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# Synthesis, Growth, Spectral, Optical and Mechanical Properties of an Organic Single Crystal: (E)-2-(4-Chlorostyryl)-1-Methylpyridin-1-Ium Iodide Hydrate

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**Keywords:** stilbazolium derivative, nonlinear optical material, slow evaporation, hardness, Z-scan technique.

**ABSTRACT.** An organic stilbazolium derivative of (E)-2-(4-chlorostyryl)-1-methylpyridin-1-ium iodide hydrate (CMPI) crystal was grown from the methanol-acetonitrile mixed solvent by slow evaporation technique at room temperature. The crystal system and cell parameters of the grown crystal are verified by single crystal X-ray diffraction analysis. The functional groups of CMPI were identified from FTIR spectrum. The optical behaviour of the grown crystal was analysed by UV-vis-NIR studies. The mechanical stability of the grown crystal was investigated by Vicker's microhardness tester. The third-order nonlinear optical property of the grown crystal was elucidated by employing the single beam Z-scan technique.

**Introduction.** The nonlinear optical (NLO) properties of organic molecular materials have been the object of intense research due to potential applications in various photonic technologies. Organic molecules with significant NLO behaviour originate from a strong donor-acceptor intermolecular interaction with high chromophore density and delocalised  $\pi$ -electron system [1]. Normally organic chromophores exhibit high and fast nonlinearities than their inorganic counterparts. The stable packing of chromophores in organic crystals, which in turn results in high thermal, mechanical and photochemical stability [2]. Stilbazolium derivatives are found to be the interesting groups of organic materials because their molecular nonlinearity can be easily preserved by varying the counter-ions to achieve the desired physical and chemical properties [3]. Among them, the organic stilbazole crystal, 4-N,N-dimethylamino-4'-N'-methylstilbazolium tosylate (DAST) is of wide interest owing to its outstanding NLO properties and electro-optical properties [4]. The variation of counter-ions in stilbazolium salt is a simple and highly successful method to create new materials with macroscopic optical nonlinearities [5]. These points motivated us to design and synthesis stilbazolium crystals having a  $\pi$ -conjugated system with the good nonlinear response. Though the information about the X-ray crystallographic structural data of (E)-2-(4-chlorostyryl)-1-methylpyridin-1-ium iodide hydrate (CMPI) is available, there is no report on the growth of this material for NLO applications. Hence, we report in this present investigation synthesis, growth, spectral, optical, mechanical, and third-order nonlinear optical properties of the organic stilbazolium derivative, CMPI.

**Material synthesis and crystal growth.** CMPI was synthesized by the Knoevenagel condensation of 1, 2 dimethyl pyridinium iodide and 4-chloro benzaldehyde taken in equimolar ratio and dissolved in methanol (10 ml) in the presence of piperidine as a catalyst. The resulting mixture was refluxed for 8 h until it crystallizes as yellow salt. The product was purified by successive recrystallization from methanol. CMPI single crystals of size 6x2x1.5 mm<sup>3</sup> were grown from the saturated solution of CMPI in methanol: acetonitrile (1:1) mixed solvent by slow evaporation technique over a period of 30 days (Fig. 1).

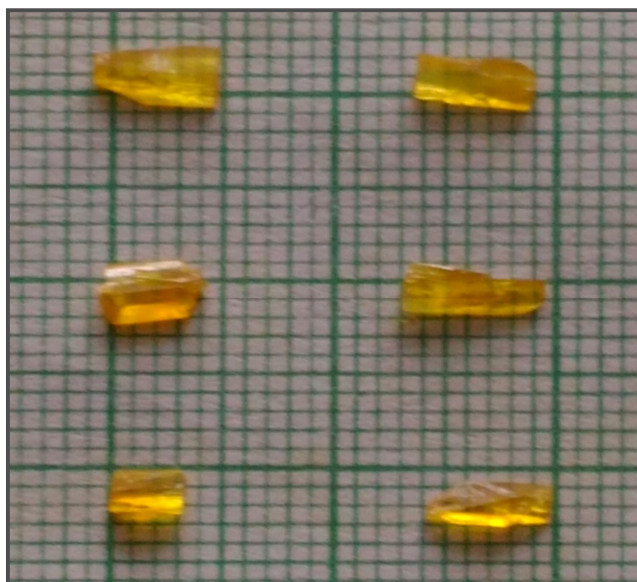


Fig. 1. Photograph of CMPI crystals.

## Results and Discussion.

**Single crystal X-ray diffraction analysis.** The XRD study confirmed the monoclinic crystal structure of CMPI with centrosymmetric space group  $P2_1/C$ . The lattice parameters obtained are  $a = 7.1043(1) \text{ \AA}$ ,  $b = 9.7805(2) \text{ \AA}$ ,  $c = 21.0801(4) \text{ \AA}$ ,  $\beta = 95.279(1)^\circ$  and  $V = 1460.24(5) \text{ \AA}^3$ . The obtained results are in concurrence with the literature [6] and thus confirm the identity of CMPI.

