Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 2
No. 2
pp. 73-80
Sep 2011

An Investigation on the Spectral and Microhardness studies of novel Morpholin-4-ium 3 carboxy-2, 3-dihydroxypropanoate NLO Single Crystal

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Abstract : Single crystals of Morpholin-4-ium 3 carboxy-2, 3-dihydroxypropanoate (M4CDP) was grown by slow evaporation of an aqueous solution at room temperature. The compound crystallizes in a noncentrosymmetric space group Cc of triclinic crystal system with cell parameters a= 7.6260 $\AA$, b= 8.2408 $\AA$, c= 10.1674 $\AA$, α = 98.462°, β = 106.282° and γ = 104.807° at 303 K. The presences of various functional groups were confirmed by FTIR, ^{1}H and ^{13}C NMR spectral analysis. The mass spectrum confirms the molecular weight of the sample. The SHG in the grown crystal was identified by Kurtz-Perry method using Nd:YAG laser as the source. The melting point of the crystal was found to be 106°C. The Meyers constant of the crystal was found to be n= 1.4285 which helps fashion the crystal towards device geometry.

Keywords : Growth from Solution, XRD, NMR, Mass, Microhardness

1. Introduction

Development of novel molecular and crystal design technique for assembling the material is a nifty concern. In particular, organic material provides many structure and bonding schemes for the molecular engineering of new materials. In recent years organic crystals are rated high as compared to inorganic in view of their large electro-optic, coefficients with low frequency dispersion, low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and intrinsic tailorability [1-2]. M4CDP is an intriguing one, since among its simple salts one finds the existence of noncentrosymmetric structures. In the present investigation we have synthesized, grown and characterized M4CDP single crystals for the first time by slow evaporation technique. In the present investigation, we report the growth of M4CDP single crystal by XRD, FTIR, ^{1}H and ^{13}C NMR, mass study, melting point measurements and microhardness studies.

2. Synthesis, Growth and Single Crystal XRD

Cold absolute methanol was added to 2,3 di hydroxyl 1,4- butdioic acid. The acid was dissolved by heating the mixture on a hot plate with stirring maintained at a temperature of 85°*C*. The solution was cooled to 25°*C* and morpholine was added drop wise. The product M4CDP was precipitated out of the solution immediately as a white tiny seed crystals by spontaneous nucleation. Optical defect free single crystal of dimensions 8x8x3xmm^3 was harvested in a period of a week. The photograph of as grown crystals of M4CDP was shown in Figure*1*.

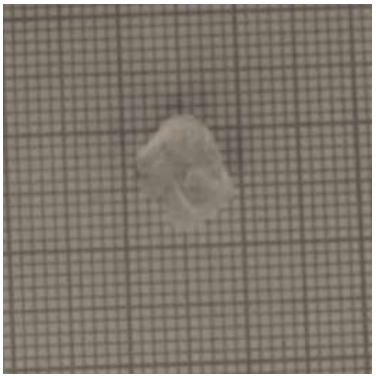

Figure 1. Photograph of as Grown Single Crystal of M4CDP

Bruker-Nonius Kappa Apex II CCD diffractometer with M_oK_α (0.71073 Å) radiation was used to obtain the accurate cell parameters of the grown crystals at room temperature. Cell parameters were obtained from least squares refinement of the setting analyses of 25 reflections. The lattice parameters are *a*= 7.6260 *Å*, *b*= 8.2408 *Å*, *c*= 10.1674 *Å*, α= 98.462°,

$\beta = 106.282°$ and $\gamma = 104.807°$. M4CDP crystal belongs to triclinic crystal system with space group *cc*. The volume of the M4CDP crystal was found to be volume = 576.25 $Å^3$.

3. FTIR Analysis

FTIR spectrum is an important analytical tool by which the functional groups present in the compound can be easily identified. The FTIR spectrum of M4CDP is shown in Figure *2*. The spectrum was recorded using the instrument PE Spectrum One FT-IR Spectrometer. The two sharp peaks at 3430 and 3311 cm^{-1} corresponds to the free –OH and –NH stretching, respectively. The spectrum also shows a peak at 1655 cm^{-1} which is due to the presence of carbonyl stretching frequency of carboxylic acid present in the tartaric acid moiety. Moreover the peak at 1551 cm^{-1} is due to –NH bending vibration of the morpholine –NH group. Additionally the spectrum also shows 1361 and 1232 cm^{-1} corresponding to ether group present in morpholine moiety.

