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# Synthesis, crystal growth and FTIR, NMR, SHG studies of 4-methoxy benzaldehyde-*N*-methyl-4-stilbazolium tosylate (MBST)

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## Abstract

A novel organic nonlinear optical material 4-methoxy benzaldehyde-*N*-methyl-4-stilbazolium tosylate has been synthesized and good optical quality crystals were grown by slow cooling solution growth technique. Powder X-ray diffraction studies have been carried out and the lattice parameters were calculated. FTIR spectra were recorded to identify the various functional groups present in the crystal. NMR spectrum studies have also been done. The powder second harmonic generation studies were done with Kurtz powder technique and the results were compared with urea.  
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## 1. Introduction

Much attention has been given to organic nonlinear optical (NLO) materials due to their promising applications including telecommunications, optical computing, and optical data-storage applications [1,2]. A generally successful and popular approach towards such materials is achieved in two steps which first imply the

synthesis of extended conjugated systems with donor and acceptor groups that can ensure the largest known second- or third-order molecular hyperpolarizability ( $\beta$ ) of any class of materials compared to inorganic NLO materials. The nonlinearity associated with a chromophore in the organic materials leads to observable bulk nonlinearity  $\chi^{(2)}$  and also only if the chromophores are oriented in a noncentrosymmetric environment [3]. So it is vital to design such a molecule with high noncentrosymmetry and one such effort has led to the development of the organic material 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate

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(DAST) crystal [4–6]. We have further extended our effort in synthesizing 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST), which is a derivative of stilbazolium tosylate and a new material having high NLO property. It was found to possess large electro-optic (EO) coefficients and NLO property. The lack of reasonably large and high-quality MBST crystals prevents real applications, such as optical sampling and EO sampling devices through frequency conversion or EO effect. In this report, we have investigated the growth of MBST crystals in order to obtain high-quality crystals and a way to obtain a reasonably large crystal has been investigated and reported in this article. MBST crystals were grown from saturated methanol solution by slow cooling technique.

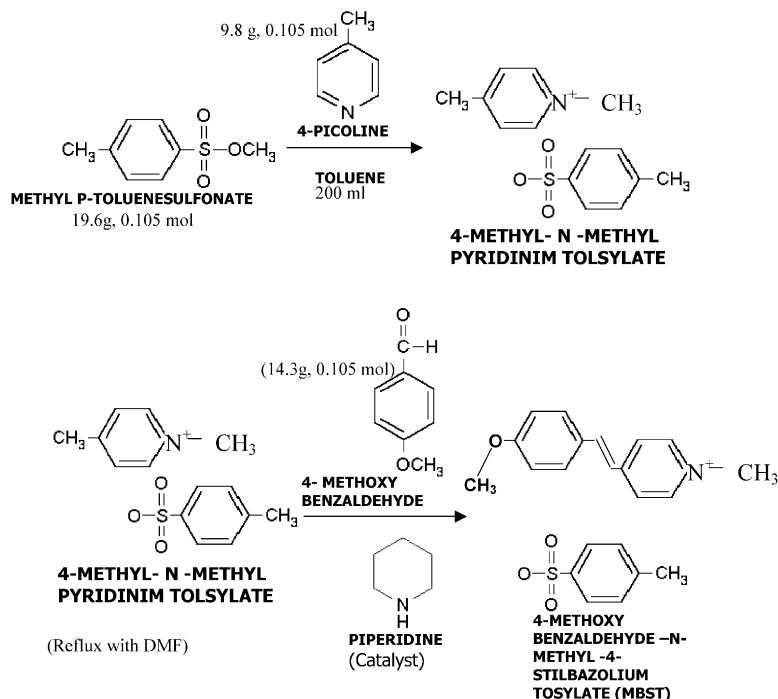
Slow cooling solution growth technique has been widely used for the growth of organic and inorganic materials [7,8]. In the present study, MBST was synthesized and the crystals were grown by slow cooling solution growth technique. The crystals were characterized using powder

X-ray diffraction, FTIR, NMR and powder SHG studies.

## 2. Synthesis

MBST was synthesized by the condensation of 4-methyl-N-methyl pyridinium tosylate, which was prepared from 4-picoline ( $C_6H_7N$ ), methyl p-toluene sulfonate ( $C_8H_{10}O_3S$ ) and 4-methoxy benzaldehyde (anisaldehyde) ( $C_8H_8O_2$ ) in the presence of piperidine as a catalyst (Scheme 1).

