

CRYSTAL GROWTH, STRUCTURAL, THERMAL, OPTICAL, AND DIELECTRIC CHARACTERIZATION OF CINCHONIDINIUM Bis(4-Methylben-Zenesulfonate) MONOHYDRATE SINGLE CRYSTAL

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Abstract

The synthesis of Cinchonidinium bis(4-methylben-zenesulfonate) monohydrate (CPT) utilized the slow evaporation solution technique (SEST) employing an aqueous solution composed of Cinchonidine and 4-methylbenzene-sulfonate at 323 K. The resulting CPT crystal, classified within the triclinic system, aligned with space group P1. Lattice parameters were verified through Powder X-ray diffraction, ensuring the crystal's structural characteristics. The determination and validation of functional groups and molecular bonds were accomplished via comprehensive FT-IR spectral analysis. Evaluation of the crystal's optical properties was conducted through UV-Visible-NIR spectrum analysis, revealing a favorable optical transmittance within the 400-1,100 nm range. Moreover, the thermal characteristics of the CPT crystal underwent thorough examination utilizing thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses.

Keywords: Crystal growth; Optical properties; Thermal properties

Introduction

In today's fast-developing technological landscape, non-linear optical (NLO) materials have a wide range of applications in a variety of fields. These applications include optical data storage, lasers, optical signal processing, and second harmonic generation. Despite the availability of diverse NLO materials, their practical applications are constrained by distinct physical and chemical properties (Aggarwal *et al.*, 2003). Effective utilization of NLO applications necessitates the presence of high-quality single crystals characterized

by substantial NLO coefficients and improved physical parameters. Among the prospective systems conducive to realizing substantial second-order non-linear coefficients are organic crystals. The scrutiny of organic materials is notable due to the microscopic origin of their NLO responses, enabling the utilization of theoretical modeling and synthetic adaptability in the innovation and production of new materials (Kitazawa *et al.*, 1994; Suresh, 2014). Recent explorations into organic NLO materials have yielded materials with

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exceptionally appealing traits. Particularly, organic crystals have been the subject of a significant amount of research. This is partly because organic crystals typically have non-linear optical coefficients that are superior to those of inorganic materials. Additionally, besides possessing significant NLO coefficients, organic NLO crystals should exhibit UV transparency (Peramaiyan *et al.*, 2014; Charoen-In *et al.*, 2015). The deployment of NLO applications requires the utilization of materials that possess wide macroscopic second-order susceptibilities. These materials are often constructed of molecules that exhibit significant molecular-first hyperpolarizability and are arranged in a configuration that is non-centrosymmetric (Pandian *et al.*, 2010). Recognized as 4-methylbenzenesulfonate is an organic acid available in a solid phase, demonstrating charge transfer facilitated by the CH_3 group as an electron donor and the sulfonate group as an acceptor in this compound. Complex formations encompassing both organic and inorganic bases may contribute to inducing heightened NLO behavior (Charoen-In *et al.*, 2013; Azeeza *et al.*, 2015). A key consideration in selecting these substances is their chirality, the property of lacking a plane of symmetry that enables the exhibition of NLO characteristics. Cinchonidine possesses this chirality, yet limited research has explored its NLO properties (Boratyński *et al.*, 2019). Conversely, the aggregation of organic molecules featuring complete conjugated bonds represents an intriguing domain within NLO material research. Over the last twenty years, a substantial amount of research efforts has been devoted to the process of understanding the NLO characteristics of organic compounds. Promising candidates among the extensive array of organic compounds investigated for their NLO behavior include cinchonidine and 4-methylbenzenesulfonate. Particular attention has been attracted to cinchonidine, an organic compound obtained from the bark of the Cinchona tree, due to its remarkable optical characteristics and chirality. It belongs to a class of compounds known as alkaloids, which possess a complex molecular framework. The presence of chiral centers in cinchonidine leads to its enantiomeric form, providing opportunities for investigating the effects of chirality on NLO properties. The unique molecular structure of cinchonidine offers the potential for nonlinear optical applications such as second harmonic generation, frequency mixing, and optical switching. However, in the current research, no studies have been found that utilize cinchonidine as a component in investigating NLO materials. Further exploration and investigation are required to determine its potential in the field of nonlinear optics.

