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# Structural, elemental and dielectric properties of an organic stilbazolium single crystal of DAAS

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**Abstract:** The synthesis and growth of an ionic organic crystal 4-N, N-dimethylamino-4-N'-methylstilbazolium 4-aminotoluene-3-sulfonate (DAAS) are reported. The chemical composition of DAAS crystal was determined using CHN analysis. The single crystal XRD data of DAAS crystal confirms triclinic structure with non-centrosymmetric space group of $P1$. The proton NMR spectrum was recorded by dissolving the sample in deuterated methanol to confirm the presence of hydrogen. Dielectric measurements in the frequency range of 50 Hz - 5 MHz suggest that the permittivity and the dielectric loss of DAAS decrease with increase in frequency at different temperatures.

**Keywords**: Ionic organic crystal; Stilbazolium derivative; Single Crystal XRD; CHN analysis; NLO material

## Inroduction:

Nonlinear optical properties similar to those of DAST but with superior growth possibilities are highly desired. Much effort has been directed towards developing new molecules with high molecular nonlinearities that would promote better noncentrosymmetric crystal packing and enable easier and faster bulk crystal growth. To design materials with large second-order optical nonlinearities, one must attempt to achieve a large molecular hyperpolarizability*(β),* alignment of the molecules in the bulk material such that the hyperpolarizability is effectively used, and transparency in the visible region of the spectrum (for near-IR frequency conversion) [1]. One strategy employed to encourage noncentrosymmetric crystallization of neutral dipolar organic chromophores is to increase their geometrical asymmetry by introducing a substituent in the ortho or meta position of one of the aromatic rings. An alternative approach involved the use of ionic chromophores, whose counterions can be metathesized, allowing one to vary the orientation of the chromophore in the crystal lattice [1]. In this manner, researchers have successfully synthesized a good number of 4-N-methylstilbazolium salts that can give rise to large powder SHG efficiencies when combined with appropriate counterion [1,2]. Though several crystals have been investigated by researchers, most of them belongs to either centrosymmetric group or hygroscopic in nature. By overcoming these demerits we have synthesized the non-centrosymmetric and environmentally stable non linear optical material of 4-N, N-dimethylamino-4-N'-methylstilbazolium 4-aminotoluene-3-sulfonate (DAAS).the structural and electrical properties of the DAAS NLO crystal are presented in this work.

## Experimental

### Material synthesis and crystal growth

The title compound (DAAS) was synthesized via metathesization reaction between 4-N, N-dimethylamino-4-N'-methyl stilbazolium iodide (DMSI) and sodium salt of 4-aminotoluene-3-sulfonate [3, 4]. The metathesization reaction was carried out as follows: Initially, DMSI (0.7324, 2 mmol) was dissolved in 100 ml of deionised water with continuous heating. Simultaneously, aqueous solution of 4-aminotoluene-3-sulfonate sodium salt was prepared by dissolving equimolar ratio of 4-aminotoluene sulfonic acid (0.375 g, 2 mmol) and NaOH (0.08 g, 2 mmol) in 50 ml of deionised water and the content was mildly heated. The already prepared hot solutions were then thoroughly mixed with continuous stirring and further heated for an hour at 70 °C. The final solution was cooled down to room temperature and kept undisturbed for a day. A red colour precipitate was obtained as a result of cation and anion exchange reaction. The left out aqueous solution of sodium iodide was later separated by vacuum filtration. For the crystal growth experiment, saturated solution was prepared by dissolving 0.5 g of the salt of DAAS in 200 ml of water-methanol mixed solvent system taken in 1:1 ratio [5]. The content was heated up to 45 ℃ and stirred continuously until the material is completely dissolved in the solvent. The as-prepared saturated solution was filtered and then shifted to a Teflon beaker. The beaker was then sealed with a cap and then housed in a constant temperature bath at 48 ℃. And temperature was reduced 0.5-1 ℃/day. After 25-30 days, crystals with size up to $3\times1\times1$ $mm^3$were harvested Fig 1.