The step-by-step synthesis procedure of MBST is as follows: 200 ml of toluene, picoline (9.8 g, 0.105 mol) and methyl para toluene sulfonate (19.6 g, 0.105 mol) was taken together in a round-bottomed flask (500 ml) of dean-stark apparatus. The mixture was heated to form a salt, which was insoluble in toluene. While heating the mixture, dimethyl formamide (DMF) was added to the toluene salt mixture until the crystals (mixture salt) are dissolved. Now 4-methoxybenzaldehyde (14.3 g, 0.105 mol) was added to the mixture salt;



Scheme 1. Synthesis of MBST.

then drops of piperidine were added as catalyst until the solution just turned to red in colour. The mixture was then refluxed for 2 days with a dean-stark apparatus trap to remove water.

After the collection of more than equivalent amount of water, the reaction was cooled to room temperature and yellow/orange colour crystals of MBST was obtained by vacuum filtration. Approximately 40 g (equivalent to 94%) substance of MBST was collected [9].

### 3. Experimental studies

#### 3.1. Crystal growth

Recrystallized salt was taken and dissolved in methanol at 45°C. According to the solubility a saturated solution of 200 ml of MBST was prepared and the solution was filtered using borosil filter paper porosity of 0.1  $\mu\text{m}$ . The beaker containing the solution was shielded hermetically to prevent the evaporation of the solvent. Growth was carried out in a constant temperature bath (CTB) with a controlling accuracy of  $\pm 0.01^\circ\text{C}$ .

Transparent and high optical quality seeds were obtained from slow evaporation method and were hung in the solution with the help of a nylon thread. A cooling rate of  $0.05\text{--}0.08^\circ\text{C}/\text{day}$  was employed during the initial and the final stages of the growth process. Once the normal ambient room temperature is reached the crystal is harvested.

#### 3.2. Powder X-ray diffraction studies

Powder X-ray diffraction studies were carried out to demonstrate the crystallinity using Rich Seifert X-ray diffractometer employing  $\text{CuK}\alpha$  of  $1.5418 \text{ \AA}$  in the range  $10\text{--}55^\circ$ . The lattice parameters were calculated.

#### 3.3. FTIR and NMR spectral studies

The FTIR spectra was recorded using Nicolet Instrument corporation in the wavelength range  $400\text{--}4000 \text{ cm}^{-1}$  by KBr pellet technique. The middle infrared (IR) spectrum of the MBST material is shown in Fig. 1. Proton NMR spectrum was recorded for the crystal dissolved in

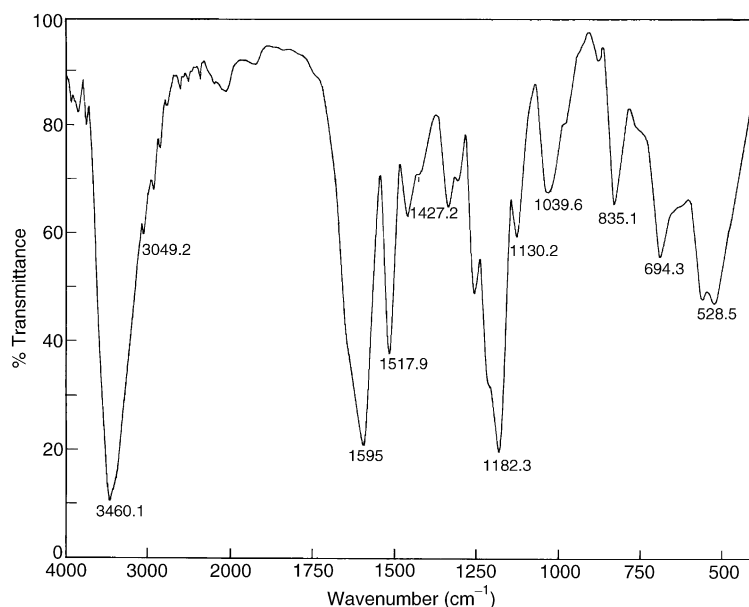


Fig. 1. FTIR spectrum of MBST.

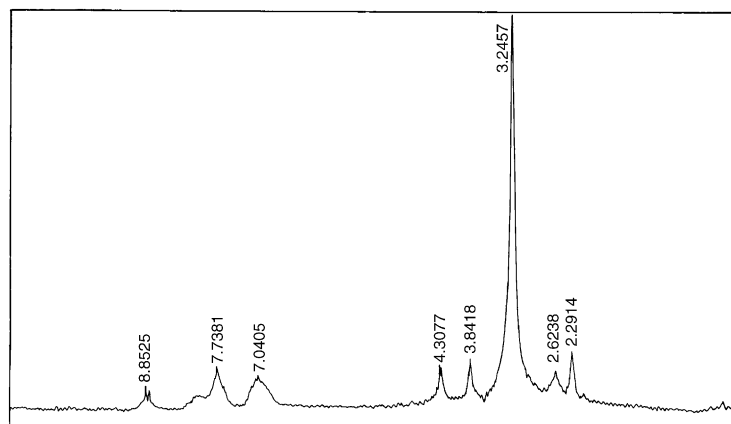


Fig. 2. NMR spectrum of MBST.