The objective of this work is to explore and enhance the nonlinear optical properties of organic

materials by employing the solution growth technique to obtain high-quality single crystals. The main focus of this study is on the formation of single crystals, specifically cinchonidinium bis (4-methylbenzene sulfonate) monohydrate (CPT). A thorough investigation of the structural, vibrational, optical, thermal, and electrical attributes of these crystals will be conducted. By utilizing characterization methods, the physical and chemical properties of the materials can be quantitatively assessed, thereby facilitating the optimization of growth processes and the enhancement of crystal quality.

Experimental Procedure

Cinchonidine is an organic compound consisting of carbon, nitrogen, oxygen, and hydrogen, with the chemical formula $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$. In this work, high-quality reagents were utilized in the process of synthesis of the CPT chemical. This was accomplished by combining cinchonidine ($\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$) and 4-methylbenzene-sulfonate ($\text{C}_7\text{H}_8\text{O}_3\text{S}$) in a proportion of 1:3 within di-water at a temperature of 323 K. This amalgamation underwent stirring for about 6 hours to ensure comprehensive reaction completion. The resulting synthesized crystal was subjected to repeated cycles of recrystallization in di-water to purify the compound. Upon reaching saturation at 323 K, the refined CPT crystal dissolved in di-water, creating a uniform solution through consistent stirring. This solution, already saturated, underwent additional refinement and evaporation at higher temperatures. Utilizing a repetitive recrystallization methodology, the synthesized material underwent further refinement. The spontaneous nucleation process fostered the development of minute, transparent seed crystals, meticulously scrutinized to select an optimal seed crystal suspended within the solution to facilitate room-temperature evaporation. This rigorous process facilitated the growth of single crystals of considerable dimensions, measuring approximately $16 \times 7 \times 2 \text{ mm}^3$, cultivated over thirty days via the gradual solvent evaporation process. Figure 1 displays an illustration of the cultivated CPT crystal.

Results and Discussion

Analysis of a Single Crystal Using X-ray Diffraction

To determine the crystal structure, X-rays of known wavelengths are directed through the sample. The lattice of the crystal diffracts these



Figure 1. Cinchonidinium bis(4-methylbenzenesulfonate) monohydrate crystal

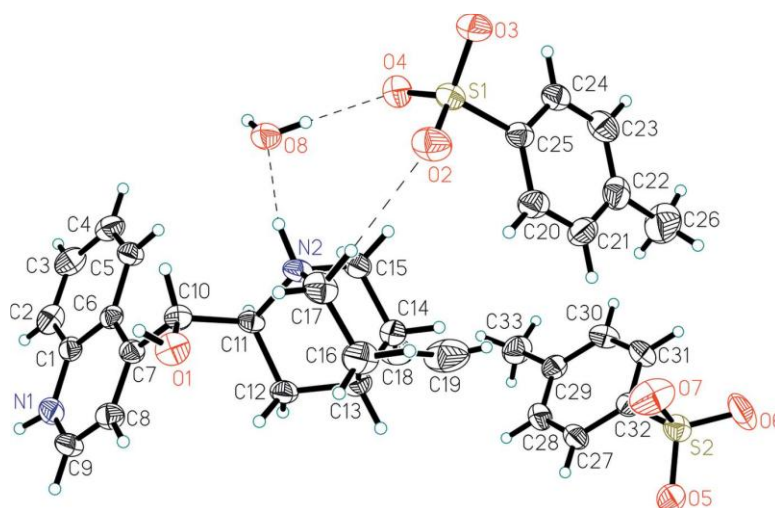


Figure 2. The molecular structure of CPT crystalline form

X-rays, resulting in a distinctive pattern of peaks with varying intensities and angles. The unit cell parameters of the CPT single crystal were obtained using a Bruker X-ray diffractometer, utilizing light having a wavelength of 1.54184 Å. A crystal was meticulously chosen and positioned on the diffractometer, maintaining its temperature at 296.15 K throughout the data collection process. Computational analysis involved employing Olex2 (Dolomanov *et al.*, 2009) for structural resolution via ShelXS (Sheldrick, 2015) utilizing Direct Methods, followed by refinement using the Olex2.refine (Puschmann *et al.*, 2013) package with Gauss-Newton minimization. The examination confirmed the CPT crystal's categorization within