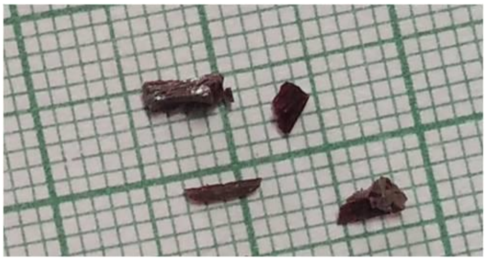

**Figure 1 Photograph of DAAS crystals grown in water-methanol (1:1) mixed solvent**

### CHN & Single crystal X-ray diffraction analysis

The chemical composition of DAAS crystal was determined using CHN analysis. The sample contains 64.69% carbon (C), 6.31% hydrogen (H) and 9.83% nitrogen (N). The calculated theoretical values of $C_{23}H_{27}N_3O_3S$ are; C = 64.92%; H = 6.39%; N = 9.87%, confirming the close agreement between the calculated and experimental data.

Single crystal X-ray diffraction data were collected by using a Bruker X8 KAPPA APEX IIX-ray diffractometer with $MoK_\alpha$ ($\lambda$ = 0.71073 Å) radiation. It indicates that the crystal is triclinic in structure and belongs to the non-centrosymmetric space group of *P*1. The cell parameters of the DAAS crystals are; a = 7.228(2) (Å),b = 8.942(3) (Å),c = 10.029(3) (Å), α = 97.729(15) °, β = 110.366(14) °, γ = 112.465(14) °, V = 534.22(3) $Å^3$ , Z = 1, ρ = 1.323 ($g/cm^3$). The single crystal XRD data for DAAS is almost in close agreement with the earlier work [4].

### NMR analysis

The proton NMR spectrum was recorded using a Bruker ADVANCE III 500 MHz FT-NMR spectrometer by dissolving the sample in deuterated methanol. In the proton NMR spectrum (Fig. 2), the singlet seen at 2.22 ppm is assigned to three $C–CH_3$ hydrogens present in the anion. The singlet observed at 4.231 ppm is attributed to the three $N–CH_3$hydrogens of pyridinium structure. The singlet at 3.09 ppm is due to the six hydrogens of $N–(CH_3)_2$. The singlet positioned at 4.613 ppm is assigned to the two hydrogens of $C–NH_2$. The doublets seen at 6.82 and 7.637 ppm are due to the four hydrogens of the $N–(CH_3)_2–C_6H_4$ aromatic ring. The doublets positioned at 7.969 and 8.522 ppm are attributed to the four hydrogens ortho to the $C_5H_4N$ aromatic ring. The doublet at 6.68 is due to the aromatic C–H hydrogen ortho to $–NH_2$. The doublet at 6.99 ppm corresponds to the aromatic C–H hydrogen ortho to $–CH_3$ group present in the anion. The doublet positioned at 7.498 is due to the aromatic C–H hydrogen ortho to $–SO_3$. The doublets seen at 7.121 and 7.866 are due to the two oliphinic hydrogens (HC=CH). The multiplet observed at 3.33 is caused by the solvent.

### Dielectric Studies

The dielectric constant and dielectric loss of the DAAS crystal were measured at different temperatures (308,328, 348 and 368 K ) using a HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5 MHz. The capacitance of the parallel plate capacitor with DAAS sample kept as dielectric medium at different temperatures (308,328, 348 and 368 K) was measured. The dielectric constant ($\varepsilon_r$) was calculated using the relation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$

Where, C the capacitance, d the thickness of the sample, $\varepsilon_0$ the permittivity of free space and $A$ the area of the crystal. Fig.3 shows the variation of dielectric constant as a function of frequency at different temperatures. It is observed that the value of both dielectric constant and dielectric loss decreases with frequency and becomes almost constant at higher frequency. The observed low dielectric constant at higher frequency may due to the loss of significance of all these polarizations gradually. The larger value of dielectric loss at low frequencies can be ascribed to the space charge polarization due to charged lattice defect [36]. The low value of dielectric constant at higher frequencies is significant for the fabrication of materials for photonics and electro-optic devices [6, 7].