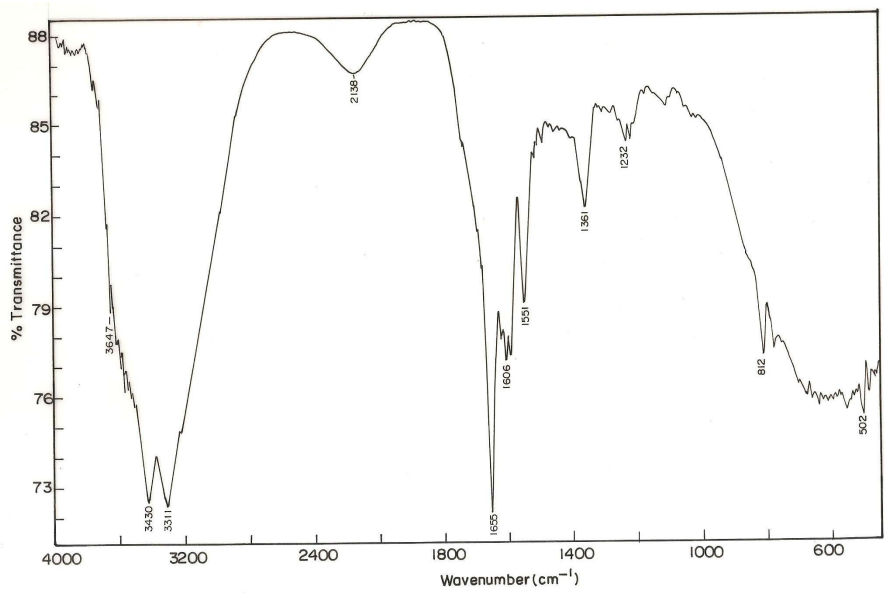

Figure 2. FTIR Spectrum of M4CDP Single Crystal

4. NMR Studies

NMR spectroscopy is widely used not only in the structural determination of synthesized compound but also its analytical purity. The ^{1}H and ^{13}C NMR spectra of M4CDP sample was recorded using a JEOL: GSX 500 instrument in H_2O solvent with tetramethylsilane (TMS) as an internal standard. Figures *3a* and *3b* represent ^{1}H and ^{13}C NMR spectra respectively. ^{1}H NMR spectrum show a triplet at 3.08*ppm* which corresponds to the protons present in the

ortho to the ammonium salt. Similarly the appearance of triplet at 3.75 *ppm* confirms the presence of protons in the meta position to the ammonium group and ortho to the oxygen ring. Similar pattern was observed in the synthesized compound containing morpholine salt tartaric acid moiety. Appearance of triplet and doublet at 6.32 and 6.74 *ppm* are attributed to the –CH and C–OH protons respectively in the tartaric acid moiety.[13]C NMR spectrum of the synthesized compound shows peaks at 42.1, 63.2, 107, 109, 138, 158, 177 *ppm*. The peaks at 42.1 and 63.2 *ppm* correspond to the presence of two different carbons in the morpholine moiety. Similarly the other peaks obtained in the range 107 – 177 *ppm* are due to the carbons of tartaric acid moiety.