**FTIR Spectral analysis.** The FTIR spectrum for CMPI crystal was recorded in the KBr pellet phase in the frequency region of  $4000\text{-}400 \text{ cm}^{-1}$  shown in Fig. 2. The spectrum confirms the formation of CMPI crystal and the characteristic frequencies and the corresponding assignments are given in Table 1.

Table 1. Spectral data and their assignments for CMPI.

Wavenumber ( $\text{cm}^{-1}$ )	Assignments
3500.80 and 3383.14	O-H stretching
3070.68 and 3041.74	Aromatic C-H stretching
2945.30, 2916.37 and 2791	Alkyl C-H stretching
1616.35	Olefinic C=C stretching
1568.13 and 1514.12	Aromatic ring vibrations
1489.05, 1458.18 and 1409.96	CH <sub>2</sub> bending
1338.60, 1284.59 and 1269.16	C-N stretching
1083.99	Olefinic =C-H bond
1000-1200 and 850-1000	Aromatic C-H inplane and out of plane bending
731.02, 769.60, 815.89, 833.25	C-Cl stretching

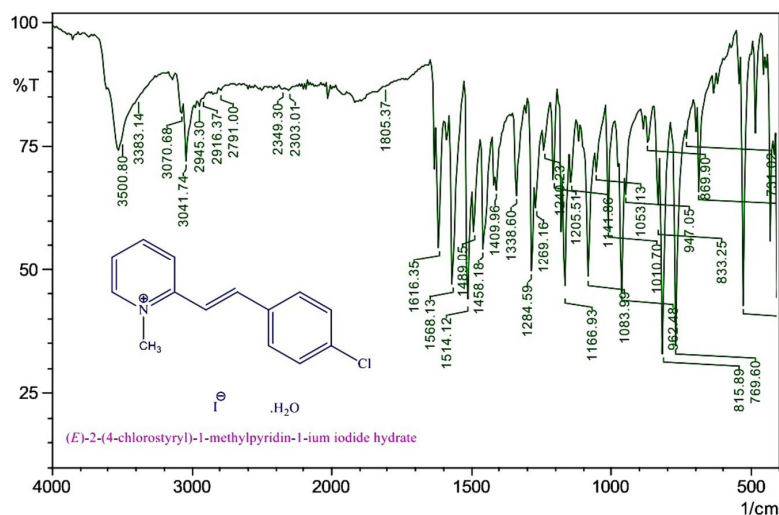


Fig. 2. FTIR spectrum of CMPI.

**UV-vis-NIR spectral analysis.** The optical absorption spectrum of CMPI as recorded for the wavelength range of 220–1000 nm is depicted in Fig. 3. The spectrum shows two absorption peaks, one at 260 nm corresponds to  $n-\pi^*$  transition and the other at 340 nm corresponds to the  $\pi-\pi^*$  transition of the stilbazolium chromophore. Moreover, negligible absorption can be seen in the entire region of 341-1000 nm suggests that the grown crystals of the title material are suitable for various nonlinear optical applications.

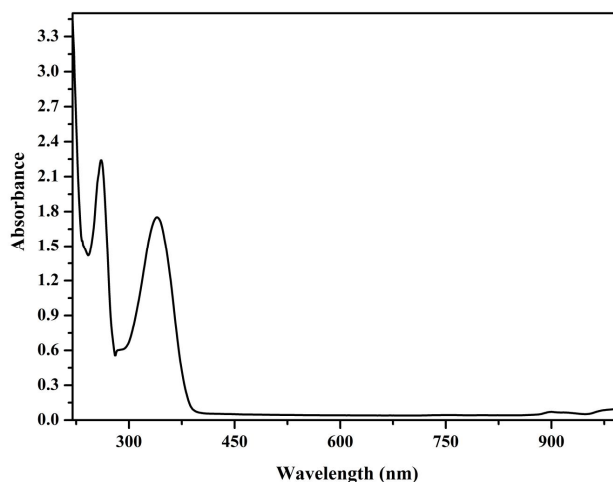


Fig. 3. Absorption spectrum of CMPI.

**Vickers microhardness studies.** Microhardness measurement was carried out on CMPI single crystals using Vickers microhardness tester fitted with a diamond pyramidal indenter. The diagonal length of the indentation in  $\mu\text{m}$  for various applied loads in kg was measured for the constant indentation time of 10 s. The Vickers hardness number ( $H_v$ ) was computed using the formula,  $H_v = 1.8544 P/d^2$ . The variation of  $H_v$  with load ( $P$ ) Fig. 4 shows that  $H_v$  increases with increase in  $P$  due to reverse indentation size effect. The Meyer index 'n' is estimated from the graph plotted against  $\log P$  vs.  $\log d$  (Inset of Fig. 4). Thus, the 'n' value of 4.26 shows the softness nature of the grown crystal satisfying Onitsch results [7].