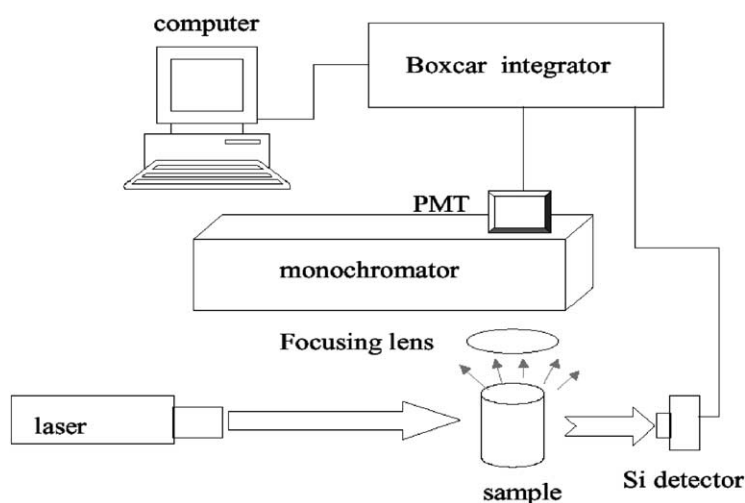


Fig. 3. Schematic of the SHG experimental setup.

deuterated methanol using Hitachi high-resolution NMR spectrometer, 60 MHz. The  $^1\text{H}$  NMR spectrum of the MBST is shown in Fig. 2.

### 3.4. Powder SHG measurements

The relative SHG efficiency of MBST and urea was measured by using the Kurtz powder technique. The set-up consists of an Nd:YAG Q-switched laser of wavelength 1064 nm whose beam falls focussed onto a thin section of the material contained in a 3 mm cuvette. The specifications of the laser source we used are 3  $\mu\text{J}$  pulse energy, 4 kW peak power, 8.62 kHz repeti-

tion rate, and pulse width 860 ps. The MBST crystals were powdered using a ball mill to get uniform particle size. The schematic of the experimental set-up used is shown in Fig. 3.

## 4. Results and discussion

The growth rate of the crystal mainly depends on the crystal growth parameters like temperature and degree of supersaturation of the solution. Efforts have been taken to increase the growth rate of the crystal by increasing the supersaturation of the solution. MBST crystals of size

$15 \times 12 \times 5 \text{ mm}^3$  exhibiting plate growth morphology with highly polished surfaces have been grown by conventional slow cooling solution growth technique. The crystals grown by slow cooling solution growth technique are shown in Fig. 4.

The middle IR spectrum recorded (Fig. 1) shows an intense envelope at  $3460 \text{ cm}^{-1}$  and it is due to OH stretch of water. Associated with its envelope are the minute peaks due to aromatic C–H stretch. These peaks are present at the lower wave number portion of the envelope. The peaks at  $1595$  and  $1517.9 \text{ cm}^{-1}$  can be assigned to aromatic ring skeletal vibration and olifinic C=C stretch,

respectively. The asymmetric and symmetric stretching modes of  $\text{SO}_2$  group are observed at  $1427.2$  and  $1182.3 \text{ cm}^{-1}$  respectively. The  $\text{CH}_3\text{--O}$  stretch is positioned at  $1039.6 \text{ cm}^{-1}$ . The para disubstituted nature of aromatic rings is evident by the bending mode of aromatic ring hydrogens at  $835 \text{ cm}^{-1}$ .

Fig. 2 shows the  $^1\text{H}$  NMR spectrum of the MBST crystals. The peak at  $8.5525 \text{ ppm}$  is assigned to pyridinium ring hydrogens. The para disubstituted nature of the aromatic rings is evident by the peaks at  $7.7381$  and  $7.0405 \text{ ppm}$ . The signal at  $4.3077 \text{ ppm}$  is due to pyridinium methyl hydrogens. The methoxy methyl hydrogens

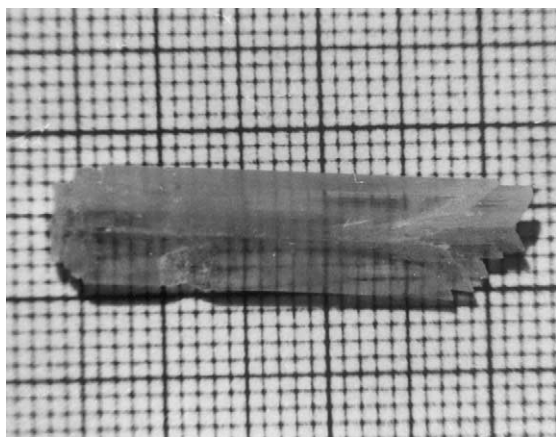


Fig. 4. Photograph of MBST crystals.