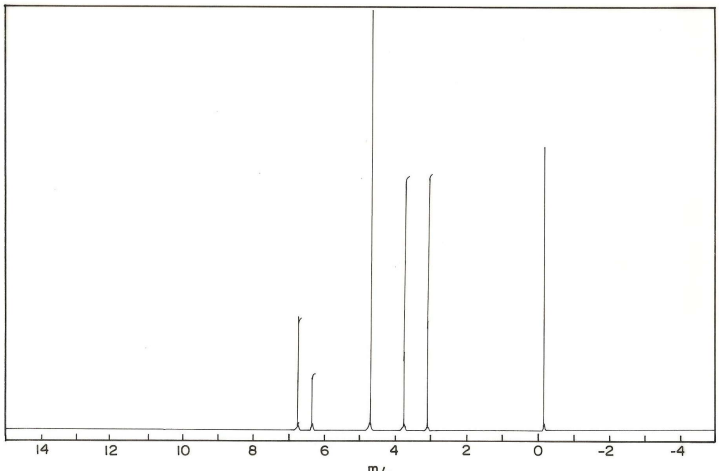

Figure 3a. [1]H NMR Spectrum of M4CDP Single Crystal

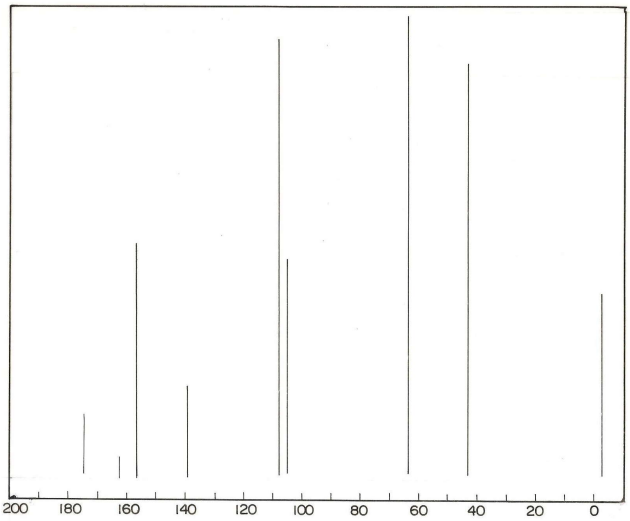

Figure 3b. [13]C NMR Spectrum of M4CDP Single Crystal

5. Mass Spectrum Analysis

The mass spectrum of M4CDP was recorded using JEOL GCmate spectrometer. The value of M/z at which the molecular ion (M^+) appears on the mass spectrum, assuming that the ion has only one electron missing, gives the molecular weight of the original molecule. The EI mass spectrum of the compound shows M/z at 235 corresponding to M^+- Z ion which confirms the molecular weight of M4CDP. Additionally the spectrum also shows a peak at M/z 203 which corresponds to the M^+- Z [3] which is attributed to molecular ion minus two hydroxyl groups. The mass spectrum of M4CDP is shown in Figure*4*.

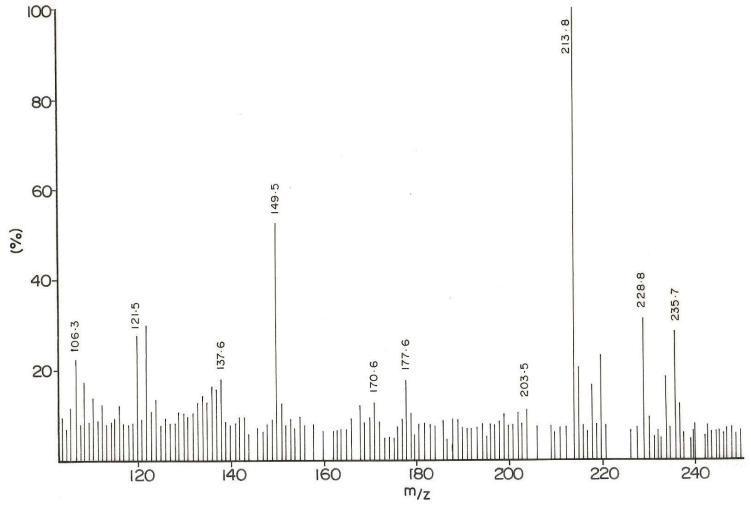

Figure 4. Mass Spectrum of M4CDP Single Crystal

6. SHG Study

The study of non linear optical conversion efficiency was carried out using the modified experimental setup of Kurtz and Perry [4]. A Q-switched Nd:YAG laser beam of wavelength 1064 *nm*, with an input power of 2.8 *mJ* and a pulse of width 8 *ns* with a repetition rate of 10 *Hz* was used. The grown single crystal of M4CDP was powdered with a uniform particle size and then packed in a micro capillary tube of uniform bore and exposed to laser radiation. The output from the sample was monochromated to collect the intensity of 532*nm* component and to eliminate the fundamental frequency. Second harmonic radiation generated randomly oriented micro crystals were focused by a lens and detected by a photo amplifier tube. The generation of second harmonics was confirmed by the emission of green light. A KDP sample was used as the reference material, and the output power intensity of M4CDP was observed. A second harmonic signal of 165 mV was obtained from M4CDP with reference to 78 mV of KDP. Thus, the SHG efficiency of M4CDP is roughly 2 times that of KDP.

7. Melting Point Measurement

The melting point of the grown M4CDP crystal was determined using a melting point apparatus (Model: TEMPO PT S100-230V). The microcapillary tube containing the powder sample was inserted into the melting point apparatus with a thermometer nearby. The temperature was gradually increased and the powder of the M4CDP started to melt into a transparent solution. The corresponding temperature was measured indicating the melting point 104.5°*C* of M4CDP. The error in the measurement was±2°*C*.