the triclinic system under the space group P1, showcasing lattice parameters consistent with the reported values as depicted in Table 1 (Hui-Min *et al.*, 2006). Figure 2 displays an illustration of the CPT single-crystal structure. In addition, a Bruker diffractometer was used to obtain the powder X-ray diffraction (PXRD) patterns of the cultivated CPT crystal. The diffractometer employed CuK α (λ = 1.5418 Å) line radiation. The scanning process ranged from 5° to 80° at a rate of 1°/min. Figure 3 displays the pattern of X-ray diffraction of CPT, where the peaks observed in the structure confirm the successful determination of the lattice parameters. The presence of apparent peaks in the X-ray diffraction confirms the

Table 1. The crystalline data for the CPT crystal

Parameters	Present work	Reported reference (Hui-Min <i>et al.</i> , 2006)
Unitcell dimensions	$a = 6.588$ (2) Å $b = 9.630$ (9) Å $c = 12.786$ (6) Å $\alpha = 97.40$ (6)° $\beta = 95.91$ (8)° $\gamma = 85.27$ (9)°	$a = 6.565$ (3) Å $b = 9.599$ (4) Å $c = 12.748$ (5) Å $\alpha = 85.25$ (3)° $\beta = 84.08$ (3)° $\gamma = 82.71$ (3)°
Volume	798.30 Å ³	790.66 Å ³
System	Triclinic	Triclinic
Space group	P1	P1

Table 2. FTIR band assignments of CPT crystal

Wavenumber (cm ⁻¹)	Descriptions of Vibrational Modes
3,400	N-H stretching
3,239	N-H ⁺ stretching
3,050	C-H symmetric stretching
2,656	C-H Asymmetric stretching
1,633	NH ₃ Asymmetric deformation
1,605	NH ₃ Asymmetric deformation
1,552	C-C Stretching
1,490	N-H asymmetric bending vibration
1,384	CH ₂ deformation
1,320	C-N asymmetric stretching
1,232	SO ₃ asymmetric Stretching
1,165	C-N symmetric stretching
1,114	Asymmetric stretching vibrations of the C-C group
923	S-O-C stretching vibration
877	O-H out of plane deformation
815	4-methyl benzenesulfonate
752	C-H out of plane bending mode
674	N-H wagging vibration
556	SO ₃ Asymmetric deformation
483	C-N-C deformation

crystalline structure of the specimens, specifically the (0 0 1) peak, which exhibits the maximum intensity per second.

Vibrational Analysis

The FT-IR analysis conducted on CPT serves to validate the presence of distinct functional groups within the developed crystal. The FTIR spectrum obtained using a BRUKER Tensor 27 FT-IR spectrometer in the attenuated total reflectance (ATR) mode is graphically depicted in Figure 4. The specific wavenumbers and their corresponding assignments may be found in Table 2. This investigation spanned from the visible light to the mid IR region, encompassing the wavenumber range of 400 to 4,000 cm⁻¹, maintaining a resolution of ± 5 cm⁻¹. Notably, the spectrum portrays essential features: the N-H stretching of cinchonidine ions manifesting as vibrations at 3,400 cm⁻¹, the C-H symmetric and asymmetric stretching vibrations at 3,050 cm⁻¹ and 2,656 cm⁻¹ respectively, and the C=C-H stretching mode of 4-methylbenzenesulfonate at 3,050 cm⁻¹. In the range of 3,500-3,000 cm⁻¹,