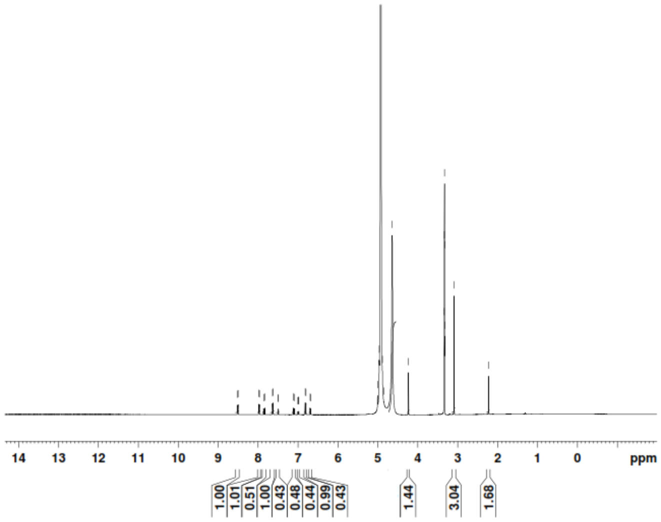

**Figure 2 NMR spectrum of DAAS crystal**

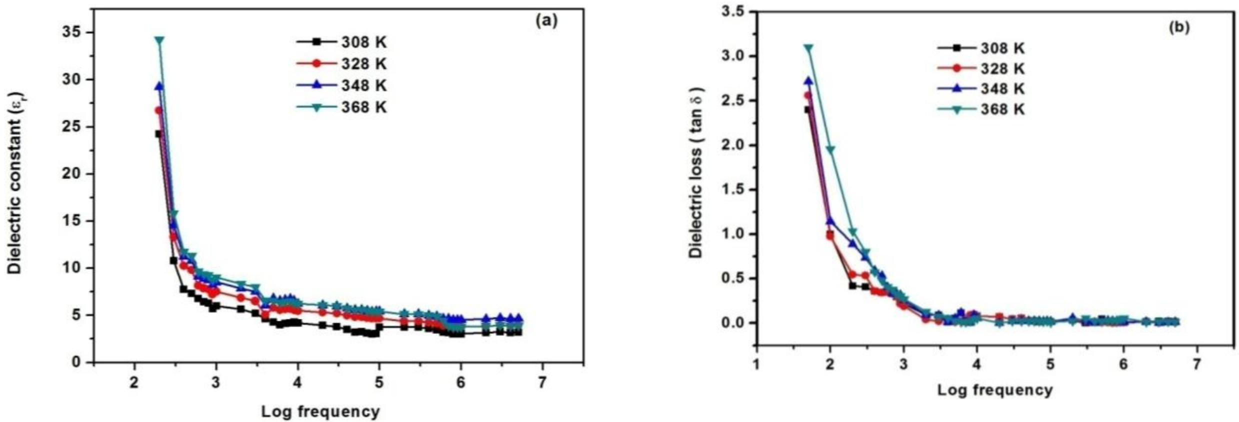

**Figure Frequency dependence of (a) dielectric constant and (b) dielectric loss of DAAS crystal**

## CONCLUSION

A derivative of stilbazolium was grown and the choice of water-methanol mixed solvent with slow cooling had favoured the growth of DAAS crystal with appreciable size. X-ray diffraction studies ascertained the *triclinic* structure of DAAS with space group *P*1. The CHN and NMR analysis confirms the elements present in the crystal. The observed low dielectric constant at high frequency region suggests the suitability of the material for photonics and electro-optic applications.

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