8. Microhardness Studies

Vicker's microhardness measurements were carried out on M4CDP crystal. The indentations were made using a Vickers pyramidal indentor for various loads from 10 g to 60 *g*. The diagonals of the impressions were measured using Vickers Microhardness Tester fitted with a diamond pyramid indenter. Vickers microhardness number was evaluated from the relation,

$$H_v = \left(\frac{1.854\ P}{d^2} \right)\ kg/mm^2$$

where H_v is Vicker's hardness number, *P* is the indenter load in kilogram and *d* is the diagonal length of the impression in millimeter. The variation of microhardness values with applied load is shown in Figure *5a*. The hardness value decreases with increasing load. For loads above 50 *g*, cracks developed on the surface of the crystal due to the release of internal stress generated locally by indentation. The phenomenon of dependence of microhardness of a solid on the applied load, at low level of testing load is known as indentation size effect (ISE). By plotting *log P* verses *log d* (Figure *5b*), the value of the work hardening coefficient (*n*) of M4CDP was found to be 1.4. According to Onitsch (1956), $1.0 \leq n \geq 1.6$ for hard materials and $n>1.6$ for soft materials. Hence, it is concluded that M4CDP is a hard material, which means the material is mechanically strong enough to be used in device fabrications.

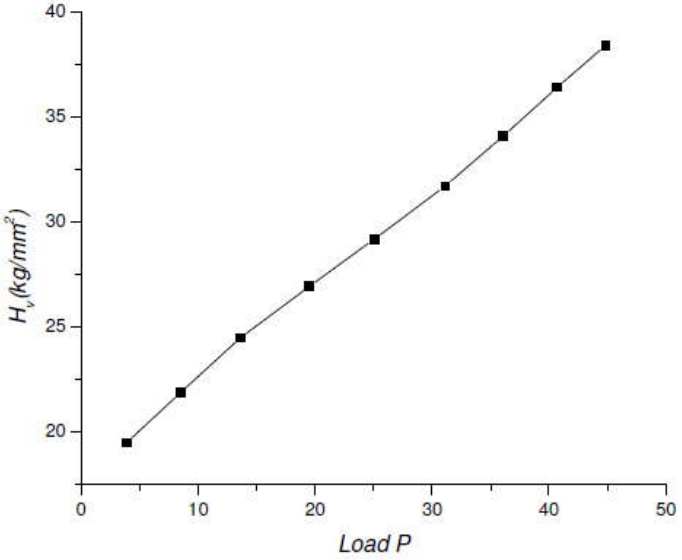

Figure 5a. Variation of Vickers Hardness Number with Applied Load for M4CDP Single Crystal

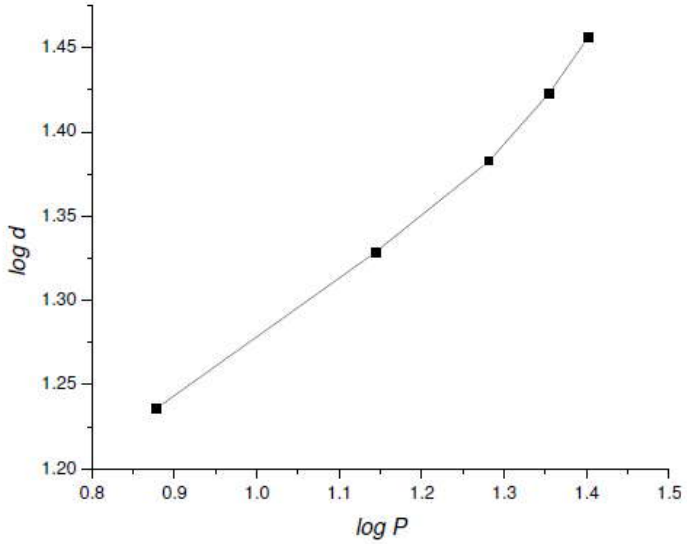

Figure 5b. Plot of log P against log d for M4CDP Single Crystal

Conclusions

The organic material M4CDP was synthesized and good optical quality single crystals were grown by slow evaporation solution growth method at room temperature. Single crystal XRD study establishes the noncentrosymmetric which is the root cause for the NLO activity in

this organic material. The presence of various functional groups stands confirmed from FTIR, ^{1}H and ^{13}C NMR spectra. From the mass spectral study the molecular weight of the sample was determined. The second harmonic generation property of the grown crystal was tested and found to be efficient compound to KDP crystal. The microhardness studies established that the M4CDP crystal is a hard material.

ACKNOWLEDGMENT

It is a pleasure to Dr. L. Joseph Milton Gaspar, Associate Scientist, ITC R&D Centre, Bengaluru, Dr. M. Palanichamy, Professor, Department of Chemistry, Anna University, Chennai and Dr. A. John Maria Xavier, Assistant Professor, Department of Chemistry, Loyola College, Chennai for their constant help, support and encouragement.

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