there are prominent peaks associated with the stretching vibrations of O-H bonds. These peaks arise from the interaction between hydrogen atoms and oxygen atoms in functional groups such as alcohols, phenols, ethers, acids, or esters. The positions and intensities of these peaks provide information about the hydrogen bonding and the presence of specific functional groups. Moreover, the NH₂⁺ deformation is indicated by peaks observed at 1,633 and 1,605 cm⁻¹, while the N-H asymmetric bending vibration appears at 1,490 cm⁻¹. Other significant absorptions include the stretching vibration of the sulphonate group, which occurs at 1,384 cm⁻¹, the deformation of CH₂ at the same wavenumber, and the asymmetric and symmetric stretching peaks for the C-N group, which are detected at 1,320 cm⁻¹ and 1,165 cm⁻¹, respectively. Lastly, the out-of-plane bending mode of the C-H group is depicted at 752 cm⁻¹ (Willard *et al.*, 1986; Peramaiyan *et al.*, 2014; Kumar *et al.*, 2016) encapsulated comprehensively in Table 2 along with the corresponding functional group assignments.

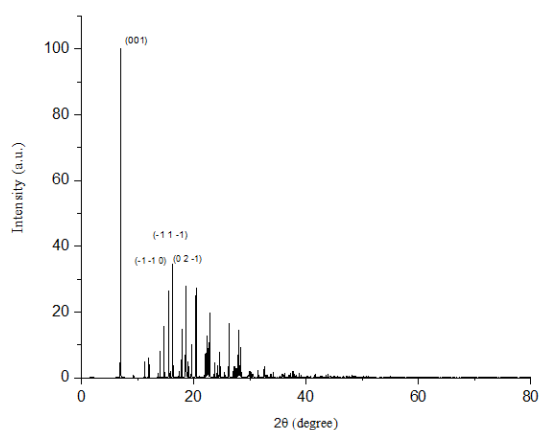


Figure 3. The X-ray diffraction of CPT

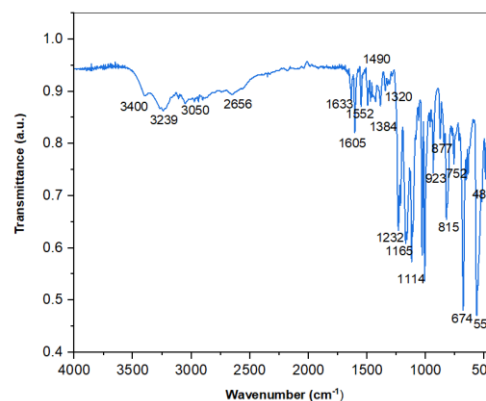


Figure 4. FT-IR spectrum of CPT crystal

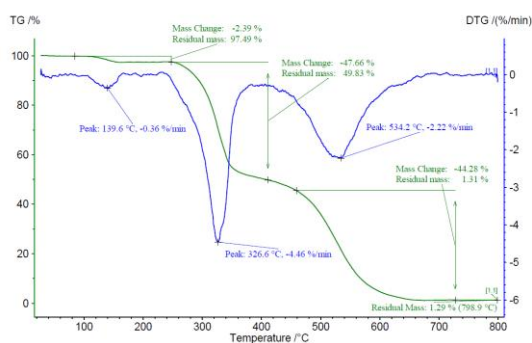


Figure 5. TG/DTG curve of CPT crystal sample

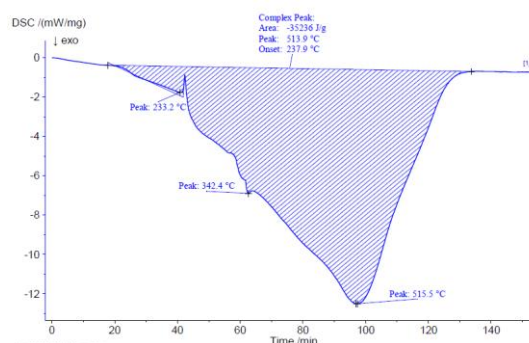


Figure 6. DSC curve of CPT crystal

Thermal Study

The investigators performed thermal investigations using a NETZSCH STA 449F5 differential thermal instrument in a nitrogen atmosphere. The measurements were taken on a powder sample of CPT weighing 5.29 mg and were acquired at a rate of 6°C/min over a temperature range of 30 to 800°C. The resulting TG/DTG and DSC curves (refer to Figure 5 and Figure 6) provide insights into the material's thermal stability and decomposition behavior. According to the DSC analysis, the compound exhibits a melting point of 233.2°C. An exothermic peak observed at 515.5°C signifies the material's decomposition, releasing volatile gases like CO₂, NO₂, and NH₂, among others. Notably, the initial mass of the material was 5.29 mg, while only 0.068 mg (1.29%) of the initial mass remained at 798.9°C, indicating significant decomposition. Based on these findings, the crystal's characteristics render it suitable for potential applications in thermal sensor applications.