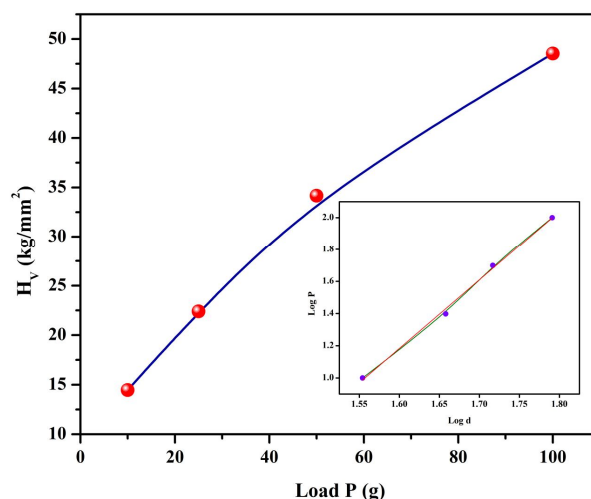


Fig. 4. Variation of  $H_v$  with load  $P$  and Meyer's plot of CMPI (inset).

**Z-scan studies.** The third-order NLO property of CMPI crystal was measured by the single beam Z-scan technique with the laser light 632.8nm from He-Ne laser was used. The open and closed aperture Z-scan methods were used for the measurement of nonlinear absorption coefficient ( $\beta$ ) and nonlinear refractive index ( $n_2$ ) for optical materials. The output beam has a Gaussian intensity profile and was focused, using a convex lens of 30 mm focal length, to a waist of radius ( $\omega_0$ ) 12.05  $\mu\text{m}$ , which corresponds to a Rayleigh length of 0.72 mm. The sample thickness of 0.60 mm was less than the Rayleigh length ( $L < Z_R$ ) and hence it could be treated as a 'thin medium'. The sample is translated in the Z-direction along the axis of a focused Gaussian beam using a motorized translation stage. The transmittance change through a small aperture at the far field position (closed aperture) can determine the amplitude of phase shift. The intensity dependent absorption is measured by moving the sample through the focus without placing an aperture at the detector (open aperture). In the open aperture pattern (Fig.5a), the decrease in transmission near the focus is an indicative of reverse saturable absorption (RSA) with a positive nonlinear absorption coefficient. In the closed aperture pattern (Fig.5b), the valley-peak configuration implies that the sign of refraction nonlinearity is positive ( $n_2 > 0$ ) i.e. self-focusing effect. The third order nonlinear optical parameters of CMPI crystal are calculated according to the reported literature [1,8]. Table 2 lists the experiment results of the third-order NLO parameters of the CMPI crystal. Here the nonlinear optical response arises due to strong delocalization of  $\pi$ -electrons within the molecular structure of CMPI.

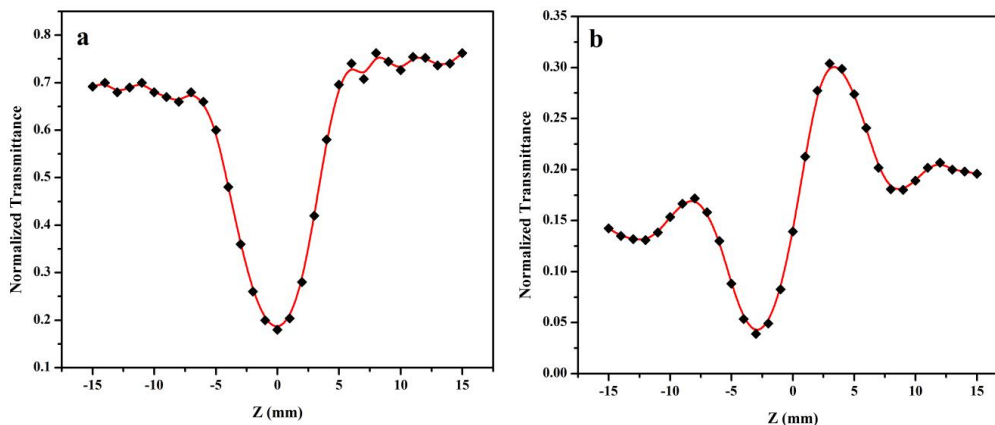


Fig. 5. Open aperture and Closed aperture Z-scan plot of CMPI crystal.

Table 2. Third-order NLO parameters of CMPI.

Nonlinear absorption coefficient ( $\beta$ )	$3.04 \times 10^{-5} \text{ m/W}$
Nonlinear refractive index ( $n_2$ )	$4.63 \times 10^{-12} \text{ m}^2/\text{W}$
Third-order nonlinear optical susceptibility ( $\chi^{(3)}$ )	$4.90 \times 10^{-5} \text{ esu}$

**Summary.** Single crystals of organic stilbazolium derivative, CMPI was grown by slow evaporation technique and characterized using single crystal XRD, FTIR, UV-vis-NIR studies, microhardness and Z-scan studies. The results of the above studies reveal that the CMPI crystal might be a potential candidate for NLO applications.

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