracks were observed for loads more than 50 g since p-CaP is a fairly-soluble compound, it is expected to be a soft material and is evident from the microhardness test.

III. Conclusions

Good quality crystals of p-CaP were grown by slow evaporation solution growth technique at room temperature. Single crystal XRD confirms that grown crystal belongs to the triclinic system functional groups present in the system were identified using FTIR technique. Optical transmission study shows above 90% transparency. Thermal stability of the grown material is upto 178 ºC. Microhardness testing evidenced the grown material is soft. All above results indicate that p-CaP can be used as potential candidate for optoelectronic applications.

References

[1] S. Boomadevi, H. P. Mittal, and R. Dhansekaran, "Synthesis, crystal growth and characterization of 3-methyl 4-nitropyridine 1-oxide (POM) single crystals," *Journal of Crystal Growth*, vol. 261, no. 1, pp. 55-62, January 2004.

[2] L. G. Prasad, V. Krishnakumar, and R. Nagalakshmi, "Growth and characterization of semi-organic nonlinear optical crystal: Sodium 2, 4-dinitrophenolate monohydrate," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 110, pp. 377-382, June 2013.

[3] L. G. Prasad, V. Krishnakumar, R. Nagalakshmi, and S. Manohar, "Physicochemical properties of highly efficient organic NLO crystal: 4-aminobenzamide," *Materials Chemistry and Physics*, vol. 128, no. 1-2, pp. 90-95, July 2011.

[4] A. E. Goeta, C. C. Wilson, J. C. Autino, J. Ellena, and G. Punte, "Hydrogen bonding in nitroanilines: Neutron diffraction study of m-nitroaniline at 100 K," *Chemistry of Materials*, vol. 12, no. 11, pp. 3342-3346, 2000.

[5] A. Afkhami, S. Masahi, and M. Bahram, "Spectrophotometric determination of nitrite based on its reaction with p-nitroaniline in the presence of diphenylamine in micellar media," *Bulletin of the Korean Chemical Society*, vol. 25, no. 7, pp. 1009-1011, 2004.

[6] R. T. Bailey, G. Bourhill, F. R. Cruickshank, D. Pugh, J. N. Sherwood, and G. S. Simpson, "The linear and nonlinear optical properties of the organic nonlinear material 4-nitro-4'-methylbenzylidene aniline," *Journal of Applied Physics*, vol. 73, no. 4, pp. 1591-1597, 1993.

[7] J. O. White, D. Hulin, M. Joffre, A. Migus, and A. Antonetti, "Ultrabroadband second-harmonic generation in organic and inorganic thin crystals," *Applied Physics Letters*, vol. 64, no. 3, pp. 264-266, 1994.

[8] M. Sigelle, and R. Hierle, "Determination of the electrooptic coefficients of 3-methyl 4-nitropyridine 1-oxide by an interferometric phase-modulation technique," *Journal of Applied Physics*, vol. 52, no. 6, pp. 4199-4204, 1981.

[9] B. F. Levine, C. G. Bethea, C. D. Thunmonal, R. T. Lynch, and J. L. Bernstein, "An organic crystal with an exceptionally large optical second-harmonic coefficient: 2-methyl-4-nitroaniline," *Journal of Applied Physics*, vol. 50, no. 4, pp. 2523-2527, 1979.

[10] J. Zyss, I. Ledoux, and J. F. Nicoud, *Molecular Nonlinear Optics Materials, Physics and Devices*, p. 129, New York Academic Press, 1994.

[11] C. Saiz-Jimenez, "Pyrolysis/methylation of soil fulvic acids: Benzenecarboxylic acids revisited," *Environmental Science & Technology*, vol. 28, no. 1, pp. 197-200, 1994.

[12] L. M. Belyaev, G. S. Belikova, A. B. Gil'varg, and I. M. Sil'vestrova, *Sov. Phys-Crystallogr.*, vol. 14, pp. 544-549, 1970.

[13] R. A. Ray, *Quantitative Analysis*, p. 555, Prentice-Hall of India, New Delhi, 2005.

[14] K. Srinivasan, K. Sankaranarayanan, S. Thangavelu, and P. Ramasamy, "Influence of organic solvents on the habit of NMBA (4-nitro-4′-methyl benzylidene aniline) crystals," *Journal of Crystal Growth*, vol. 212, no. 1-2, pp. 246-254, 2000.

[15] K. U. Lakshmi, and K. Ramamurthi, "Growth and characterization of 2,6-dibenzylidenecyclohexanone single crystal," *Crystal Research & Technology*, vol. 40, no. 12, pp. 1165-1178, 2005.

[16] P. Kalsi, *Spectroscopy of Organic Compounds*, Wiley Eastern, New Delhi, p. 65, 1985.

[17] W. Kemp, *Organic Spectroscopy*, 3rd ed., ELBS, Macmillan, p. 62, 1993.

[18] H. H. Willard, L. L. Merritt Jr., J. A. Dean, and F. A. Settle Jr., *Instrumental Methods of Analysis*, 6th ed., Wadsworth Publishing Company, USA, p. 609, 1986.

[19] V. Kannan, R. B. Ganesh, and P. Ramasamy, "Growth of new nonlinear optical crystals of hydrochlorides of L-histidine from solution," *Crystal Growth and Design*, vol. 6, no. 8, pp. 1876-1880, 2006.