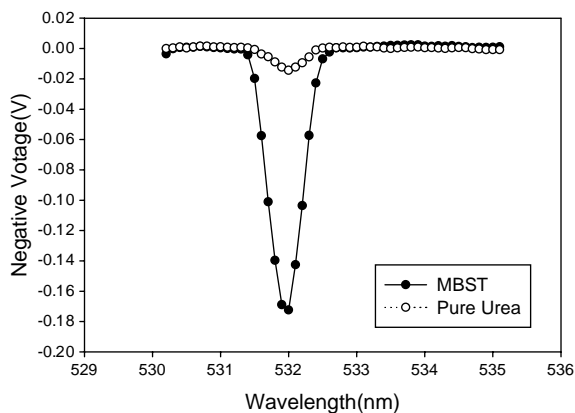


Fig. 5. SHG peak intensity of urea and MBST.

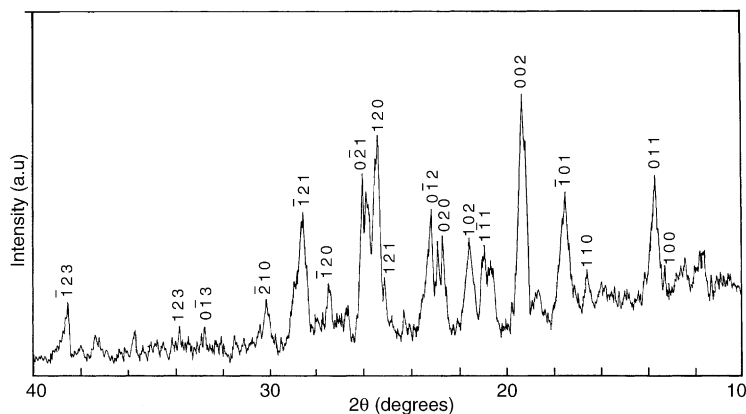


Fig. 6. Powder X-ray diffraction spectrum of MBST.

are observed as a singlet at 3.8413 ppm. The methyl group of *p*-toluene sulfonate molecule has produced a signal at 2.6228 ppm. The signal due to olefinic protons is observed at 2.2918 ppm. The intense peak at 3.2452 ppm is due to solvent.

During the SHG measurement using a 1064 nm laser beam MBST shows intense emission of green light. The peak intensity of MBST powder was observed to be 17 times higher than urea. Fig. 5 shows the SHG peak intensity curves of urea and MBST.

The crystal belongs to triclinic system with space group P1. The powder XRD studies (Fig. 6) confirm the crystallinity of the synthesized crystal salt. The calculated lattice parameters are  $a = 6.796 \text{ \AA}$ ,  $b = 7.908 \text{ \AA}$ ,  $c = 9.624 \text{ \AA}$  and  $\alpha = 78.98^\circ$ ,  $\beta = 80.56^\circ$ ,  $\gamma = 83.61^\circ$  and volume  $V = 499.05 \text{ \AA}^3$ .

## 5. Conclusion

MBST was synthesized and crystals have been grown by slow cooling solution growth technique. Powder X-ray diffraction studies were carried out and lattice parameters values were calculated. FTIR and NMR spectra recorded identify the various functional groups present in the material. The Kurtz powder SHG measurements show that

the peak intensity is 17 times more than that of urea. The growth parameters of MBST were optimized for the growth of large single crystals.

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## References

- [1] D.S. Chemla, J. Zyss, Nonlinear Optical properties of Organic Molecules and Crystals, Academic Press, Orlando, FL, 1987.
- [2] D.J. Williams, ACS Symposium Series, 1983, p. 233.
- [3] D.J. Williams, Ang.Chem. Int. Ed. Engl. 23 (1984) 690.
- [4] H. Nakanishi, H. Matsuda, S. Okada, M. Kato, Mater. Res. Soc., Int. Mtg. Adv. Mater. 1 (1989) 97.
- [5] S.R. Marder, J.W. Perry, W.P. Schaefer, Science 245 (1989) 626.
- [6] S.R. Marder, J.W. Perry, C.P. Yakymyshyn, Chem. Mater. 6 (1994) 1137.
- [7] S. Aravazhi, R. Jayavel, C. Subramanian, Mater. Chem. Phys. 50 (1997) 233.
- [8] G. Arunmozhi, R. Jayavel, C. Subramanian, J. Crystal Growth 178 (1997) 387.
- [9] N. Patrick Wang, T.M. Leslie, Chem. Mater. 7 (1995) 185.