Investigation of Dielectric Constant and Loss

The study of the electrical properties of dielectrics in connection to their composition and structure not only establishes a basis for the development of new materials with distinctive qualities but also provides significant insights into the bonding nature of the material through the analysis of the dielectric constant. The dielectric properties of the CPT underwent characterization through a process involving cutting and polishing the grown crystal using fine grits and a lubricant. After the preparation of the specimen into a square shape with a thickness of 1.2 mm, further measurements were carried out using a Hewlett Packard 4194 A Impedance/Gain phase analyzer. This allowed the determination of the dielectric constant across a frequency spectrum ranging from 100 Hz to 1.5 MHz at ambient temperature. Coating the CPT specimen on both sides with silver paste facilitated further analysis. The dielectric constant was computed using the formula Equation 1.

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (1)$$

where ϵ_0 represents the permittivity of free space, C stands for capacitance, d signifies the sample thickness, and A denotes the cross-sectional area. As depicted in Figure 6, the dielectric constant of CPT single crystals exhibits a frequency-dependent behavior. At 100 Hz, the maximum dielectric constant for the grown CPT crystal reached approximately 56, significantly diminishing with an increase in frequency. As shown in Figure 7, the behavior of dielectric loss at lower frequencies is subject to various controllable factors, such as defects, temperature variations, and crystal size, evident from the high dielectric loss value of 80 at 100 Hz, dropping to 0.3 at 1.5 MHz. This trend is further illustrated in Figure 8, which provides a comprehensive view of the dielectric loss characteristics of the material, reinforcing the strong dependence of dielectric loss on frequency. The notably low dielectric loss observed in the grown

CPT crystal underscores its improved optical quality with minimal defects (Pandian and Ramasamy, 2010), showcasing its relevance in the production of IR detectors.

UV-Vis NIR Study

The spectrophotometer utilized to acquire the optical absorption spectra was the Shimadzu UV-3600, which operated at room temperature and maintained a spectral resolution of 1 nm. In this study, the UV-visible transmission of the CPT crystal spanning 200 to 1000 nm is depicted in Figure 9, providing crucial insights into the material's electronic transitions and facilitating comprehension of its electronic structure and optical band gap. Analysis of the transmission spectrum reveals a notable transmittance of approximately 78%, persisting throughout the entire visible spectrum. Notably, the optical cut-off wavelength for this crystal is identified at 240 nm within the UV region, signifying the likelihood of $n-\pi^*$ electronic transitions in this state. Employing the transmittance

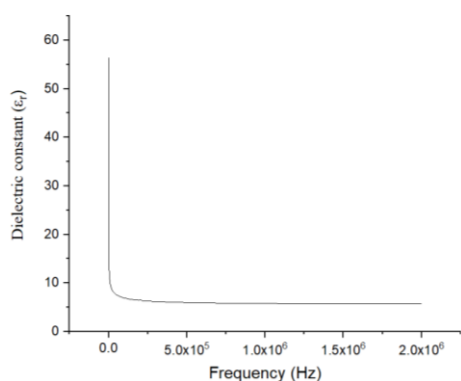


Figure 7. An investigation into the dielectric constant of the CPT crystal

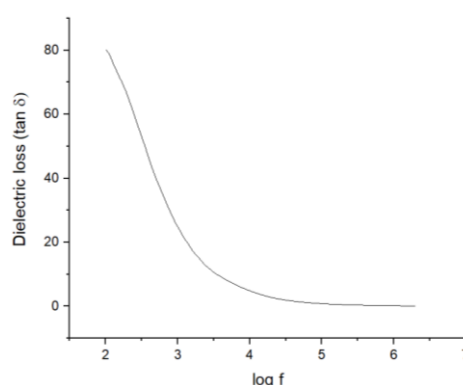


Figure 8. The measurement of the dielectric loss of the CPT crystal

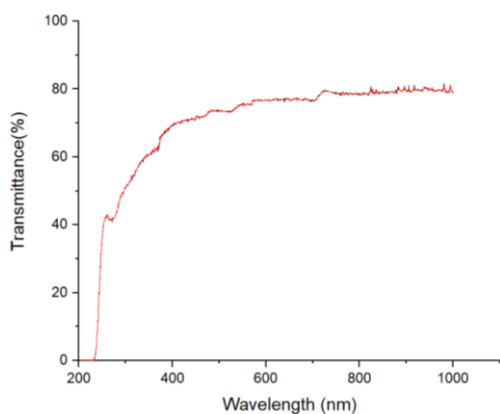


Figure 9. Optical Transmittance Spectrum of CPT crystal

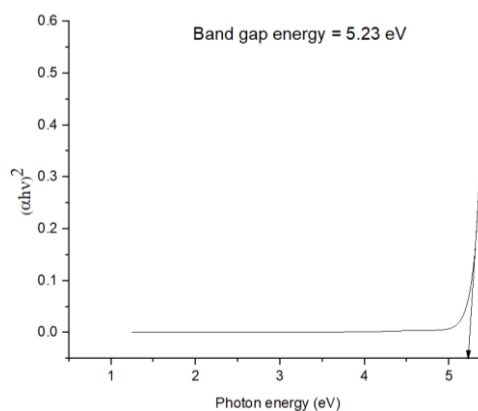


Figure 10. Tauc's Plot of CPT crystal

value and the crystal sample's thickness, the determination of the absorption coefficient (α) was derived using a specific equation.

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (2)$$

In the above equation, T to denote the transmittance percentage, while t signifies the crystal's thickness, measured at 1.8 mm. Specifically, the absorption coefficient for CPT is determined at 138.06 m^{-1} . To compute the optical band gap energy (E_g), Tauc's plot Equation (2) is employed, a formula specifically tailored for calculating the material's optical band gap energy.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3)$$

A in the equation denotes the band edge constant, while $h\nu$ represents the photon energy, and n signifies the index characterizing the electronic transition's nature during the absorption process. The resulting Tauc's plot, depicted in Figure 10, provides crucial insights. From this plot, the determined optical bandgap value stands at 5.23 eV. Notably, the CPT crystal exhibits a commendable optical bandgap energy along with a high transmittance value, signifying its significant utility within optoelectronic applications (Moses *et al.*, 2019).

Conclusions

In this work, cinchonidinium bis(4-methylbenzenesulfonate) monohydrate (CPT) was successfully synthesized using the conventional slow evaporation solution method, requiring a time span of over two months, followed by a comprehensive evaluation of the crystal system and cell parameters via single crystal X-ray diffraction analysis. The resulting crystal was categorized within the triclinic crystal system, specifically under space group P1. The assignment of various vibrational modes was conducted through FTIR investigations. FTIR spectrum shows functional group peaks, the major peaks in the $3,500\text{-}3,000 \text{ cm}^{-1}$ range are linked to O-H bond stretching vibrations. In functional groups including alcohols, phenols, ethers, acids, and esters, hydrogen and oxygen atoms interact to form these peaks. The placements and intensities of these peaks reveal hydrogen bonding and functional groups. In addition, peaks due to sulfonate group vibrations can be seen between $1,200\text{-}1,000 \text{ cm}^{-1}$. Moreover, thermal analysis confirmed the crystal's remarkable thermal stability up to 232°C . Despite the material's

high heat resistance and impressive optical transparency of 78%, limitations in experimental equipment for nonlinear optical material assessments resulted in a lack of specific data. Nevertheless, this research work provides insights into cinchonidine, suggesting its potential for future developments in nonlinear optical material advancements.

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